

## IS CHEMICAL INDEX OF ALTERATION (CIA) A RELIABLE PROXY FOR CHEMICAL WEATHERING IN GLOBAL DRAINAGE BASINS?

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**ABSTRACT.** The chemical weathering of silicate rocks in continents as an important sink of atmospheric CO<sub>2</sub> is of great significance for global environmental change. Rivers play a key role in earth surface processes and are regarded as the most important carrier of terrigenous materials into the sea. The chemical index of alteration (CIA) has been widely used as a proxy for chemical weathering in sediment source area. In this paper, the CIA values of suspended particulate matters from 44 rivers worldwide are recalculated. The CIA values vary significantly, with the highest average value occurring in African rivers and the lowest in North American rivers. The correlation analyses suggest that on a global scale the CIA is sensitive to land surface temperature, latitude at river mouth and soil depth in the drainage basins, but poorly correlated with drainage area, precipitation, average elevation and runoff. However, the CIA of the rivers draining east China are closely related to temperature, precipitation, latitude and runoff, primarily reflecting the dominant control of monsoon climate on chemical weathering in the catchments. It is therefore unrealistic to find a simple law of regulating chemical weathering in continents. The CIA actually reflects the integrated weathering history in the drainage basins and therefore, caution should be taken while using it as a direct and quantitative proxy for evaluating the intensity of instantaneous chemical weathering in continents.

### INTRODUCTION

Atmospheric CO<sub>2</sub> is one of the most important greenhouse gases and regulated largely by chemical weathering of silicate rocks in continents (Bernier and others, 1983; Raymo and Ruddiman, 1992; Suchet and Probst, 1993; Kump and others, 2000). Rivers, as an important carrier of terrigenous matters into the sea, play a key role in earth surface processes. Globally, physical erosion in drainage basins and suspended sediment discharges of major rivers in continents have been well documented. The total load of terrigenous suspended sediment into the sea transported by global rivers is estimated to be about  $13.5 \times 10^9$  tons/yr (Milliman and Meade, 1983). The mechanism and controls of chemical weathering in drainage basins, however, remain to be clarified (Gaillardet and others, 1999; West and others, 2005).

Many variables including geologic, climatic and topographic settings and even anthropogenic activity may potentially affect chemical denudation rates in continents (Gibbs, 1970; Stallard and Edmond, 1983; Meybeck, 1987; Grantham and Velbel, 1988). The search for causal links between weathering rates and geomorphological and/or climatic variables is obscured by the strong statistical correlations between the variables (for example, runoff, precipitation and temperature) (Blum and Erel, 1995; Gaillardet and others, 1999; West and others, 2005). The mechanism of chemical weathering processes revealed by previous studies, therefore, remains problematic and even controversial (Raymo and Ruddiman, 1992; White and Blum, 1995; Huh and Edmond, 1999; Gaillardet and others, 1999; Yang and others, 2004). Gaillardet and his group suggested that runoff is the most important driver of silicate chemical weathering, while the role of temperature is less clear, with a majority of rivers showing increasing weathering rates of silicates with increasing temperature, but a couple of rivers, especially the tropical lowland rivers, deviating from the global trend (Gaillardet and others, 1999). A simple model of how temperature and runoff driving silicate

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weathering has been established by Dupré and others (2003). Nevertheless, Oliva and others (2003) suggested that the positive impact of temperature on chemical weathering is obvious only when runoff is higher than 1000 mm/yr. Besides runoff and temperature, basin relief is regarded as another insensitive control of chemical weathering in catchments (White and Blum, 1995). Many studies argued that basin relief is also strongly coupled with both mechanical and chemical denudation rates, especially for those tectonic active areas, such as the Himalaya region (Raymo and Ruddiman, 1992; Dalai and others, 2002; Hren and others, 2007). The well-known “Uplift-Weathering Hypothesis” proposed that the uplift of large plateaus such as the Himalayas intensified the Asian monsoon, and the large amount of rainfall combined with steep relief and high mechanical erosion rates has resulted in intense chemical weathering, which finally consumed atmospheric CO<sub>2</sub>, thus weakening the global greenhouse effect and causing the growth of continent-spanning ice sheets at both poles over the past 40 million years (Raymo and Ruddiman, 1992).

Another remarkable finding is that a strong positive correlation exists between chemical weathering and physical denudation (Edmond and Huh, 1997; Gaillardet and others, 1999; Millot and others, 2002). Nevertheless, Yang and others (2004) argued that strong physical denudation in drainage basins is not always accompanied by intense chemical weathering, based on a case study on the Changjiang (Yangtze River) and Huanghe (Yellow River) sediments. Despite the extraordinarily strong soil erosion in the Loess Plateau of the Huanghe drainage basin, the soil depth in the catchment is generally shallower than that of the Changjiang valley. Grantham and Velbel (1988) suggested that the variation of CIA in rivers can also be attributed to differences in regolith exposure ages in the drainage basins.

Various geochemical proxies have been proposed to estimate the intensity of chemical weathering in continents (Duzgoren-Aydin and others, 2002; Price and Velbel, 2003). Some of them are based on dissolved loads in rivers, which directly indicate weathering status at present but cannot reflect an integrated weathering history (Grantham and Velbel, 1988; Johnsson and Stallard, 1989). Furthermore, correction is required considering that lithology and anthropogenic activity in the catchment may exert a strong influence on river water chemistry (Négrel and others, 1993; Gaillardet and others, 1999). In view of this, other geochemical indices, which focus on solid phase of rivers were proposed to investigate weathering intensity. The Chemical Index of Alteration (CIA) was pioneered by Nesbitt and Young (1982) to quantitatively evaluate weathering history recorded in sediments and sedimentary rocks. CIA is defined as  $Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O) \times 100$  (molar contents, with CaO\* being CaO content in silicate fraction of the sample). Over the last two decades, the CIA has been used for the evaluation of chemical weathering in specific drainage basins (McLennan, 1993; Vital and Statterger, 2000; Yang and others, 2004). McLennan (1993) found a negative correlation between sediment yield and weathering history, based on the CIA statistics of 16 rivers in the continents. Although a general pattern of CIA variations in different catchments has been proposed by his pioneering work, the implication and controls of CIA in fluvial sediments remain enigmatic. In this paper, we re-calculate the CIA values of suspended particulate matters from 44 rivers worldwide (fig. 1; table 1). In particular, the small rivers and circumpolar rivers that were largely neglected in McLennan's work are considered in the present study and compared with those large rivers. In addition, Chinese rivers will be discussed in more detail considering that these rivers have unique geology, geography and climate. The main objectives of this study are to reveal the differences among CIA values of global rivers and further to answer whether this proxy is applicable for evaluating chemical weathering intensity in drainage basins.

#### DATA SOURCES AND METHODS

In order to obtain a global pattern, we collected recently published geochemical data of 44 rivers from five continents (fig. 1). Details of these rivers, including drainage area, runoff, temperature, precipitation, sediment yield, average elevation and soil

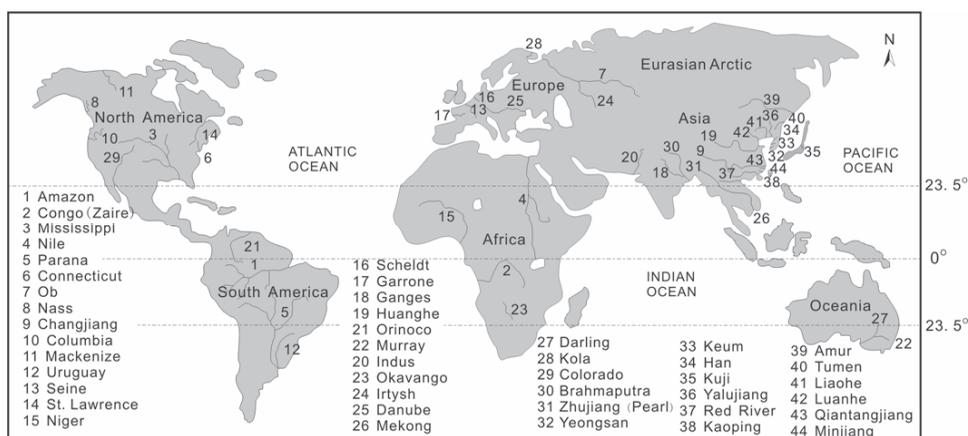


Fig. 1. A schematic map showing the major rivers worldwide selected for this study; numbers correspond to the river name as listed.

depth, are given in table 1. The total drainage area of these representative rivers is about  $42 \times 10^6 \text{ km}^2$ , occupying about 28 percent of the Earth's land area. The total sediment discharge reaches  $5720 \times 10^6 \text{ tons/yr}$ , about 31 percent of total suspended sediment flux into the sea (Milliman and Syvitski, 1992). It is well accepted that suspended particulate matter may better reflect the whole weathering history of source rocks within a specific drainage basin relative to the bank, floodplain and river bed sediments. To explore the weathering history of the whole basin, only the data of river samples taken from estuarine and delta areas or lower reaches were considered. One thing must be kept in mind: the rivers we present in this study cover highly variable basinal settings of climate, topography, hydrology and geology. Furthermore, different sampling and measuring methods were used by different authors. Uncertainty may also pertain to the measurements and statistics of climatic variables including mean values of temperature and precipitation over very extensive drainage areas (Velbel, 1993).

As shown above, the  $\text{CaO}^*$  used in the calculation of CIA refers to the amount of CaO incorporated in silicate fraction of sediments. Therefore, it is necessary to correct the measured CaO concentrations for  $\text{CaO}^*$  since most of the published CaO data are bulk concentrations. Due to the lack of  $\text{P}_2\text{O}_5$  and calcium carbonate contents for many river samples,  $\text{CaO}^*$  correction was only made by mole ratios of  $\text{Na}_2\text{O}/\text{CaO}$  for consistency according to the correction method proposed by McLennan (1993).

The CIA actually reflects changes in the proportion of feldspar and various clay minerals in the weathering product (Nesbitt and Young, 1982). It is well known that aluminous minerals such as kaolinite, gibbsite and beidellite are secondarily formed while Na- and Ca-bearing silicate minerals are significantly removed from the weathering profile during intense chemical weathering, resulting in high CIA values in the weathered sediments. As a consequence, CIA values of about 45 to 55 indicate virtually no weathering, whereas the value of 100 indicates intense weathering with complete removal of alkali and alkaline earth elements (McLennan, 1993). Nevertheless, Price and Velbel (2003) found that the CIA in the unweathered high-grade metamorphic rocks in the southern Appalachian Mountains may be as high as 65 to 88, and correspondingly, the eroded metasediments would have high CIA even without further chemical weathering before entering riverine environments.

## RESULTS AND DISCUSSION

### *Regional Variability of CIA Values among Global Rivers*

The concentrations of  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , CaO and  $\text{K}_2\text{O}$  in river sediments and calculated CIA values of global rivers are listed in table 2. The CIA values of global

TABLE 1  
*Geographic, climatic, and topographic characteristics of the world's major rivers*

Rivers	Latitude <sup>1</sup>	Drainage area <sup>2</sup> 10 <sup>3</sup> km <sup>2</sup>	Runoff <sup>3</sup> mm/yr	Temp. <sup>4</sup> °C	Prec. <sup>5</sup> mm/yr	Sediment yield <sup>6</sup> ton/km <sup>2</sup> /yr	Average elevation <sup>4</sup> m	Soil depth <sup>7</sup> cm	Sediment load <sup>3</sup> 10 <sup>9</sup> kg/yr
<b>North America</b>									
Mississippi	32.3	3270	150	13	760	64.2	661	214	210
Mackenzie	67.5	1810	170	-4	380	23.2	618	184	42
St. Lawrence	45	1030	435	4	890	3.9	271	210	4
Columbia	45.6	670	375	10	640	14.9	1293	232	10
Colorado	32.7	640	32	16	250	0.2	1537	176	0.1
Connecticut	43 <sup>8</sup>	25 <sup>9</sup>	570 <sup>9</sup>	8.3 <sup>9</sup>	1130 <sup>9</sup>	-	396 <sup>32</sup>	-	-
Nass	55.2	19.2 <sup>10</sup>	1000 <sup>10</sup>	2.5 <sup>10</sup>	1625 <sup>10</sup>	-	1000 <sup>10</sup>	-	-
<b>South America</b>									
Amazon	2	6150	100	27	2030	195	467	226	1200
Parana	32.7	2830	165	21	1140	27.9	557	228	79
Orinoco	8.1	990	1100	24	1400	152	373	228	150
Uruguay	31.4	240 <sup>3</sup>	604 <sup>17</sup>	-	1400 <sup>25</sup>	45.8	475 <sup>25</sup>	-	11
<b>Europe</b>									
Danube	45.2	810	250	10	760	82.7	501	154	67
Seine	49.3	43 <sup>11</sup>	164 <sup>17</sup>	12.5 <sup>11</sup>	550 <sup>11</sup>	-	100 <sup>11</sup>	-	-
Scheldt	51 <sup>8</sup>	22 <sup>12</sup>	-	-	813 <sup>26</sup>	-	-	-	-
Garrone	44.4	55 <sup>13</sup>	320	11.5 <sup>7</sup>	900 <sup>27</sup>	-	483 <sup>7</sup>	139	-
<b>Africa</b>									
Congo	4.3	3820	340	24	1520	11.3	751	-	43
Nile	29.7	2960	30	27	510	40.5	856	221	120
Niger	11.9	1210	160	29	1140	33.1	364	294	40
Okavango	19 <sup>8</sup>	192 <sup>14</sup>	-	-	-	-	400 <sup>14</sup>	-	-
<b>Eurasian Arctic</b>									
Ob	66.6	2500	130	-1	380	6.4	208	216	16
Irtysh	66 <sup>8</sup>	1643 <sup>15</sup>	-	0 <sup>23</sup>	275 <sup>23</sup>	9.3	120 <sup>23</sup>	-	15.2 <sup>34</sup>
Kola	69 <sup>8</sup>	3.85 <sup>16</sup>	-	-1 <sup>16</sup>	554 <sup>16</sup>	-	70 <sup>16</sup>	-	-
<b>Asia</b>									
Changjiang	30.8	1940	513 <sup>17</sup>	16	1100 <sup>18</sup>	261.2 <sup>36</sup>	1601	196	-
Ganges	24.5	493 <sup>17</sup>	470 <sup>17</sup>	21 <sup>5</sup>	2030	1055	890 <sup>5</sup>	153	520
Brahmaputra	25.2	510 <sup>17</sup>	879 <sup>17</sup>	15 <sup>5</sup>	2030	1059	2734 <sup>5</sup>	-	540
Indus	25.4	970	245	24	380	60.8	1807	92	59
Mekong	15.1	790	590	21	1270	203	875	210	160
Huanghe	35.2	770	55 <sup>17</sup>	13	460 <sup>18</sup>	2126.4 <sup>36</sup>	1860	179	-
Zhujiang	23.5	454 <sup>18</sup>	831 <sup>17</sup>	21	1550 <sup>18</sup>	205.87 <sup>36</sup>	670	198	-
Red river	22 <sup>8</sup>	120	1000	24	1520 <sup>28</sup>	1083	987	306	130
Yalujiang	42 <sup>8</sup>	61 <sup>19</sup>	491.5 <sup>36</sup>	8 <sup>36</sup>	930 <sup>18</sup>	73.68 <sup>36</sup>	-	-	-
Yeongsan	35 <sup>8</sup>	2.8 <sup>19</sup>	-	-	1222 <sup>29</sup>	443	280 <sup>33</sup>	-	1.24 <sup>35</sup>
Keum	36 <sup>8</sup>	9.9 <sup>19</sup>	-	-	1220 <sup>29</sup>	130	-	-	1.3 <sup>24</sup>
Kuji	36.5 <sup>8</sup>	1.49 <sup>20</sup>	-	-	1360 <sup>20</sup>	-	500 <sup>20</sup>	-	-
Han	37.5	26 <sup>19</sup>	-	-	1050 <sup>29</sup>	154	-	-	4 <sup>22</sup>
Kaoping	22 <sup>8</sup>	3	2700	24.7 <sup>37</sup>	3000 <sup>30</sup>	12000	2000 <sup>30</sup>	-	36
Amur	50 <sup>8</sup>	1855 <sup>18</sup>	180	-1	500 <sup>18</sup>	28	-	-	52
Tumen	43 <sup>8</sup>	33 <sup>18</sup>	270.5 <sup>36</sup>	5.3 <sup>36</sup>	570 <sup>18</sup>	-	-	-	-
Liaohe	45 <sup>8</sup>	229 <sup>18</sup>	49.55 <sup>36</sup>	7 <sup>36</sup>	470 <sup>18</sup>	246.54 <sup>36</sup>	-	-	-
Luanhe	39 <sup>8</sup>	44 <sup>18</sup>	106.7 <sup>36</sup>	8.25 <sup>36</sup>	560 <sup>18</sup>	513.59 <sup>36</sup>	-	-	-
Qiantangjiang	31 <sup>8</sup>	42 <sup>18</sup>	883.2 <sup>36</sup>	16.7 <sup>36</sup>	1600 <sup>18</sup>	156.76 <sup>36</sup>	-	-	-
Minjiang	27 <sup>8</sup>	61 <sup>18</sup>	992.7 <sup>36</sup>	18 <sup>36</sup>	1700 <sup>18</sup>	122.97 <sup>36</sup>	-	-	-

TABLE 1  
(Continued)

Rivers	Latitude <sup>1</sup>	Drainage area <sup>2</sup> 10 <sup>3</sup> km <sup>2</sup>	Runoff <sup>3</sup> mm/yr	Temp. <sup>4</sup> °C	Prec. <sup>5</sup> mm/yr	Sediment yield <sup>6</sup> ton/km <sup>2</sup> /yr	Average elevation <sup>4</sup> m	Soil depth <sup>7</sup> cm	Sediment load <sup>3</sup> 10 <sup>9</sup> kg/yr
<b>Oceania</b>									
Murray	34.6	1060	21	18	466 <sup>22</sup>	28.3	243	161	30
Darling	34 <sup>8</sup>	650 <sup>21</sup>	–	–	700 <sup>31</sup>	–	–	–	–

Temp. = temperature; Prec. = precipitation; – indicates no data available; Data without note are referred from caption's reference.

Data sources: 1. Dai and Trenberth, 2002; 2. Milliman and Meade, 1983; 3. Milliman and Syvitski, 1992; 4. Pinet and Souriau, 1988; 5. Summerfield and Hulton, 1994; 6. Sediment yield data are calculated based on drainage area and sediment load (McLennan, 1993); 7. Ludwig and Probst, 1998; 8. Estimated from Google earth software; 9. Canfield, 1997; 10. Gaillardet and others, 2003; 11. Roy and others, 1999; 12. Zwolsman and Eck, 1999; 13. Audry and others, 2006; 14. Mendelsohn and Obeid, 2004; 15. Vinokurov and others, 2005; 16. Pekka and others, 2004; 17. Gaillardet and others, 1999; 18. Chen and Wang, 1996; 19. Schubel and others, 1984; 20. Nagao and others, 2003; 21. Olley and Caitcheon, 2000; 22. Chang and Oh, 1991; 23. Pisarenko and others, 2001; 24. Yang and others, 2003; 25. Collischonn and others, 2005; 26. Billen and others, 2005; 27. Veyssy and others, 1999; 28. Pinet and Souriau, 1988; 29. Chough and Kim, 1981; 30. Chung and others, 2009; 31. Thoms and Sheldon, 2000; 32. Connecticut River Joint Commissions; 33. Nahm and others, 2008; 34. Lisitzina, 1974; 35. Hong and others, 2002; 36. Li, ms, 2003; 37. Lai, ms, 2003.

ivers vary between 48.2 and 89.9 with an average of 72.1, close to previous estimation of 71.6 to 75.5 (McLennan, 1993; Savenko, 2006; Viers and others, 2008). The average CIA value of African rivers reaches 83.4, higher than those in other continents, while North American rivers have the lowest CIA of 66.0 on average (fig. 2). The CIA values of Asian rivers average at 71.7, much closer to the world average of 72.1. Among these rivers, the Congo River in tropic Africa has the highest CIA of 89.9 whereas the Kola River in the Arctic area has the lowest of 48.2. Interestingly, the CIA value of a specific river may vary considerably depending on different studies. For example, the CIA of the Mississippi River varies from 61.5 to 81.5, with a standard deviation of about 10.5. The large variation of CIA may primarily arise from different sample characters (sample homogeneity) and analytic uncertainties in previous studies. Nevertheless, this study focused on the suspended particulate matters that were primarily collected from the river mouths and lower reaches, and hence, can overall represent the average compositions of weathered source rocks in the whole catchments.

According to the classification of weathering intensity by Nesbitt and Young (1982, 1984), these river sediments presented in this study constitute a broad and consistent spectrum of chemical weathering from early to late stages, while most of them belong to intermediate stage of silicate weathering. The Al<sub>2</sub>O<sub>3</sub>-(CaO\*+Na<sub>2</sub>O)-K<sub>2</sub>O (A-CN-K) diagram has been widely used to reflect silicate weathering trends (Nesbitt and Young, 1982). The ternary diagram distinctly indicates that African rivers more approach the Al<sub>2</sub>O<sub>3</sub> apex relative to other rivers, probably reflecting strong removal of Ca- and Na-bearing silicate minerals from the source rocks (fig. 3). Overall, the weathering trend is parallel to the A-CN line, which suggests that removal of Ca and Na (for example, plagioclase dissolution) dominates silicate weathering in these drainage basins, and K-bearing minerals remain less attacked. Nevertheless, some of African and Asian rivers do deviate the A-CN line and are somewhat parallel to the A-K line, revealing significant loss of K-bearing minerals during chemical weathering (fig. 3). It is noteworthy that despite variable weathering intensities registered in these river-borne sediments, most of the river samples seem to be weathered from similar parent rocks, which is close to the average composition of the upper continental crust (UCC, Taylor and McLennan, 1985; fig. 3). This observation again confirms the notion that the fine-grained suspended sediments of rivers, especially those large rivers, can reflect the average compositions of diverse source rocks in the specific catchment,

TABLE 2  
Major elemental concentrations and calculated CIA values of suspended particulate materials of global rivers

Rivers	Al <sub>2</sub> O <sub>3</sub> (%)	Na <sub>2</sub> O (%)	CaO (%)	K <sub>2</sub> O (%)	CIA	CIA- mean	References
<b>North America</b>						66.4	This study
Mississippi	15.49	0.75	1.47	1.92	77.2	73.4	Canfield, 1997
	17.38	0.53	2.11	2.05	81.5		Canfield, 1997
	11.50	1.36	2.37	2.51	61.5		McLennan, 1993
Mackenzie	13.26	0.50	7.92	2.25	76.4	74.4	Gaillardet and others, 1999
	15.70	0.32	5.35	4.53	72.5		McLennan, 1993
St. Lawrence	12.66	1.93	4.49	2.34	58.7	53.3	Gaillardet and others, 1999
	16.30	3.73	3.57	3.40	50.5		McLennan, 1993
	14.73	3.37	3.22	3.01	50.6		Martin and Meybeck, 1979
Connecticut	21.53	1.81	0.62	3.78	72.4	72.4	Canfield, 1997
Colorado	8.28	0.66	4.85	1.84	66.5	66.5	McLennan, 1993
Columbia	16.90	2.90	3.30	2.90	57.1	57.1	McLennan, 1993
Nass	13.86	1.98	0.85	1.78	67.3	67.3	Gaillardet and others, 2003
<b>South America</b>						75.5	This study
Amazon	14.60	1.10	1.10	2.20	70.9	74.9	Vital and Statterger, 2000
	22.90	1.11	2.36	2.28	78.9		McLennan, 1993
Parana	16.76	1.21	1.04	2.90	70.4	73.2	Depetris and Pasquini, 2007
	16.70	1.30	1.00	2.90	70.1		Depetris and others, 2003
	20.90	0.94	0.87	2.27	79.0		McLennan, 1993
Orinoco	11.30	0.65	0.57	1.16	77.0	74.8	Lewis and Saunders, 1989
	17.30	1.62	0.80	2.22	72.6		McLennan, 1993
Uruguay	17.73	0.69	1.40	0.97	84.2	80.3	Depetris and Pasquini, 2007
	14.22	0.97	1.32	1.12	76.4		Depetris and others, 2003
<b>Europe</b>						73.3	This study
Danube	12.10	2.38	6.39	2.51	53.4	53.4	McLennan, 1993
Seine	11.58	0.26	13.18	1.47	82.5	83.0	Gaillardet and others, 1999
	10.55	0.19	17.36	1.36	83.4		Roy and others, 1999
Scheldt	8.42	0.54	5.73	1.88	68.8	68.8	Zwolsman and others, 1999
Garrone	15.90	0.47	5.10	2.64	78.3	78.3	Audry and others, 2006
<b>Africa</b>						83.4	This study
Congo	25.10	0.32	1.34	1.64	89.9	89.9	McLennan, 1993
Nile	18.80	1.00	5.68	2.32	76.4	76.4	McLennan, 1993
Okavango	4.99	0.16	0.68	0.49	71.0	71.0	Huntsman-Mapila and others, 2005
Niger	21.31	0.46	0.72	1.95	85.4	89.8	Gaillardet and others, 1999
	30.90	0.13	0.48	1.36	94.2		McLennan, 1993
<b>Eurasian Arctic</b>						66.7	This study
Ob	8.17	0.53	1.97	1.08	73.7	73.7	Gordeev and others, 2004
Kala	55.65	13.75	25.76	13.38	48.2	48.2	Pekka and others, 2004
Irtys	11.60	0.49	1.80	1.51	78.1	78.1	Gordeev and others, 2004

TABLE 2  
(Continued)

Rivers	Al <sub>2</sub> O <sub>3</sub> (%)	Na <sub>2</sub> O (%)	CaO (%)	K <sub>2</sub> O (%)	CIA	CIA- mean	References
<b>Asia</b>						66.4	This study
Changjiang	15.96	0.94	3.78	2.74	72.5	77.0	Gaillardet and others, 1999
	15.45	0.09	4.05	2.46	83.8		Chen and Wang, 1996
	17.81	0.77	4.13	3.25	74.6		This study
Ganges	16.00	1.58	4.07	2.77	66.1	65.9	McLennan, 1993
	15.76	1.27	3.16	3.73	65.7		Singh and others, 2005
Indus	17.63	2.04	2.37	4.07	61.3	63.8	Ahmad and others, 1998
	15.40	1.48	12.50	2.73	66.3		McLennan, 1993
Mekong	15.92	0.77	3.05	2.66	74.6	77.1	Gaillardet and others, 1999
	22.30	0.74	0.87	3.04	79.5		McLennan, 1993
Huanghe	13.34	1.32	9.32	2.38	65.8	66.4	Gaillardet and others, 1999
	13.69	1.43	8.13	2.22	65.8		Chen and Wang, 1996
	10.63	1.19	6.78	2.23	62.7		this study
	17.30	1.05	6.62	3.25	71.2		McLennan, 1993
Red River	18.60	0.51	1.42	3.05	78.8	78.8	Gaillardet and others, 1999
Da River	23.08	0.35	0.52	3.84	81.3	81.3	Gaillardet and others, 1999
Zhujiang	8.84	0.32	0.81	0.98	80.6	82.4	This study
	20.99	0.47	1.83	2.22	84.1		Chen and Wang, 1996
Keum	22.78	0.97	0.78	3.34	77.4	76.4	Choi and Cho, 2001
	18.89	1.08	1.12	2.41	75.4		Cho, ms, 1994
Brahmaputra	19.08	1.48	1.06	3.31	70.5	70.5	Stummeyer and others, 2002
Kuji	15.90	0.91	1.47	1.61	77.0	77.0	Nagano and others, 2003
Yalujiang	13.69	1.31	3.25	3.46	63.0	63.0	Chen and Wang, 1996
Han	17.55	0.69	0.90	2.39	78.3	78.3	Choi and Cho, 2001
Yeongsan	21.48	0.92	0.66	3.19	77.7	77.7	Choi and Cho, 2001
Kaoping	10.52	1.23	1.27	2.05	62.7	62.7	Lai, ms, 2003
Amur	11.84	1.29	2.70	3.00	61.2	61.2	Chen and Wang, 1996
Tumen	13.62	1.17	2.81	3.09	65.4	65.4	Chen and Wang, 1996
Liaohe	12.84	1.25	4.21	2.60	64.9	64.9	Chen and Wang, 1996
Luanhe	11.24	1.37	3.57	2.95	59.3	59.3	Chen and Wang, 1996
Qiantangjiang	14.13	0.69	1.02	2.31	74.8	74.8	Chen and Wang, 1996
Minjiang	18.45	0.66	0.91	1.95	81.1	81.1	Chen and Wang, 1996
<b>Oceania</b>						77.1	This study
Murray	16.23	1.32	0.85	2.07	73.1	73.1	Douglas and others, 1995
Darling	20.20	0.92	1.08	1.56	81.1	81.1	Olley and Caitcheon, 2000
UCC	15.19	3.90	4.20	3.37		48.0	Taylor and McLennan, 1985
World rivers (44)	16.4	1.21	3.57	2.55		72.1	This study
World rivers (16)	17.98	1.33	3.84	2.60		71.6	McLennan, 1993
World rivers	16.47	0.96	3.63	2.04		75.5	Viers and others, 2008
World rivers	17.76	0.96	3.01	2.41		75.5	Martin and Meybeck, 1979
World rivers	16.30	1.11	3.64	2.59		71.7	Savenko, 2006

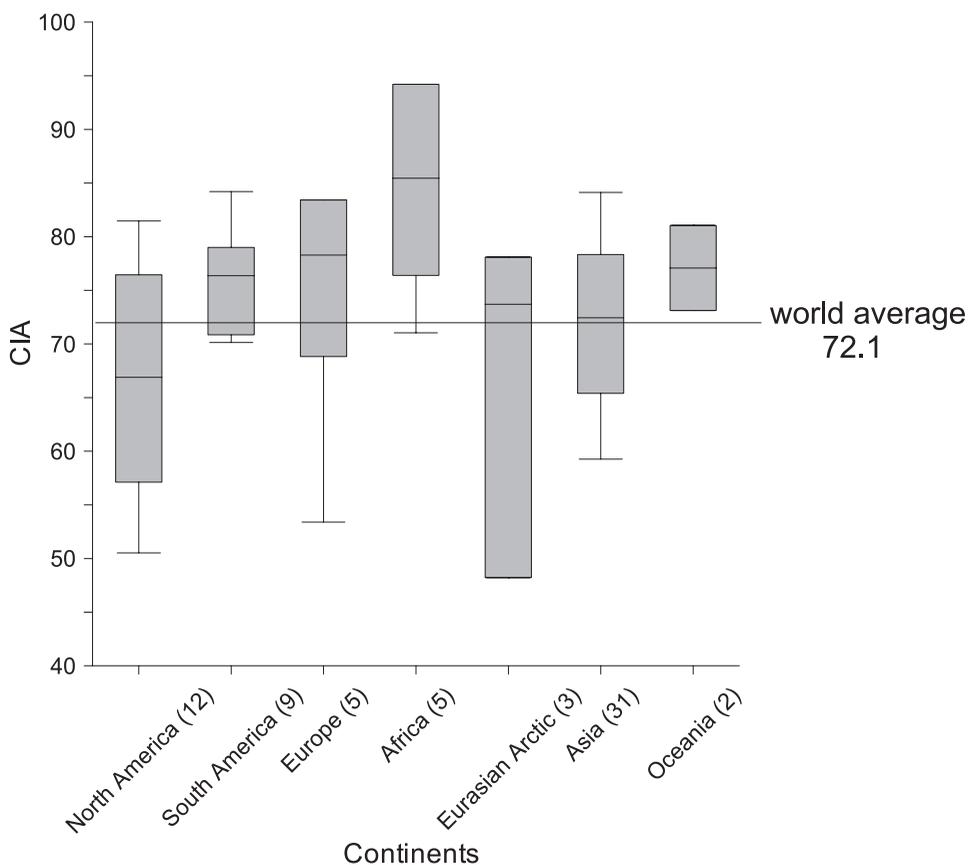


Fig. 2. Comparison of mean CIA values among the rivers from different continents. Numbers in brackets indicate the river samples referred.

and overall represent the weathered UCC (Taylor and McLennan, 1985; Yang and others, 2004).

#### *Constraints of CIA Variations Among Global Rivers*

As suggested above, chemical weathering in continents is basically controlled by many factors including source rock type, climate regime, tectonic and topographic settings, vegetation, soil development, and human activities as well. Many previous studies suggest that rock type plays an important, if not dominant role, on chemical denudation (Garrels and Mackenzie, 1971; Amiotte-Suchet and Probst, 1993; Bluth and Kump, 1994; Edmond and others, 1996; Price and Velbel, 2003). However, it is impossible to quantitatively define the influence of rock type on chemical denudation rate because of complicated and diverse compositions of source rocks in different drainage basins. Similarly, the effects of tectonic and topographic settings and vegetation on chemical denudation are difficult to determine considering much variable geological and geographical settings in the world's major catchments.

*Climatic constraint.*—Continental weathering is strongly coupled with climate and tectonics (Raymo and Ruddiman, 1992), and warm and humid climate generally favors strong chemical weathering (White and Blum, 1995). Velbel (1993) found that temperature alone is a dominant factor controlling differences in chemical weathering

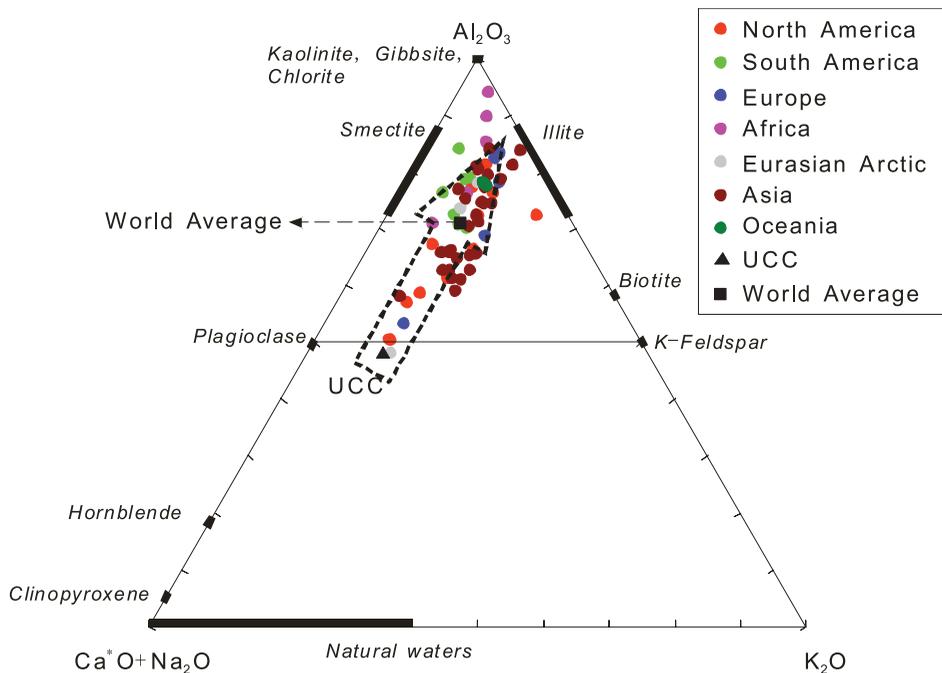


Fig. 3. The A-CN-K diagram of global rivers. Note that most of the investigated rivers show the similar weathering trend in parallel with the A-CN line.

rates while isolating the effects of any other factors. In this study, a negative correlation ( $R=-0.43$ , fig. 4A) between latitude at river mouth and CIA apparently suggests that the drainage basins in low latitudes are more sensitive to chemical weathering than those in the high latitudes. Correspondingly, a positive correlation ( $R=0.46$ , fig. 4B) is clearly observed between temperature and CIA. Therefore, land surface temperature can be regarded as an important control of continental weathering (Gaillardet and others, 1999), which to a great extent explains why tropical African rivers generally have higher CIA values than the rivers in Eurasian Arctic region and North America (fig. 2). Furthermore, these two correlation coefficients can reach as high as  $-0.57$  and  $0.64$  if the Mackenzie, Ob, and Irtysh rivers were excluded. These three rivers are all located at high latitude. The very low temperature and cryogenic processes in the high latitudes may cause a unique weathering environment (Huh and others, 1998). These findings are in agreement with the long-held view that chemical weathering is not active at high latitude areas (Curtis, 1990). The weathering mechanism and patterns in arctic/subarctic areas may be quite distinct from those in the relatively well-studied hot and humid tropics (Huh and others, 1998). Oliva and others (2003) observed a similar correlation between land temperature and chemical weathering, although they suggested that the positive influence of temperature is remarkable only when runoff is higher than  $1000 \text{ mmyr}^{-1}$ . It should be noted that the average temperature used in this study can vary significantly in a specific catchment, for example, from  $0$  to  $25 \text{ }^\circ\text{C}$  for the Amazon River basin (Gaillardet and others, 1999), and from  $-4$  to  $18 \text{ }^\circ\text{C}$  for the Changjiang drainage basin.

Although precipitation is another important climatic parameter, its effect on chemical weathering, has seldom been considered in previous studies. Pinet and Souriau (1988) argued that precipitation is one of the most important factors that control weathering rate in the catchments, based on the contents of dissolved ions in river water. Our study reveals a poor correlation between CIA and annual precipitation

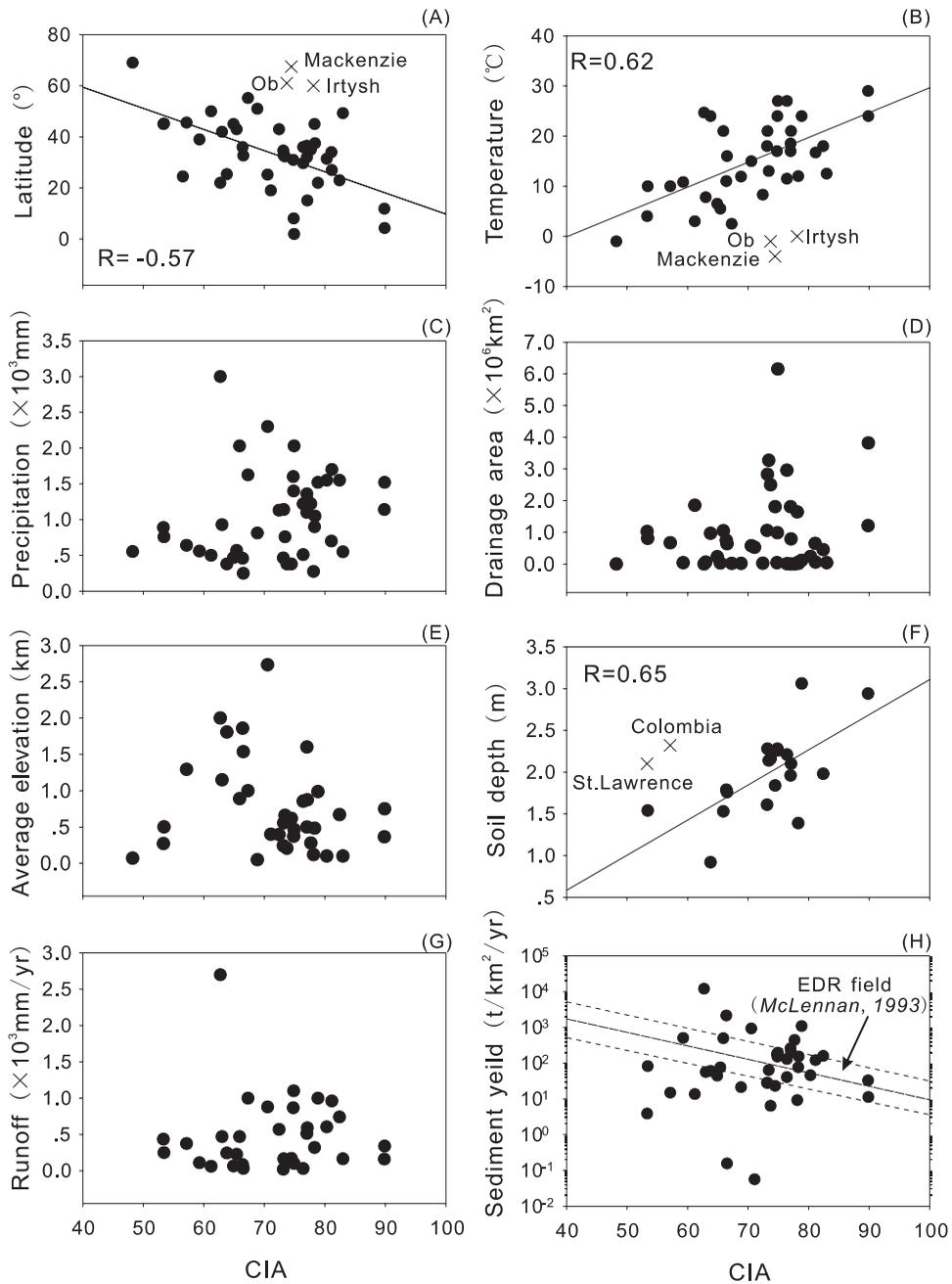


Fig. 4. Correlations of the CIA values with geographic, climatic, topographic and hydrological parameters of global rivers. The EDR (equilibrium denudation regions) field defined by the dashed line was proposed by McLennan (1993).

(fig. 4C). There is no doubt that precipitation can provide aqueous solution for weathering reactions. However, reactive solutions involved in weathering processes are not simply determined by precipitation. It can be complicated by many factors, like

precipitation infiltration and groundwater mobility. The equilibrium saturation state of feldspar hydrolysis is also of great influence on weathering reactions (Velbel, 1989).

*Geographic and topographic constraints.*—Drainage area seems to be poorly related with weathering intensity, which can be seen from the scattered data in figure 4D. Nevertheless, large drainage basins span wide ranges of climatic, geographic and topographic environments, and the suspended particulate matters in these rivers undergo well-mixed weathering processes, which result in the CIA values more close to the world average.

Analogous poor correlation between average elevation and CIA (fig. 4E) probably implies that chemical denudation in the drainage basin is either not sensitive to elevation, which has early been proven by Gaillardet and others (1999). Although no obvious relation is found, the regions with rapid tectonic uplift, steep channel slopes, and high stream power, for example the Himalayan and Tibetan areas, do reveal a distinct weathering pattern (Raymo and Ruddiman, 1992; Dalai and others, 2002; Hren and others, 2007). Generally, rapid surface uplift and exhumation result in frequent exposure of fresh rocks and thus, increase chemical weathering rates (Raymo and Ruddiman, 1992). Together with heavy monsoonal precipitation, high rates of chemical weathering occur along the southern and eastern Himalayas (Sarin and others, 1989; Galy and France-Lanord, 2001). Therefore, for a given precipitation and temperature, tectonic uplift may be an important regulator of chemical weathering, particularly in areas where supply-limited or transport-limited weathering prevails (Carson and Kirkby, 1972; Stallard and Edmond, 1983; Riebe and others, 2003; West and others, 2005). Nevertheless, topographic/tectonic effect on chemical weathering is only regional, rather than a global pattern.

As particulate matter in rivers is predominantly derived from soils, the degree of chemical weathering is expected to be consistent with global soils distribution (Grantham and Velbel, 1988; Curtis, 1990; Summerfield, 1991). A good positive correlation ( $R=0.65$ ) between soil depth and CIA (fig. 4F) ignoring the rivers at high latitudes, such as the St. Lawrence and Colombia Rivers, implies that thick soils may have long residence time for water and can allow weathering reactions to reach chemical equilibrium, which consequently leads to a high CIA value (Gaillardet and others, 1999).

*Hydrological constraint.*—Besides temperature, runoff is also widely accepted as an important control of silicate weathering (Grantham and Velbel, 1988; Pinet and Souriau, 1988; Summerfield and Hulton, 1994; Ludwig and Probst, 1998; Gaillardet and others, 1999; West and others, 2005). However, the poor correlation between runoff and CIA (fig. 4G) suggests that runoff is not a dominant control of chemical weathering in drainage basins. It is noteworthy that most of the previous estimates of chemical weathering rate are based on ionic compositions of river water, which may be closely related to runoff. The CIA calculated from sediment chemistry, however, as suggested above, is not a direct indicator of chemical weathering rate in the present catchment, but a proxy of indicating integrated weathering history (recycled sediment) during the formation of sediment.

Previous attempts to estimate weathering rate rely heavily on measurements of sediment yield. McLennan (1993) had constructed a simple model to correlate sediment yield with CIA values of 16 rivers from different continents. According to this model, rivers with sediment yields varying within a factor of  $\pm 3$  uncertainty for a given CIA value belong to equilibrium denudation regions (EDR), while the others belong to the nonequilibrium denudation regions (NDR). In our study, 44 rivers are considered, and it is obvious that most rivers are located in the NDR field rather than EDR (fig. 4H). This implies that the correlation between sediment yield and CIA value is not as simple as previously thought, especially when more rivers are considered. These rivers are widely distributed in five continents, with much variable lithological, topo-

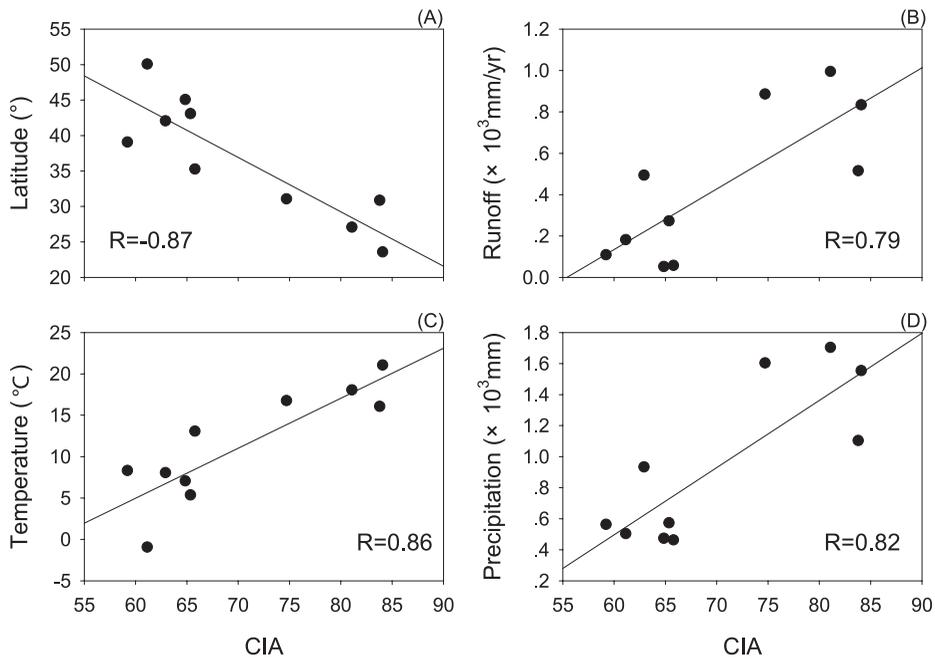


Fig. 5. Correlations of the CIA values with land surface temperature, latitude, precipitation and runoff of major rivers in China.

graphical and climatic conditions, which probably result in a great uncertainty according to this simple model.

#### *CIA Variations In Chinese Rivers*

As discussed above, the controlling of CIA variations among different drainage basins is quite complex, and no simple parametric laws can be deduced on a global scale. Yang and others (2004) studied silicate weathering in the Changjiang and Huanghe drainage basins and proposed that climate is the predominant control, while source rocks and relief are subordinate. Regional case studies on major rivers in China, therefore, may provide more direct links between CIA and climatic, tectonic, topographic and hydrological constraints.

With highlands in the west and plains in the east, almost all of the major rivers in mainland China flow eastward into the East Asian marginal seas. A total of 10 large rivers in eastern China, namely, from north to south (fig. 1), the Amur, Tumen, Yalujiang, Liaohe, Luanhe, Huanghe (Yellow River), Changjiang (Yangtze River), Qiantang, Min, and Zhujiang (Pearl River), were considered for CIA calculations. The basins of these rivers, accounting for about 50 percent of the total land area of China, cover a wide spectrum of physical geographical zones from cold snowy forest climate and dark brown earth in the northeast to moist subtropical-tropical climate and red earth in the southeast (Chen and Wang, 1996).

Unlike the global pattern, the CIA variations among Chinese rivers reveal some unique characters. The CIA of Chinese rivers exhibit much higher correlations with latitude ( $R = -0.87$ ), temperature ( $R = 0.86$ ), precipitation ( $R = 0.82$ ) and runoff ( $R = 0.79$ ), than those of global rivers (figs. 3 and 5). The three largest drainage basins of the Huanghe, Changjiang and Zhujiang span the giant landform structure of China with three-grade relief terraces, that is, highlands with an average elevation above 2000 m in

the west and low-lying plains with an average elevation below 500m in the east. The other rivers with relatively small catchments are all located in eastern China and the coastal plains where rivers meet the sea. They have a mean elevation of less than 50 m. On the other hand, almost all these Chinese rivers originate in the west and flow eastward to the sea, in parallel with the latitude. Consequently, these river basins span different climatic zones including frigid, warm temperate, temperate, subtropic, and tropic zones from north to south, which are of typical continental climate regime and influenced by East Asian monsoon to different extents. The distinct climatic zones in these river basins may result in variable chemical weathering processes that have been registered in the river-borne suspended materials. The river basins in the south and low latitudes where stronger summer monsoon brings more precipitation and high runoff, are subjected to more intense chemical weathering than those in the north where monsoonal precipitation is minor. Therefore, the CIA of Chinese rivers can better reflect the basinal climate than those of the world's other rivers, despite much variable geological, geographical and hydrological settings of these rivers. In other words, chemical weathering in Chinese river basins is more sensitive to continental climate, rather than other controls such as basin area, source rock types, and water and sediment discharges.

#### CONCLUSIONS

A total of 44 rivers worldwide were selected for the calculation of chemical index of alteration (CIA) of suspended particulate matter, with an aim to present a general view of CIA variations in global rivers and to determine its controls on global and regional scales. The mean CIA value of global rivers is 72.1, with a large range from 48.2 (Kola River in Arctic area) to 89.9 (Congo River in tropic Africa). Overall, the CIA values of African rivers are higher than those in other continents, while North America rivers have the lowest CIA on average. According to the definition of CIA, these investigated rivers constitute a broad and consistent spectrum of chemical weathering from early to late stages, while most of them belong to intermediate stage of silicate weathering, shown by large loss of Ca- and Na-bearing silicate minerals from source rocks. Most of the river samples seem to be weathered from the similar parent rocks, close to the average composition of the upper continental crust, despite variable weathering intensities registered in these river-borne sediments.

Chemical weathering in continents is controlled by many factors including source rock type, climate regime, tectonic and topographic settings, vegetation, soil development, and human activities as well. The correlation analyses suggest that on a global scale CIA is sensitive to land surface temperature, latitude at river mouth and soil depth in drainage basins. No significant correlations exist between CIA and drainage area, precipitation, runoff and elevation. However, the CIA variations of the rivers draining east China are closely related to temperature, precipitation, latitude and runoff. Different CIA variations on global and regional scales imply that chemical weathering in the drainage basins are constrained by complicated factors. It is difficult, if not impossible, to find a simple law of regulating chemical weathering in continents, given that chemical weathering is dominated by a complicated combination of all parameters rather than a single constraint. Nevertheless, chemical weathering in major drainage basins in China are more climatic limited, primarily due to the dominance of monsoon climate within these latitudinal drainage basins. One thing to keep in mind is that the CIA actually reflects the integrated weathering history, rather than present weathering intensity in the drainage basins as revealed by ionic compositions of river water. Therefore, caution should be taken while using CIA as a direct and quantitative proxy for instantaneous chemical weathering intensity, although it indicates the variability of continental weathering from a global perspective or from a long geologic history.

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