



Records of chemical weathering and volcanism linked to paleoclimate transition during the Late Paleozoic Icehouse

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ABSTRACT

The late Paleozoic ice age (LPIA) was the longest-lived glaciation of the Phanerozoic, and the demise of LPIA is the Earth's only recorded transition from an icehouse to a greenhouse state. In order to explore the records of chemical weathering and volcanism linked to paleoclimate, an integrated multi-proxy study from the Pennsylvanian to the earliest Cisuralian in the Western Shandong from the North China Craton (NCC) was conducted, including results of chemical weathering indices (CIA, CIW, PIA, WIP, CIX, and τ_{Na}), element indicators (Sr/Ba, Sr/Cu, and Rb/Sr), Hg concentration, total organic carbon (TOC), and organic carbon isotope ($\delta^{13}C_{org}$). The chemical weathering indices show a peak of chemical weathering intensity during the early Asselian (~298 Ma), indicating a warming event occurred at that time. Hg/TOC shows one obvious peak of volcanic intensity, corresponding with the rapid increase of chemical weathering. Moreover, the peak in volcanic intensity coincides with negative excursions of $\delta^{13}C_{org}$, hinting at volcanic drivers for the perturbations of carbon isotope and the change of paleoclimate. This phenomenon coincides with the change of conodont oxygen isotope ($\delta^{18}O$), a shift in atmospheric partial pressure of CO_2 (pCO_2), sea-level variation, and late Paleozoic deglaciation records that together document the earliest Permian climate warming-cooling perturbation with a temperature maximum. We suggest that the climate warming in the early Asselian may be driven by volcanism through released greenhouse gas. Our result provides an important contribution to enabling the correlation of volcanic and climatic events during glacial and interglacial cycles.

1. Introduction

The late Paleozoic icehouse is the most serious glaciation in the Phanerozoic (Isbell et al., 2003; Horton et al., 2007; Fielding et al., 2008; Isbell et al., 2012; Montañez et al., 2016; Isbell et al., 2021). The late Paleozoic ice age (LPIA) records the only transition from a greenhouse to an icehouse with complex terrestrial ecosystems to a full greenhouse world, beginning in the Famennian and ending in the Wuchiapingian, spanning ~106 million years (Isbell et al., 2021; Rosa and Isbell, 2021). Multiple episodes of glacial expansion and interglacial shrinkage occurred in the late Paleozoic ice age (Isbell et al., 2003; Fielding et al., 2008; Gulbranson, 2011; Metcalfe et al., 2015; Griffis et al., 2019; Griffis et al., 2021; Dietrich et al., 2021; Le Heron et al., 2021; Sun et al., 2022). Many studies focused on the records of carbonate rocks and marine

biological fossils to reconstruct sea level (Miller et al., 2005; Haq and Schutter, 2008), biodiversity (Gastaldo et al., 1996; Shen et al., 2006; Davydov, 2014; Groves and Wang, 2013; Groves and Yue, 2009), stable-isotope excursions (Korte et al., 2005; Grossman et al., 2008; Isozaki et al., 2007; Chen et al., 2013; Chen et al., 2018; Chen et al., 2022), change of paleotemperature (Yang et al., 2014; Yang et al., 2016), paleo-fires and atmospheric oxygen levels (Shao et al., 2012; Yan et al., 2019). Some studies proved a further coupling of atmospheric partial pressure of CO_2 (pCO_2) and surface temperatures with changing global ice volume during the LPIA (Montañez et al., 2016; Richey et al., 2020; Isbell et al., 2021; Lu et al., 2021; Chen et al., 2022). Recently, volcanism has been considered a causal mechanism for the increasing atmospheric pCO_2 and changing the global climate in the Paleozoic (Soreghan et al., 2019; Yang et al., 2020; Lu et al., 2021).

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The climate shifts have been linked to the atmospheric $p\text{CO}_2$ (Montañez et al., 2007; Montañez et al., 2016; Chen et al., 2018; Richey et al., 2020), tectonically paced rock weathering regimes (Goddéris et al., 2017; Yang et al., 2020), and volcanism (Yin et al., 2007; Korte et al., 2010; Korte and Kozur, 2010). Continental weathering trends have a discernable relationship to climate change, i.e., intensified chemical weathering corresponds to higher temperature and precipitation, while weakened weathering intensity to lower temperature and precipitation (Wang et al., 2020; Yang et al., 2020). Volcanism can discharge large volumes of CO_2 and CH_4 into the atmosphere, increasing atmospheric greenhouse gas concentration will result in global warming (Yin et al., 2007; Bond and Grasby, 2017), but the negative radiative forcing of volcanic sourced sulfate aerosols can also lead to global cooling (Soreghan et al., 2019; Lu et al., 2021).

Volcanic eruptions can release large amounts of Hg and cause enrichment of Hg in the Earth-surface system, which can easily overwhelm the background detrital Hg flux (Pyle and Mather, 2003; Zambardi et al., 2009). The residence time of Hg in the atmosphere has enough time (0.5 to 2 yrs) to ensure its wide dispersal after a major volcanic eruption (Selin, 2009; Driscoll et al., 2013). Mercury element derived from volcanism has the potential to be recorded in contemporaneous sedimentary rocks (Lu et al., 2021). Therefore, Hg concentrations have been extensively considered as an indicator of ancient volcanism (Nriagu and Becker, 2003; Pyle and Mather, 2003; Sial et al., 2013; Percival et al., 2015). For example, Lu et al. (2021) suggested that volcanism was an important driver for late Pennsylvanian to earliest Cisuralian shifts in global climates. Climate warming in southern North China at the Permo-Carboniferous transition likely tightly corresponds

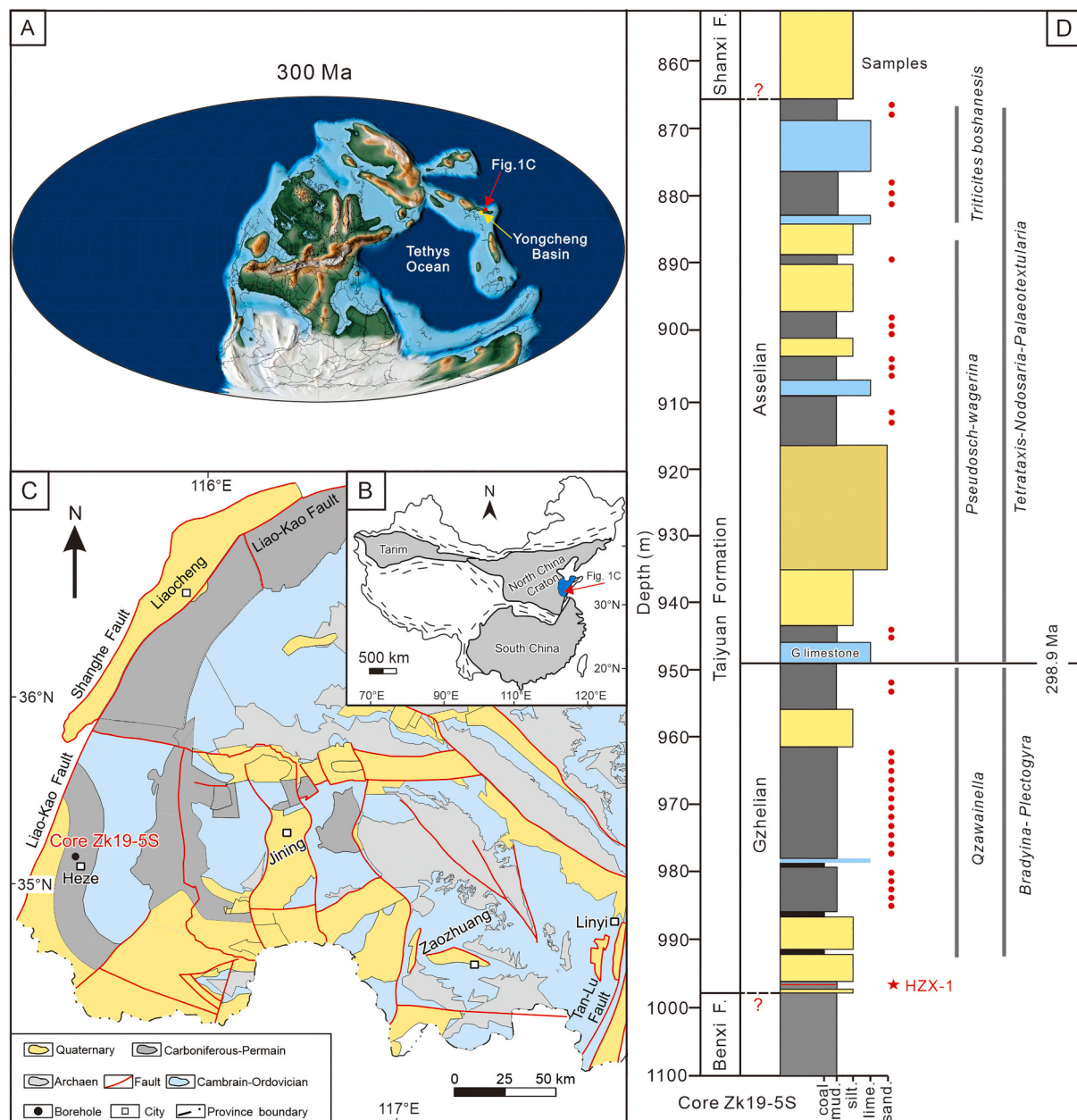


Fig. 1. Location and stratigraphic column for the study area. (A) ~300 Ma paleogeographic reconstruction from Scotese (2014) showing the positions of the studied area and the Yongcheng Basin (Yang et al., 2020). (B) Present location of the Western Shandong in North China Craton (NCC). (C) Regional geologic map of the Western Shandong showing the position of the core Zk19-5S. (D) Stratigraphic column of the core Zk19-5S with biological fossils (Zhang et al., 1989; Li et al., 2015). The red dots represent mudstone samples. The red five-pointed star represents the tuffaceous claystone sample. Benxi F. = Benxi Formation, Shanxi F. = Shanxi Formation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with the LIP event in the Skagerrak center, which is correlated using high precision zircon U—Pb ages and weathering trends (Yang et al., 2020). However, this hypothesis lacks the record of mercury as valid evidence of volcanism.

In the present study, we investigate the Pennsylvanian to early Cisuralian Taiyuan Formation to show the relationships between volcanism and climate transitions. Focusing on the core Zk19-5S in the Western Shandong of the North China Craton (NCC), we report U—Pb zircon ages and derive a record of chemical weathering indices from a cored uppermost Carboniferous through the lower Permian succession. This study also analyzes mercury concentrations to identify intervals of volcanism and organic carbon isotope ($\delta^{13}\text{C}_{\text{org}}$) values to evaluate perturbations in the global carbon cycle. Our data suggest that this climate warming event at the Permo-Carboniferous transition may correspond with the volcanism.

2. Geological setting

During the Permo-Carboniferous the NCC was surrounded by the Inner Mongolia uplift (IMU) to the north, the North Qinling Belt (NQB) to the south, warm waters of the Tethys Ocean to the west, and the Panthalassic Ocean to the east, was located in the northeastern margin of the Paleotethys Ocean (PTO) (Fig. 1A), with a latitude of approximately 5–15°N (Embleton et al., 1996; Muttoni et al., 2003; Muttoni et al., 2009; Dong et al., 2011; Huang et al., 2018; Yuan and Yang, 2015; Dong and Santosh, 2016). The Western Shandong is located in the east of the NCC, bounded by the Tan-Lu fault zone in the east and the Liao-Kao fault in the west (Jin et al., 1999; Niu et al., 2004; Fig. 1B).

Fold structures and fault structures are widely distributed in the Western Shandong. The main fold structure is a monoclinical structure, and the stratigraphic strike is NE-SW and NW-trending (Fig. 1B). The eastern part of the Western Shandong is bounded by the Tan-Lu fault zone, which had a significant effect on tectonic magmatic activity and mineralization in the Western Shandong. The fault structures in the southern and central hills and mountains are well exposed, and the faults in the north and west are mostly covered by quaternary sediments (Jin et al., 1999). Core Zk19-5S was recovered from the Heze city of Shandong province in eastern North China (Fig. 1B). It is preserved in a dedicated core storage facility and is thus free of modern surface weathering, making it very convenient for examination. The stratigraphic succession and rock types in the target strata in the core Zk19-5S of the Heze city are shown in Fig. 1C. The Taiyuan Formation is a broadly coastal and shallow marine deposit of very similar aspects to the cyclothymic successions of North America and Europe (Wang, 1985; Lv et al., 2011; Davydov, 2014; Lv and Chen, 2014; Yang et al., 2020). The sedimentary lithology of the Taiyuan Formation is mainly successions of sandstones, siltstones, mudstones, and coal seams. It is separated from the Benxi Formation by a layer of gray, thick-bedded coarse-grained quartz sandstone, with the remainder of the Taiyuan Formation comprising mudstones, limestones, and sandstones deposited in a range of carbonate and detrital coastal depositional environments. It is also separated from the Shanxi Formation by a mudstone. The bottom of the Taiyuan Formation contains a thin layer of tuffaceous claystone (Fig. 1C).

3. Sampling and analytical methods

A total of 35 mudstone samples were collected from the Taiyuan Formation from core Zk19-5S. Vertical sampling locations are shown in Fig. 1C. The samples were crushed using an agate ball and sieved through a < 200 mesh and divided for total organic carbon (TOC) analysis, $\delta^{13}\text{C}_{\text{org}}$ analysis, major elements analysis, trace elemental analyses, and mercury concentration analysis. The major elements, trace elements, and TOC were detected in Tianjin Center, China Geological Survey, the $\delta^{13}\text{C}_{\text{org}}$ analysis, and mercury concentration analysis were detected in Beida Zhihui Microstructure Analysis and Testing Center Co.,

LTD. Samples for TOC were first treated with phosphoric acid to remove inorganic carbon, and then the TOC values were measured using a carbon-sulfur analyzer (CS580-A) with the lower detection limits of 100 mg/g and an absolute analysis error of $\pm 0.2\%$. $\delta^{13}\text{C}_{\text{org}}$ analysis was performed using a stable isotope mass spectrometer (MAT253), and $\delta^{13}\text{C}_{\text{org}}$ values are expressed in per mil (‰) with respect to the Vienna Pee Dee Belemnite (VPDB) standard, with the absolute analysis error of $\pm 0.1\%$. The X-ray fluorescence spectrometry (PW2404) with the relative analysis error of $\pm 5\%$ was used to determine the content of major-element oxides (SiO_2 , Al_2O_3 , CaO , K_2O , Na_2O , Fe_2O_3 , MnO , MgO , TiO_2 , and P_2O_5). The trace elements were determined using an Inductively-coupled plasma mass spectrometer (LA-ICPMS).

Mercury concentration was undertaken using a Lumex RA-915 + mercury analyzer with lower detection limits of 2 ng/g and a relative analysis error of $\pm 5\%$. More details of the analytical method are described by Liao et al. (2016), Hu et al. (2019), and Chu et al. (2020). In this study, mercury enrichment anomalies have been used to indicate the presence of volcanic activity due to their relationship with volcanic eruptions and magmatic intrusions (Sanei et al., 2012; Grasby et al., 2013; Chen and Xu, 2019). At the same time, mudstones can retain information not only about the nature of the source material but also about its weathering history (Garver and Scott, 1995; Yang et al., 2020).

In order to establish an age model for the Permo-Carboniferous succession in the Western Shandong in NCC, the tuffaceous claystone sample (Fig. S1) from the Taiyuan Formation was obtained by using the zircon U—Pb dating method in this study. After crushing, grinding, sieving, and heavy liquid and magnetic separation, euhedral zircon crystals with clear oscillatory zoning under the cathodoluminescence (CL) microscope were selected for U—Pb zircon isotope analysis. Zircon grains were then analyzed for U, Th, and Pb isotopes by LA-ICPMS at Langfang Yuneng Rock Mineral Separation Technology Service. Data Cal and Isoplot 3.0 software were used for the age analysis, calculation, and the drawing of Concordia diagrams from the LA-ICPMS data. Zircon grains were then analyzed for Th, and Pb isotopes by LA-ICPMS at the Wuhan Shangpu Analysis Technology Co., Ltd. Further details of this technique are given by Lu et al. (2021).

4. Result

4.1. Zircon U—Pb dating

One tuffaceous claystone was sampled from the lowermost part of the Taiyuan Formation which is similar to other Late Paleozoic tuffs from the NCC (Yang et al., 2020; Lu et al., 2021). One hundred zircon crystals were separated from the sample in the core Zk19-5S from the NCC in the Western Shandong (HZX-1), with crystal sizes varying from 50 to 150 μm . Individual zircon crystals show euhedral morphology and clear oscillatory zoning in cathodoluminescence (CL) distinctive of magmatic zircon (Fig. 2A). Results of zircon U—Pb laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) dating are shown in Fig. 2 and Table S1. From sample HZX-1 a total of 78 concordant age values were determined with a bimodal age distribution (Fig. 2B); the younger peak has a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 301.3 ± 1.1 Ma (MSWD = 1, $n = 64$), while the older peak has a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 437.5 ± 2.8 Ma (MSWD = 0.83, $n = 14$).

We interpret the weighted mean ages from the younger peaks as the sedimentary ages of the tuffaceous claystone horizon for the following reasons. Firstly, sample HZX-1 yielded 64 concordant age values, which were distributed in a younger peak (Fig. 2). Secondly, during the Pennsylvanian frequent volcanic activity provides the possibility for the frequent inputs of tuffaceous and pyroclastic materials into the depositional basin, and the ages of the younger peaks are consistent with a Pennsylvanian age. Finally, the distribution of the younger peak weighted mean ages is consistent with the Permo-Carboniferous ages determined from biostratigraphy. These ages indicate that the lowest

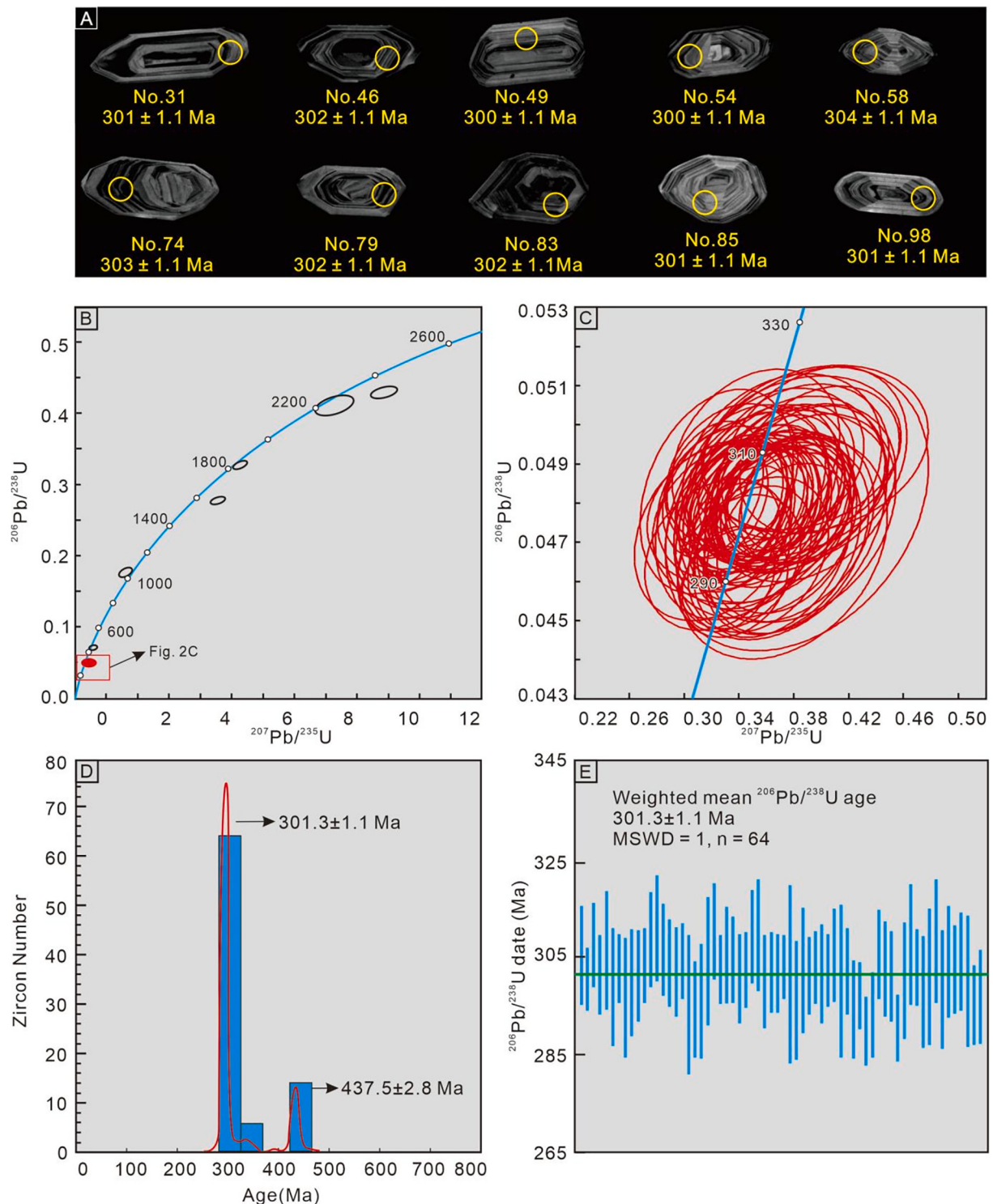


Fig. 2. Zircon U–Pb age distribution diagrams. (A) Typical zircon crystals of sample HZX-1 sample. (B–C) Zircon U–Pb of sample HZX-1 sample diagrams of sample HZX-1. (D) Zircon $^{206}\text{Pb}/^{238}\text{U}$ histogram of sample HZX-1. (E) The calculation of the weighted mean age of sample HZX-1.

Taiyuan Formation belongs to Middle Gzhelian.

4.2. Mudrock weathering index values and element indicators

Weathering indices of ancient detrital sediments can track changes in chemical weathering (Nesbitt and Young, 1982; Fedo et al., 1995; Scheffler et al., 2003; Rieu et al., 2007; Bahlburg and Dobrzinski, 2011; Yang et al., 2020). Various chemical weathering indices were used in

this study. We combine chemical index of alteration (CIA, Nesbitt and Young, 1982), weathering index of Parker (WIP, Parker, 1970), chemical index of weathering (CIW) (Harnois, 1988), chemical index of alteration without CaO (CIX, Dinis et al., 2017), plagioclase index of alteration (PIA, Fedo et al., 1995), and sodium depletion index (τ_{Na} , Rasmussen et al., 2011) to quantify the chemical weathering intensity experienced by the sources to the mudrocks. These indices involve different elements and thus can get rid of many sources of interference

and allow for evaluation of the potential influences exerted on sediment compositions. The major and trace elements are in Table S2 and Table S3, respectively. The detailed formulations and results for chemical weathering indices are listed in Table S4.

The geochemical weathering index values and element index values of Taiyuan Formation in Heze city core Zk19-5S are shown in Figs. 3 and 4, and all chemical weathering indices and element indexes are given in Table S4. CIA ranges from 77.9 to 92.4, with a mean of 85.7; WIP from 15.1 to 36.5, with a mean of 26.0; CIW ranges from 87.0 to 98.9, with a mean of 95.5; CIX from 81.7 to 93.0, with a mean of 87.0; PIA from 85.3 to 98.7, with a mean of 94.8; τ_{Na} from -0.97 to -0.67 , with a mean of -0.89 . Sr/Ba from 0.14 to 4.45, with a mean of 1.48; Sr/Cu from 0.44 to 2.3, with a mean of 0.69; Rb/Sr from 0.05 to 0.63, with a mean of 0.29.

To simplify the discussion and interpretation of the results, we defined two intervals in the Heze city core Zk19-5S profile: VA-I (Upper part of Taiyuan Formation; ~ 910 – 900 m) and VA-II (Lower part of Taiyuan Formation; ~ 985 – 955 m), as indicated by the colored bands in Fig. 3. In VA-I, the chemical weathering indices of the CIA, CIX, CIW, PIA, Sr/Ba, and Sr/Cu have extremely high values, the WIP, τ_{Na} , and Rb/Sr are extremely low. In VA-II, the chemical weathering indices of the CIA, CIX, CIW, PIA, Sr/Ba, and Sr/Cu are in the high range, while the values of WIP, τ_{Na} , and Rb/Sr are in the low range.

4.3. TOC, mercury, and $\delta^{13}C_{org}$ values

Results for TOC and mercury are shown in Table S5 and Fig. 4. TOC values vary from 0.31%–5.61% (mean average = 2.11%). Hg concentrations vary from 2 ppb–205.00 ppb (mean average = 85.5 ppb). Mercury is generally hosted by organic matter, sulfide, and clay minerals in continental strata (Grasby et al., 2013, 2019; Racki et al., 2018; Shen et al., 2019a; Shen et al., 2019b). Organic matter is the major host of Hg according to the consistent changing trends of TOC and Hg (Fig. 4) (Grasby et al., 2013, 2019; Wang et al., 2018; Wang et al., 2019; Shen et al., 2019a; Shen et al., 2019b; Hammer et al., 2019). Therefore, Hg/TOC can discern enrichments independent of variations in TOC. Hg/

TOC ratios vary from 0.41 ppb/% to 448.4 ppb/% (mean average = 71.87 ppb/%). Results for $\delta^{13}C_{org}$ are shown in Table S5 and Fig. 4. $\delta^{13}C_{org}$ values vary from -22.4% to -28.2% (mean average = -23.96%). In this study, there is a negative isotope excursion during the early Asselian (named CIE-I).

At the same time, the episodes of Hg enrichment correspond to negative carbon isotope excursion. Thus, we determined the mercury peak values in the study area can be reliable proxies of volcanism. The peak of Hg enrichment corresponds to negative carbon isotope excursion of CIE-I. The negative carbon isotope excursions of CIE-I coincide with the mercury peak from which volcanism is likely to be a causal mechanism for the perturbations in the carbon cycle.

5. Discussion

5.1. Chronostratigraphy construction

The age of the Permo-Carboniferous strata in NCC is only broadly constrained based on biostratigraphy with enormous uncertainty (Zhu et al., 2005). However, the Carboniferous-Permian boundary has been well constrained by foraminifera in the Western Shandong (Zhang et al., 1989; Li et al., 2015). The paleontology in our core Zk19-5S is from Zhang et al. (1989) and Li et al. (2015), which provided a detailed paleontological analysis of the Taiyuan Formation in our studied area. Li et al. (2015) found that one marked limestone bed called “G limestone” in the middle of the Taiyuan Formation can be defined as the Carboniferous-Permian boundary in our studied area based on the biological fossils. The Carboniferous-Permian boundary is located at the bases of the *Pseudosch-Wagerina* and *Tetrataxis-Nodosaria-Palaeotextularia* assemblages, which were debuted at the bottom of the “G limestone” in the Taiyuan Formation in our studied area (Fig. 1D; Zhang et al., 1989; Li et al., 2015).

The sample HZX-1 was collected at the bottom of the Taiyuan Formation, with a weighted mean $^{206}Pb/^{238}U$ age of 301.3 ± 1.1 Ma (Middle Gzhelian). Based on the ages of the sample HZX-1 and the

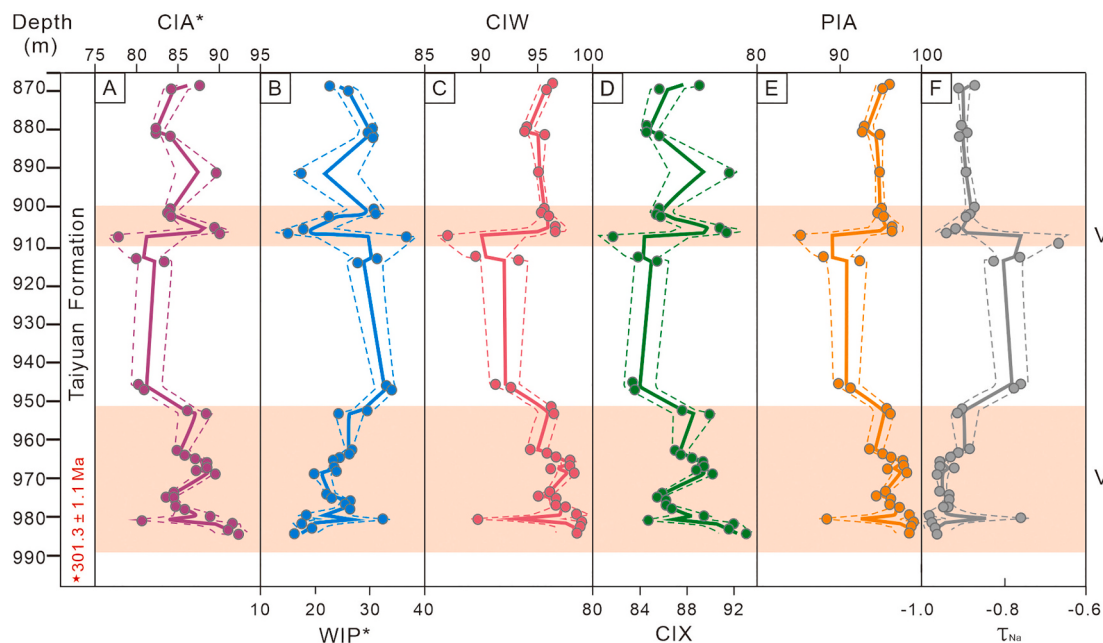


Fig. 3. Stratigraphic variations of geochemical proxies for the analyzed Zk19-5S mudrock samples. Locally estimated scatterplot smoothing trendlines using Acycle software (Li et al., 2019, 0.1 smoothing, solid lines) with 1σ bootstrapped errors (dashed lines) are shown for CIA*, CIW*, PIA, WIP, CIX, and τ_{Na} values (see the Table S4 for details). CIA = chemical index of alteration (Nesbitt and Young, 1982), WIP = Weathering index of Parker (Parker, 1970), CIW = Chemical index of weathering (Harnois, 1988), CIX = Chemical index of alteration without CaO (Dinis et al., 2017), PIA = Plagioclase index of alteration (Fedo et al., 1995), τ_{Na} = Sodium depletion index (Rasmussen et al., 2011), CIA* = Corrected CIA, WIP* = Corrected WIP. The two pink bands indicate the potential warming events. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

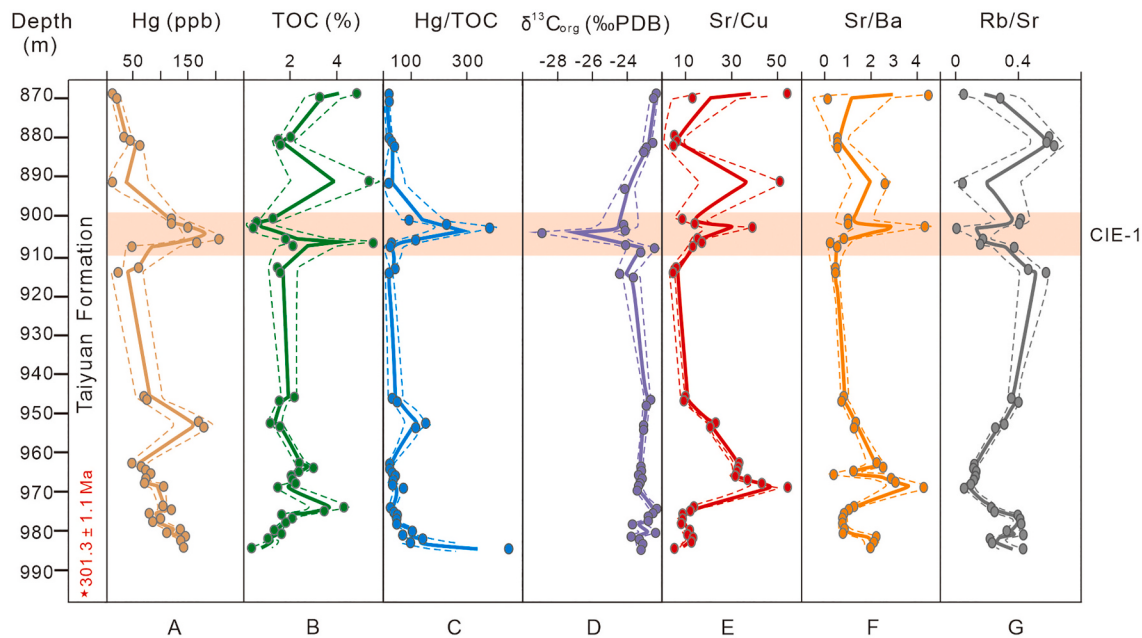


Fig. 4. Locally estimated scatterplot smoothing trendlines using Acycle software (Li et al., 2019, 0.1 smoothing, solid lines) with 1σ bootstrapped errors (dashed lines) are shown for Hg concentration, total organic carbon (TOC) values, Hg/TOC, organic carbon isotope ($\delta^{13}\text{C}_{\text{org}}$) values, Sr/Cu, Sr/Ba, and Rb/Sr in core Zk19-5S mudrock samples from the North China Craton. The pink band indicates a negative carbon isotope excursion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Carboniferous-Permian boundary, an average depositional rate of 19.2 ± 1.1 m/Myr can be calculated for the Taiyuan Formation in our studied area. Similarly, Wu et al. (2021) and Lu et al. (2021) calculated the average depositional rate of the Taiyuan Formation in NCC at 19.1 m/Myr and 25.6 m/Myr based on the zircon U—Pb ages, respectively. This age model tightly constrains the Taiyuan Formation in our studied area to the middle Gzhelian-early Asselian (301.3 ± 1.1 Ma - 296.2 ± 1.1 Ma). However, because the depositional rate could be variable in consideration of the difference in lithology, the proposed age model should have uncertainty. Despite this deficiency, a model age of ~ 295 Ma acquired for the top of the Taiyuan Formation is consistent with a tuff zircon U—Pb age of 295.65 ± 0.08 Ma collected from the upper Taiyuan Formation in the Yongcheng Basin (Yang et al., 2020). Our zircon U—Pb age provides an age constraint for the Taiyuan Formation in the Western Shandong in NCC.

5.2. Weathering and paleotemperature trends

5.2.1. Eliminating the interference of non-weathering factors on weathering indices

Mudrocks have the potential to provide valuable weathering intensity information on their important source landscapes (Nesbitt and Young, 1982; Scheffler et al., 2003; Garzanti et al., 2013; Garzanti et al., 2014). Chemical weathering on continents is primarily controlled by temperature and moisture levels (Wronkiewicz and Condie, 1987; Johnsson and Basu, 1993; Sheldon, 2006; Sheldon and Tabor, 2009). Authigenic illite, montmorillonite chlorite, and carbonate minerals (calcite dolomite and siderite) have resulted in the change of chemical composition of the muddy sediments during diagenesis (Awwiller, 1993; Land et al., 1997; Lynch et al., 1997). For example, the potassium metasomatism of kaolinite often affects the mudstone composition during diagenesis (Awwiller, 1993; Fedo et al., 1995; Bloch, 1998; Rieu et al., 2007). The CIA is sensitive to potassium metasomatism and WIP is affected by sedimentary recycling and sorting-induced accumulation of quartz and zircon (Garzanti et al., 2013; Yang et al., 2020). Potassium metasomatism has no effect on the CIW (Gaillardet et al., 1999; Garzanti et al., 2013). Therefore, the Permo-Carboniferous climatic fluctuations

of NCC can be revealed by chemical weathering indices without the interference of non-weathering factors or due to post-depositional metasomatism.

5.2.1.1. Diagenetic alteration. Some studies have shown that the dominant source for the early Permian sedimentary rocks in the Western Shandong corresponds with the composition of the upper continental crust of the interior of the NCC (INC; Chen and Liu, 1997; Fang, 1994). In this study, most analyses plot along with the predicted weathering trend of the INC in the $\text{Al}_2\text{O}_3\text{--CaO}^* + \text{Na}_2\text{O--K}_2\text{O}$ (A-CN-K; where CaO^* represents CaO in the silicate fraction only) diagram (Fig. 5A; Fedo et al., 1995). Therefore, the provenance inference of the study area is valid and reasonable. A-CN-K diagram indicates the existence of potassium metasomatism in the diagenetic process, which is caused by the conversion of kaolin (residual weathering product) to illite by reaction with K^+ -bearing pore waters (Fedo et al., 1995). This K-enrichment results in samples plotting towards the K apex of the A-CN-K triangle, with lower CIA and higher WIP values.

Thus, a correction of the potassium metasomatism of some samples deviating from the weathering trend is significant. Corrections for K-metasomatism can obtain the original weathering trend of each data point. In this study, according to the method of Yang et al. (2018a, 2018b), CIA and WIP values were corrected by potassium metasomatism on the A-CN-K diagram (Fig. 5B). CIA^* values after correction ranged from 77.9 to 92.4, with a mean of 85.7, while WIP^* from 15.1 to 36.5, with a mean of 25.3. In the Western Shandong, most of these corrected CIA values are >80.0 (Table S4). Our CIA^* and WIP^* values minimized the diagenetic influence of potassium metasomatism on the CIA and WIP, which indicates that CIA^* and WIP^* can serve as a more reliable proxy than CIA and WIP for reconstructing the paleoclimate (Yang et al., 2018a, 2018b). Therefore, the uncorrected CIA and WIP were not considered in the following discussion.

5.2.1.2. Sedimentary recycling. Sedimentary recycling refers to the process of weathering, denudation, transport, and deposition of sediments after deposition or diagenesis (McLennan, 1993; Cox et al., 1995; Jian et al., 2013). Stable minerals such as quartz and zircon accumulate

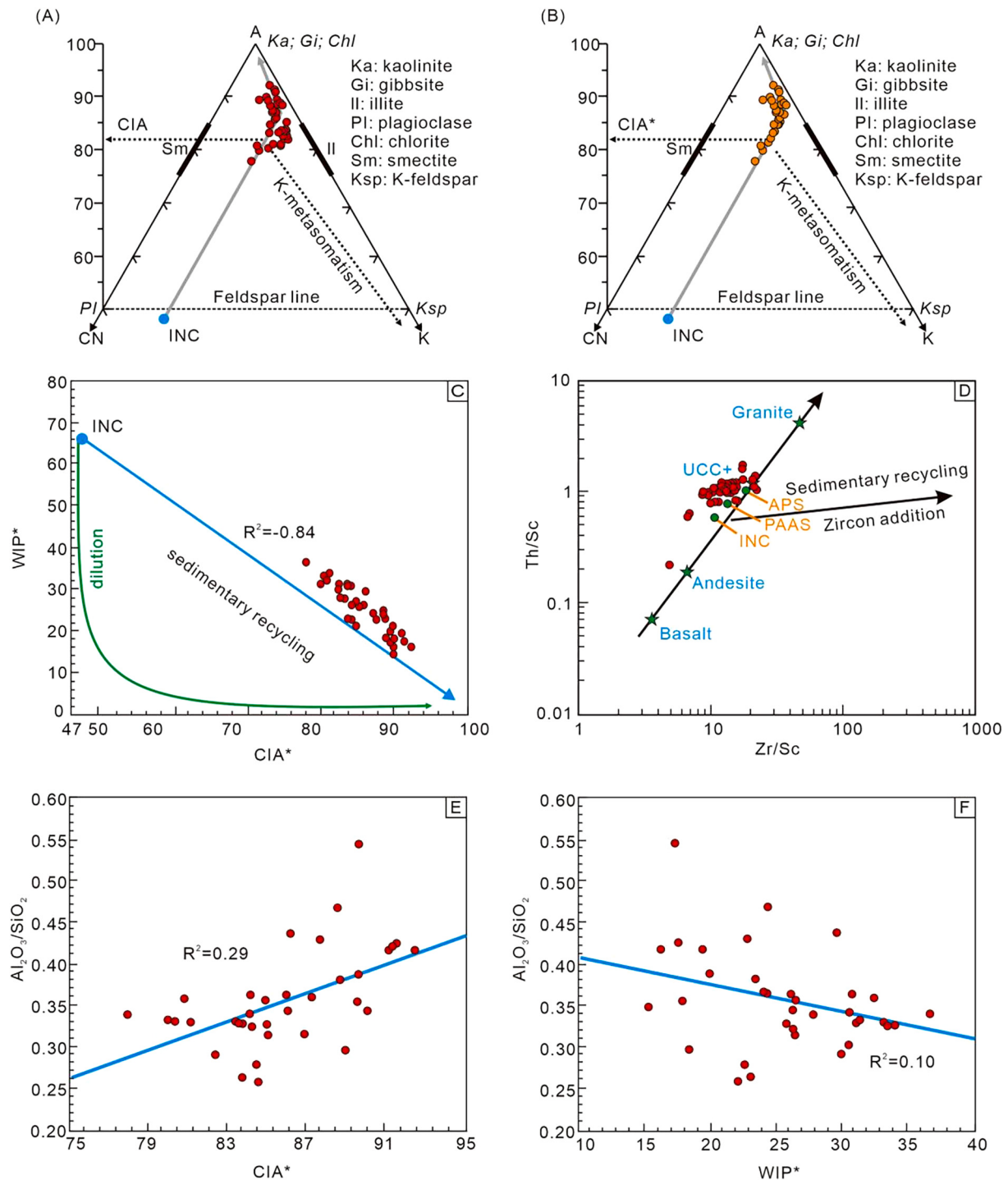


Fig. 5. Plots of analyzed mudstones. (A) Ternary diagrams of A-CN-K for core Zk19-5S mudrock samples from the North China Craton (NCC), based on the method described by Fedo et al. (1995). In the A-CN-K diagram, mudrock samples plot in the intermediate-intense weathering zones and generally mimic the ideal weathering trend of the upper continental crust of interior of the NCC (INC, Gao et al., 1998). (B) Corrected core Zk19-5S mudrock samples in Ternary diagrams of A-CN-K from the INC. A = Al₂O₃, CN = CaO* + Na₂O, K = K₂O, CIA = chemical index of alteration (Nesbitt and Young, 1982), CIA* = corrected CIA. (C) CIA*-WIP* plot for the analyzed core Zk19-5S mudrock samples for discriminating sedimentary recycling chemical weathering influence. WIP = Weathering index of Parker (Parker, 1970), WIP* = corrected WIP. (D) Crossplot of Th/Sc vs. Zr/Sc of the Taiyuan Formation mudstone samples compared to average ratios in typical source rocks and to the predicted trend from zircon enrichment during sediment recycling. UCC = average Upper Continental Crust (Rudnick et al., 2003); PAAS = Post-Archaean average Australian Shale (Taylor and McLennan, 1985); APS = Average Proterozoic Shale (Condie, 1993); Granite, Andesite and Basalt (Fedo et al., 1995). (E) Crossplot of the CIA* with Al₂O₃/SiO₂ in the Taiyuan Formation mudstone sample set. (F) Crossplot of the WIP* with Al₂O₃/SiO₂ in the Taiyuan Formation mudstone sample set.

in the sediments during polycyclic reworking processes, thus diluting other components (McLennan, 1993; Cox et al., 1995; Armstrong-Altrin et al., 2004). Besides potassium metasomatism, it is another factor leading to the change in rock composition (Metcalf et al., 2015). Therefore, this study attempts to exclude the effects of sedimentary recycling. As sedimentary recycling increases, the WIP (weathering index of Parker), which uses only the concentrations of Na, Mg, K, and Ca decreases linearly (Parker, 1970). The CIA, which uses concentrations of Al to calculate, is not affected by the process (Garzanti et al., 2013, 2014). CIA* was negatively correlated with WIP* in Taiyuan Formation in the Western Shandong ($R^2 = -0.84$), most samples showed a covariant relationship between CIA* and WIP* along with the projected INC weathering trend (Fig. 5C). It implies little effect from sedimentary recycling on the compositional trends.

Another additional proxy to evaluate possible recycling during deposition is the interaction diagram of Zr/Sc and Th/Sc (McLennan, 1993). The Zr/Sc ratio is low, meanwhile, the Th/Sc cross plot of the samples (Fig. 5D) has a good correspondence with the general trend determined by the parent rocks (Most samples are around UCC). It indicates that most components of the sedimentary rocks were not affected by recycling.

5.2.1.3. Hydraulic sorting. In addition to weathering, sorting is

particularly crucial for sedimentary rocks. Mineral sorting generally tends to increase the abundance of non-clay-clastic minerals with clay minerals as carriers (Sun et al., 2011; Singh and Rajamani, 2001; Roddaz et al., 2006). For example, as quartz and zircon minerals become enriched in the deposition of coarse-grained sediments, clay minerals are enriched in the residual finer-grained sediments during the sedimentation and sorting process (McLennan, 1993; Singh and Rajamani, 2001; Roddaz et al., 2006; Garzanti et al., 2013). The enrichment of quartz reduces the WIP value.

The Al_2O_3/SiO_2 ratio is widely applied as an indicator of hydraulic sorting and as a proxy for grain size (Bouchez et al., 2011; Yang et al., 2016). The Al_2O_3/SiO_2 ratios of all samples had a weak correlation with CIA* and WIP* (Fig. 5E; Fig. 5F). The lack of a correlation of the Al_2O_3/SiO_2 ratio with CIA* or WIP* implies that sedimentary sorting has a slight effect on the CIA* or WIP*.

5.2.1.4. Provenance interpretation. The state of element enrichment in sediments will change with the change of provenance, however, most immobile elements suffer minor losses during chemical weathering (Yang et al., 2016; Sun et al., 2022). The ratios between them are sensitive to the sedimentary provenance composition rather than to the chemical weathering intensity. For example, Th/Sc is a sensitive and simple index for identifying the overall source of terrigenous detritus

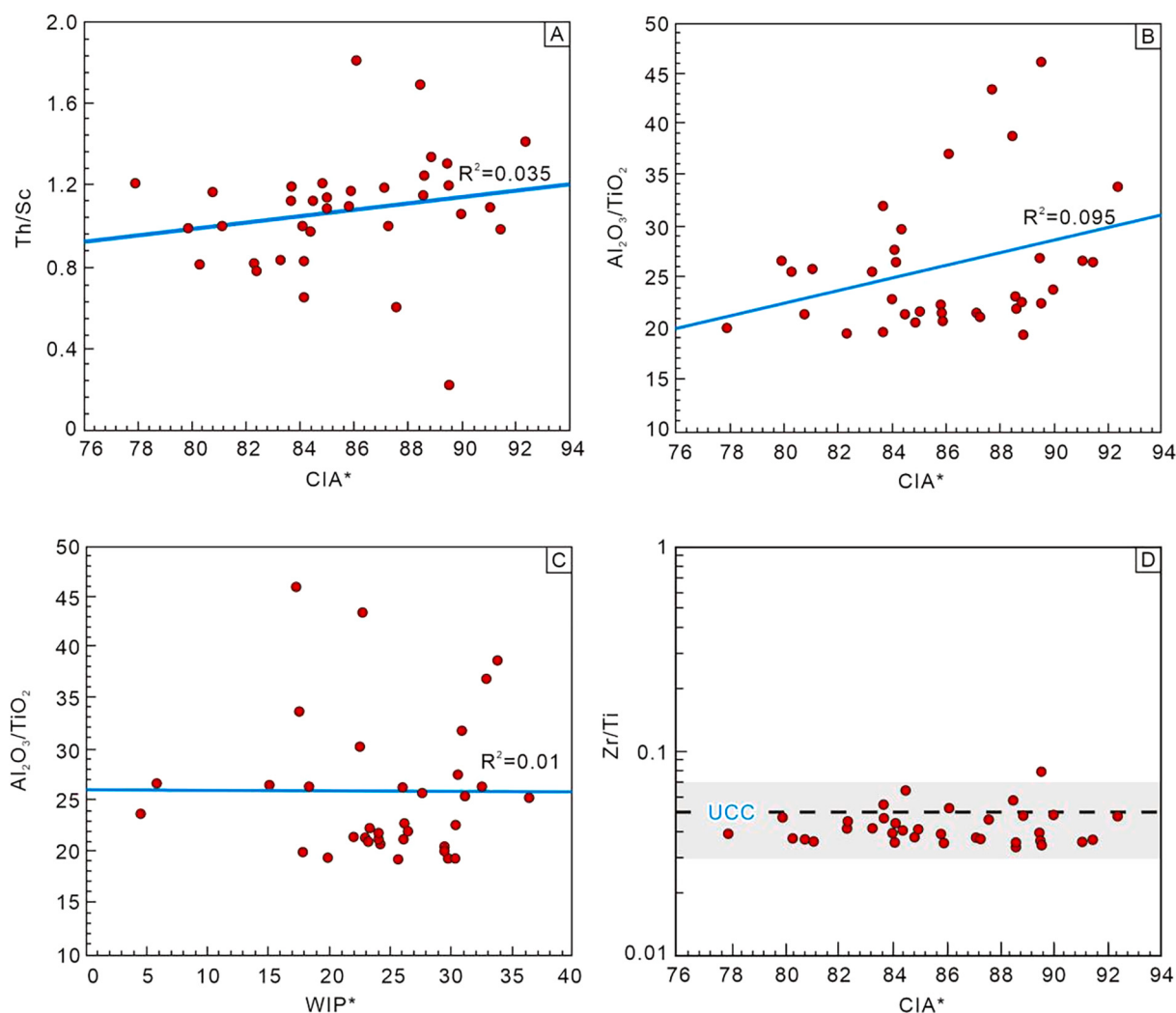


Fig. 6. (A) Cross plot of the CIA* with Th/Sc in the Taiyuan Formation mudstone sample set. CIA* = corrected chemical index of alteration. (B) Cross plot of the CIA* with Al_2O_3/TiO_2 in the Taiyuan Formation mudstone sample set. (C) Cross plot of the WIP* with Al_2O_3/TiO_2 in the Taiyuan Formation mudstone sample set. WIP* = corrected weathering index of Parker. (D) Cross plot of the CIA* with Zr/Ti in the Taiyuan Formation mudstone sample set.

because Th/Sc ratios vary >100 folds in detrital sediments with different provenances (Taylor and McLennan, 1985; McLennan, 1993; Cawood et al., 2003). There is no obvious correlation between CIA* and Th/Sc, indicating that the variations in CIA* were not affected by possible changes in provenance (Fig. 6A).

$\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio and Zr/Ti ratio are used to monitor the potential changes in source rock composition because they are controlled by source rock composition (Yang et al., 2018a, 2018b; Qi et al., 2020). Through the succession, CIA*, WIP* values have no explicit correlations with $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio ($R^2 < 0.10$), and this argues against weathering indices being influenced by sedimentary provenance (Fig. 6B; Fig. 6C). Zr/Ti ratio flattens close to the upper continental crust (UCC, Rudnick et al., 2003) and has no correlation with CIA*, which indicates the samples were unaffected by source composition (Fig. 6D).

5.2.2. Implications for Permo-Carboniferous paleoclimate and temperature changes

After eliminating the interference of non-weathering factors on weathering indices, the screened mudrock samples retain source chemical weathering signals. The sequential variations of CIA*, WIP*, CIW, CIX, PIA, and τ_{Na} values should accordingly reflect the chemical weathering trends of the source region (Nesbitt and Young, 1982; Johnsson and Basu, 1993; Scheffler et al., 2003; Garzanti et al., 2013; Garzanti et al., 2014).

These variations in chemical weathering trends reveal a remarkably consistent high peak in the upper part of Taiyuan Formation (early Asselian; ~298 Ma–297.5 Ma; numbered VA-I) and high values in the lower part of Taiyuan Formation (late Gzhelian; numbered VA-II) (Fig. 7A; Fig. 7B). The CIA* values of VA-II were relatively high, oscillating between 80.74 and 92.40. The CIA* in the upper part of Taiyuan Formation (early Asselian; VA-I) reveals a remarkable increase, followed by an immediate decrease of similar magnitude in weathering intensity.

A peak value of CIA* occurred at the depth of 906.5 m (~298 Ma), indicating that there was an obvious warming event (VA-I).

Reconstruction of paleoclimate and paleotemperature have utilized stable isotopes (Mii et al., 2001; Korte et al., 2005; Buggisch et al., 2008; Grossman et al., 2008; Korte and Kozur, 2010; Korte et al., 2010; Chen et al., 2018, 2022), Biological palynology (Cai et al., 2012; Miao et al., 2013; Davydov, 2014), organic geochemistry (Meyers, 1994; Meyers, 1997) and sea-level change (Isbell et al., 2003; Miller et al., 2005; Fielding et al., 2008; Haq and Schutter, 2008). Modern large-river estuary suspended-sediment analyses show CIA values changing with latitude and land surface temperature (Yang et al., 2014). Yang et al. (2014) derived an empirical relationship between CIA and temperature and obtained global continental weathering trends and temperatures across an Early Permian glacial to post-glacial transition. Therefore, we applied this relationship to estimate the Taiyuan Formation paleotemperature trends on the NCC (Fig. 7A; Fig. 7B). An estimated warming of ~7 °C (18 °C to 25 °C) occurred in the upper part of Taiyuan Formation (early Asselian; ~298 Ma - 297.5 Ma; numbered VA-I). An estimated temperature increase of approximately 6 °C (20 °C to 26 °C) occurred in the lower part of Taiyuan Formation (late Gzhelian; numbered VA-II) with indications of oscillations.

Yang et al. (2016) proposed that the dependence of land surface soil chemical weathering intensity on the air temperature can be described by a τ_{Na} -MAT (mean annual temperature) transfer function. However, the formula needs to fulfill the following preconditions: 1) Because the surface soil chemical weathering in arid regions (annual rainfall <400 mm/yr) is controlled by humidity, there is no correlation with land surface temperature. Thus, the formula needs to be performed with precipitation >400 mm/yr, but not >4000 mm/yr; 2) Physical erosion rate < 100 m/Myr; 3) The transport process is not affected by sedimentary recycling and diagenesis.

Many studies showed that the climate in the Western Shandong was

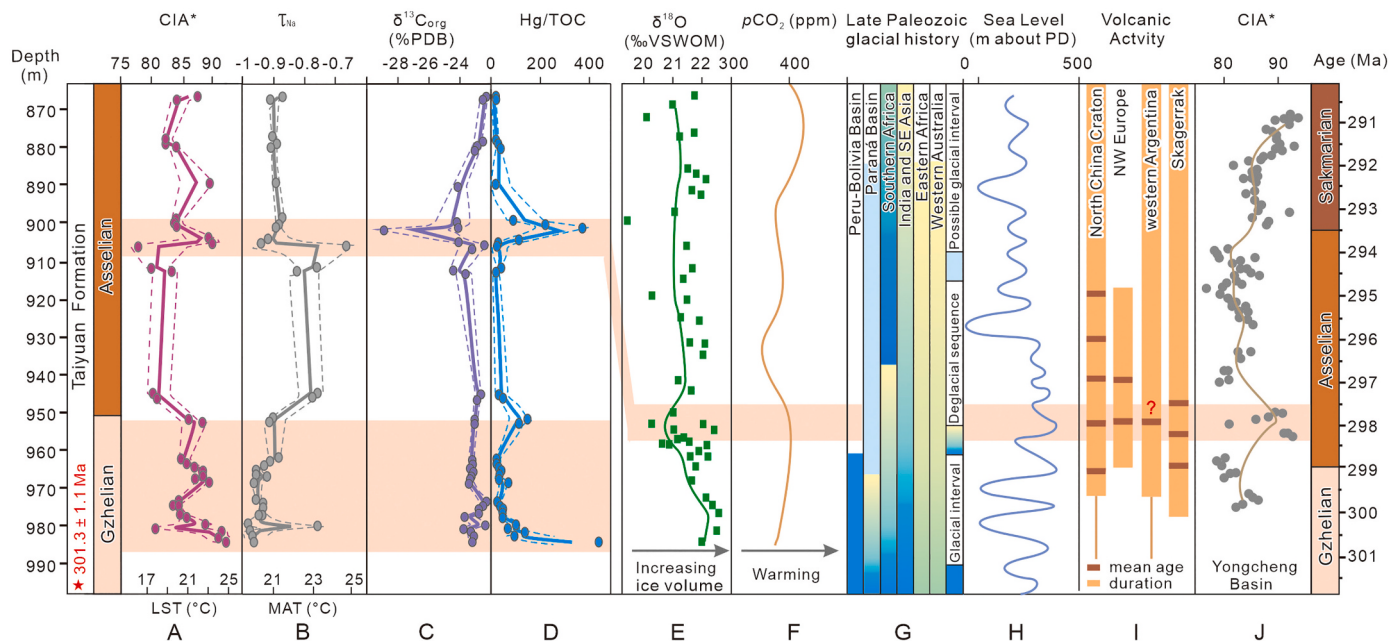


Fig. 7. Correlation of climate and weathering records of Permo-Carboniferous transition with global proxies. Locally estimated scatterplot smoothing trendlines using Acycle software (Li et al., 2019, 0.1 smoothing, solid lines) with 1 σ bootstrapped errors (dashed lines) are shown for CIA*, τ_{Na} , and $\delta^{13}\text{C}_{\text{org}}$. (A) CIA* record and LST change in this study. CIA* = corrected chemical index of alteration (Fedó et al., 1995), LST = Land Surface Temperature (Yang et al., 2014). (B) τ_{Na} record and MAT change in this study. τ_{Na} = Sodium depletion index (Rasmussen et al., 2011), MAT = Mean Annual Temperature (Yang et al., 2016). (C) Organic carbon isotope ($\delta^{13}\text{C}_{\text{org}}$) variation in this study. (D) Hg/TOC ratios from the core Zk19-5S of the Western Shandong in the NCC. (E) Sequential variation of conodont oxygen isotope ($\delta^{18}\text{O}$) from the Naqing Section of South China (Chen et al., 2016). (F) Atmospheric partial pressure of CO_2 ($p\text{CO}_2$) from Montañez et al. (2007). (G) Sea level change from Haq and Schutter (2008). (H) Spatial and temporal distribution of the main record of the late Paleozoic deglaciation for Paraná Basin, Southern Africa, India, and SE Asia, Eastern Africa, and Western Australia (Rosa and Isbell, 2021; Isbell et al., 2021). (I) Timing of volcanic activity (Sato et al., 2015; Torsvik et al., 2008; Zhang et al., 2009). (J) The trend of CIA* values in Yongcheng Basin in NCC (Yang et al., 2020).

tropical-subtropical during the sedimentary period of the Taiyuan Formation (Chen et al., 2001a), with precipitation of about 1000–4300 mm/yr. North China had a wet coal-forming climate during the Early Permian (Fu et al., 2016), and the trend of weathering may not be controlled by rainfall supply. Therefore, the correlation between surface chemical weathering and the land surface temperature of the Taiyuan Formation in the Western Shandong was likely unaffected by rainfall. The estimated global average physical erosion rates range from 10 to 20 m/Myr in the early Permian (Wilkinson, 2005). For the source region of our studied formation, the physical erosion rate could be relatively stable because no evidence of dramatic changes in tectonic uplift around the Western Shandong during the early Permian. It applies to the second condition. We also discussed the weak effect of sedimentary recycling and diagenesis on the compositional trends.

It is indicated that the τ_{Na} -MAT transformation equation can be used to calculate the land surface paleotemperature of the Taiyuan Formation in the Western Shandong. Using the interior of the NCC as an average source composition (Gao et al., 1998), the τ_{Na} of Taiyuan Formation samples in the Western Shandong ranges from -0.67 to -0.97 , with an average of -0.89 , which transforms to a MAT of 15.3 °C– 22.8 °C, with an average of 20.7 °C. And a warming of ~ 7 °C (15 °C to 22 °C) occurred in the upper part of Taiyuan Formation (early Asselian; numbered VA-I). A temperature increase of approximately ~ 5.5 °C (17.5 °C to 23 °C) occurred in the lower part of Taiyuan Formation (late Gzhelian; numbered VA-II) with indications of oscillations.

5.3. Implication for an early Asselian climate warming

A record of source weathering trends for the end-Carboniferous to early Permian in the Western Shandong in NCC provides evidence for an oscillating warm period (VA-II) during the Gzhelian and a significant warming event (VA-I) during the early Asselian. Yang et al. (2020) previously identified a warming event in the Yongcheng Basin equivalent to the VA-I event. However, Lu et al. (2021) did not find this warming event in the Liujiang Basin which is in the northeast of NCC. In this study, the zircon dating and sedimentation rate restricted the age of the warming event to approximately 298 Ma. The warming events in Yongcheng Basin were limited to about 298 Ma (Yang et al., 2020; Fig. 7J). Therefore, we conclude that the two warming events are the same event. In our study, a relatively warm event may have already been initiated in the late Gzhelian (VA-II; Fig. 6). The slight enrichment of Hg at ~ 955 m and ~ 985 m (VA-II) may be related to local and small-scale volcanic eruptions near our studied area, which have not caused recordable changes in paleoclimate as shown by CIA and $\delta^{13}C_{org}$ data. There is no more definitive evidence for this warming event, so VA-II will not be discussed in this study.

Modern surface soils in a supply-limited weathering regime tend to be chemically depleted to an extent (weathering intensity) largely controlled by precipitation and temperature (Riebe et al., 2004; Ferrier et al., 2016; Yang et al., 2020). Because there was a stable wet coal-forming climate in NCC during the early Permian (Tabor and Poulsen, 2008; Montañez and Poulsen, 2013; Yang et al., 2020), we can reconstruct land surface temperature from CIA and τ_{Na} . Using the CIA and τ_{Na} based transfer function (Yang et al., 2014; Yang et al., 2016), a reconstructed land surface temperature trend through the sampled succession suggests distinct warming of ~ 7 °C in the early Asselian, immediately followed by rapid cooling (Fig. 7A; Fig. 7B).

Coincidentally, there is a short-term rise in sea level in the earliest Asselian (Fig. 7H; Haq and Schutter, 2008). Moreover, conodont oxygen isotope ($\delta^{18}O$) values from South China suggest a $\sim 1\%$ increase and a subsequent decrease in the earliest Asselian (Fig. 7E; Chen et al., 2016), it showed a consistent pattern for the tropical sea water temperature change. In the record of global CO_2 , a peak in CO_2 still corresponds to the warming event in the Asselian (Fig. 7F; Montañez et al., 2007). Therefore, we received the same result as that of the conclusion of Yang et al. (2020).

The warming event in the early Asselian is also correlated with a spatial and temporal distribution of the main record of the late Paleozoic deglaciation and thus reflects significant deglaciation records in Paraná Basin, Southern Africa, India, and SE Asia, Eastern Africa, and Western Australia (Isbell et al., 2021; Rosa and Isbell, 2021). Although glaciation may have continued in the central and northern parts of the Paraná Basin, Antarctica, and Eastern Australia around 298 Ma (Isbell et al., 2008; Frank et al., 2015; Mottin et al., 2018), many sites show reduced glaciation at that time. A coincidence of deglaciation, increased CO_2 content, higher temperature and sea-level high stand likely defined a climate warm interval in the Asselian, which existed in the late Paleozoic maximum icehouse (Fig. 7).

In modern sediments, some sensitive element indicators are successfully applied to reconstruct paleoclimate (Gan et al., 2018; Mathews et al., 2020). The elements Sr, Cu, Ba, and Rb ratios are often used to analyze the paleoclimate characteristics (Lerman et al., 1995). Ratios of Sr/Ba indicate paleosalinity are used to investigate the paleoenvironment, while the ratios of Rb/Sr and Sr/Cu indicate paleoclimate. Sr/Cu ratio of 1.3–5.0 indicates warm and humid climate, and over 5.0 reflects drought conditions (Lerman et al., 1995). High Sr/Ba value represents high salinity, while low Sr/Ba value represents low salinity (Deng and Qian, 1993). High Rb/Sr value represents warm and humid climate, while low Rb/Sr value represents arid climate (Chen et al., 2001b). The increase of CIA indicates warmer and wetter climates (Nesbitt and Young, 1982). Therefore, normally the trends of Sr/Ba and Sr/Cu are opposite to CIA, while the trend of Rb/Sr is consistent with CIA. However, the results of the three elements proxies of samples from the Western Shandong are contrary to the expected conclusion (Fig. 4F; G; H). Perhaps the unnormal phoneme is affected by the paleogeographical environment in NCC, as high enrichment of Sr can not only be formed by concentrated deposition of lake water in arid and hot climates but also may be caused by transgression in warm and humid climates (Wang et al., 2009).

The transgressive events occurred in the late Paleozoic epicontinental basin of NCC (Li and Shan, 2000; Lv et al., 2011; Lv and Chen, 2014). In this study, we have analyzed sedimentary environments of samples from the Western Shandong by elements proxies. The relative contents of S, Ga, and Rb will change regularly from freshwater to seawater with different sedimentary environments (Degens et al., 1957; Zhang et al., 2021). Our sample reflects that the environment of the Western Shandong reached the salinity of the marine environment during the Late Paleozoic (Fig. 8A). B/Ga ratio of low 3.3 indicates continental facies, and over 4.4 reflects marine environment (Degens et al., 1957). And other sedimentologists also found Taiyuan Formation in the Western Shandong was in an epicontinental sea environment (Li and Shan, 2000; Lv and Chen, 2014; Lv et al., 2021). In this study, we arrived at this conclusion from the geochemistry characteristics (Fig. 8B). However, the B/Ga index needs to be combined with the geological background, as the inland saline lake environment is also characterized by high B/Ga (Zhang et al., 2021). Thus, combined with the changing trend of the CIA*, it can be determined that the Western Shandong is an epicontinental marine environment. The trend of Sr/Ba, Sr/Cu, and Rb/Sr are abnormal due to transgression, which is controlled by the sea level rose.

In the VA-I period (Early Asselian), the sea level rose due to the influence of climate warming, which led to increases of Sr/Cu and Sr/Ba values due to the influence of transgression in the Western Shandong. The shifts in $\delta^{18}O$ and $\delta^{13}C_{org}$, atmospheric pCO_2 , sea-level variations, distribution of the main record of the late Paleozoic deglaciation, and CIA of the Yongcheng Basin confirmed a climate warm interval during the early Asselian.

5.4. Volcanism and $\delta^{13}C_{org}$ values linked to atmospheric pCO_2 and paleoclimate

Mercury concentration has developed as a reliable proxy for the

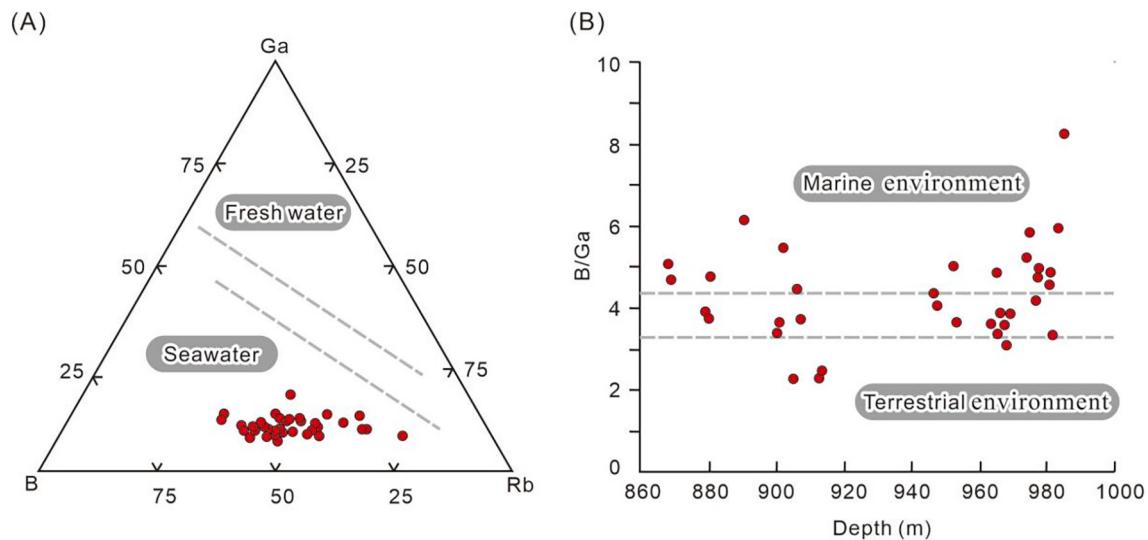


Fig. 8. Graphical analysis of the sedimentary environment. (A) Ternary diagrams of Ga-B-Rb for core Zk19-5S mudrock samples from the North China Craton (NCC), based on the method described by Yan et al. (1979). (B) Distributing disciplinarian of B/Ga in core Zk19-5S mudrock samples from the NCC (Degens et al., 1957).

evaluation of ancient volcanic fluxes (Grasby et al., 2019; Shen et al., 2019a; Shen et al., 2019b; Zhao et al., 2022). Volcanic emissions of Hg easily overwhelm the background detrital Hg during ancient large volcanic events (Pyle and Mather, 2003). The residence time of Hg in the atmosphere is long enough (0.5 to 2 yrs.; Selin, 2009) to be widely dispersed after major volcanism. Mercury in sediment can be adsorbed and removed quickly by organic matter and/or other minerals once deposited on the ocean surface (Zhao et al., 2022). Therefore, Hg can be used as a high-resolution volcanic proxy.

The record of terrestrial organic carbon isotopes is an effective proxy of the composition of CO₂ in ancient atmospheres (Wang, 2010; Turner, 2018; Vervoort et al., 2019). The eruptions and intrusions of volcanism will release significant amounts of Hg and comparatively isotopically heavy CO₂ (Javoy et al., 1984; Javoy et al., 1986), resulting in increasing atmospheric pCO₂ and Hg enrichment (Grasby et al., 2019; Vervoort et al., 2019). Magma can intrude into organic-rich sediments and release massive volumes of ¹³C-depleted CO₂ (−22‰), CH₄ (−60‰), and large amounts of Hg (Grasby et al., 2019; Vervoort et al., 2019; Lu et al., 2021). It would cause an increase of Hg enrichment and atmospheric pCO₂, with decreasing δ¹³C values in the atmosphere (McElwain et al., 2005; Hesselbo et al., 2007).

The volcanic intensity curve inferred from the Hg/TOC ratios is shown in Fig. 7D and includes a significant peak in volcanic activity, intervals of obvious volcanic activity during the early Asselian (Fig. 7D; Fig. 7I). Subsequent rapid warming (~298 Ma) in the earliest Asselian is indicated by the weathering trends in NCC and the δ¹⁸O data from South China (Fig. 7E). This warm event is associated with a rapid increase of atmospheric pCO₂ (Montañez et al., 2007) and a rise in short-term sea level (Haq and Schutter, 2008; Fig. 7H). Contemporaneous with coeval volcanism peak CIE-I in the study area (Fig. 7D), increases in atmospheric pCO₂ values (Fig. 7F; Montañez et al., 2007) show that the increased atmospheric pCO₂ and climate warming during the early Asselian. In the study area, a peak in volcanic activity corresponds to the negative excursion of δ¹³C_{org} (CIE-I), suggesting a common source in heating organic-rich sediments by magma intrusion (Shen et al., 2019a; Shen et al., 2019b). All of these indicate that the early Asselian warming is probably related to volcanism.

During the Pennsylvanian, volcanism was globally widespread. The worldwide climate warming event at the Permo-Carboniferous transition may correspond with the volcanism in the Skagerrak-Centered Large Igneous Province (LIP), northwest Europe, western Argentina (pre-Choiyoi magmatism), or northern margin of the NCC (Sato et al., 2015; Torsvik et al., 2008; Zhang et al., 2009; Fig. 7I). Although the

uncertainties on these compiled ages for these volcanic activities are larger, which need to be improved in the future. As a consequence of an imprecise timescale of these volcanic eruptions, the peak of Hg in this study is only a sudden trend, which may also indicate that Hg is the result of regional volcanic activities in North China Craton, or volcanic activities had not been recorded in such a short period. However, compared with other climate indicators around the world at the same time range (CIA, δ¹³C_{org}, δ¹⁸O, TOC, pCO₂, and sea-level variations), it is more likely to be a global volcanic activity caused warming event.

In conclusion, the above volcanisms may extend from the Late Carboniferous to the early Permian (Sato et al., 2015; Torsvik et al., 2008; Zhang et al., 2009). The LIP event with the CO₂ outgassing may have resulted in an increased release of voluminous CO₂ into the atmosphere, leading to a rapid rise in atmospheric pCO₂. Yang et al. (2020) estimated that the magma at the Skagerrak-Centered LIP may have released 1.4×10^3 Pg CO₂ by using a conservative volume estimate of $\sim 1.5 \times 10^5$ km³ for the erupted basalts in Skagerrak-Centered LIP (Neumann et al., 2004; Torsvik et al., 2008) and scaling based on data estimated for the Deccan basalts (Self et al., 2006). Obviously, this is only a rough estimate. It is difficult to quantify the amount of CO₂ emitted without knowing crucial information like the original volume, eruptive rate, and magmatic process of the LIP (Yang et al., 2020). The early Asselian warming event may be driven by several of the volcanic activities mentioned above, or unrecorded volcanic activity for a short period of time. Due to the lack of an accurate age constrain of volcanic eruption, it is difficult to confirm the certain volcanic activity, which needs to be refined in future study.

However, the atmospheric pCO₂ during the Permo-Carboniferous transition is relatively low (Montañez et al., 2007; Montañez et al., 2016) and would be sensitive to the change of magmatic CO₂ input (Yang et al., 2020). At the same time, the change of the Hg also confirmed the existence of volcanic activity during the warming event. Taken together, the release of CO₂ from volcanic events was a critical driver of climate warming in the early Asselian.

An immediately cooling after the early Asselian warming (~298 Ma - 297.5 Ma) is indicated by the weathering trends in NCC (Fig. 7). It may have been the result of rapid post-eruptional weathering of the recently formed basaltic rocks in the Skagerrak-Centered LIP, which would drive the indicated atmospheric CO₂ drawdown and promoted a return to cooler icehouse conditions (Yang et al., 2020; Lu et al., 2021).

6. Conclusion

- 1) One tuffaceous claystone horizon was dated using zircon U—Pb method, yielding ages of 301.3 ± 1.1 Ma. The new dates allow for a boundary of the Carboniferous-Permian for the target strata in the Taiyuan Formation from the Western Shandong to be developed. This age model combined with biostratigraphy tightly constrains the studied succession of the Taiyuan Formation within the late Gzhelian-Asselian (301.3 ± 1.1 Ma - 296.2 ± 1.1 Ma).
- 2) The trends in multiple chemical weathering indices are calculated from the geochemical composition of mudstones within the Taiyuan Formation to demonstrate climatic change in the West Shandong of NCC during the Permo-Carboniferous. The potential effects of provenance change, diagenesis, sedimentary recycling, and hydraulic sorting were excluded by using the specific chemical ratios through the interval. The published empirical relationship of the corrected chemical index of alteration (CIA*) and τ_{Na} with the temperature of the source region indicates the rapid onset of warming in the middle-upper part of the Taiyuan Formation, which is dated as early Asselian. The high-temperature interval is consistent with the warm events in Yongcheng Basin in southern NCC.
- 3) The initiation of the high-temperature event during the middle-upper Asselian was accompanied by the occurrence of major warm events. The trends coincide with temperature changes, shifts in $\delta^{18}O$, atmospheric pCO_2 , sea-level variations, distribution of the main record of the late Paleozoic deglaciation, and CIA of the Yongcheng Basin, which suggest the earliest Permian climate perturbation with a temperature maximum at ~ 298 Ma.
- 4) Hg/TOC ratios vary from 0.41 ppb/% to 448.3 ppb/% and include one obvious peak (VA-I) that recorded increased volcanic intensity during the early Asselian. $\delta^{13}C_{org}$ values vary from -22.4‰ to -28.2‰ (mean average = -23.96‰) and present a negative excursion. Hg/TOC ratios peaks of volcanic intensity VA-I coincide with the negative carbon isotope excursions (CIE-I) and also intervals of high atmospheric pCO_2 and the relatively high sea level. The study indicates that volcanism is a causal mechanism for increasing atmospheric pCO_2 and driving the global climate cycles through greenhouse gas emissions in the Paleozoic.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gloplacha.2022.103934>.

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