

Reply to interactive comments on “Temporary and net sinks of atmospheric CO₂ due to chemical weathering in subtropical catchment with mixing carbonate and silicate lithology” (bg-2019-310)

Responses to Anonymous Referee #1:

Thank you for your time and sincere evaluation for our manuscript. Thank you very much for your constructive comments, and they are very useful for improving our manuscript. We have revised the manuscript according to the suggestions and comments, and the responses to questions one by one are as follows.

Responses to the questions:

Question 1: During the calculation of chemical weathering rates, the authors ignore the anthropogenic origins of major ions except for SO₄²⁻, show reasons.

Answer 1: Thank you for your question.

There are two reasons.

(1) Two main characteristics of much polluted rivers are that TDS is greater than 500 mg/L and the Cl⁻/Na⁺ molar ratio is greater than that of sea salts (about 1.16) (Cao et al., 2016; Gaillardet et al., 1999). The TDS in the study area ranged from 73.79 to 230.16 mg·L⁻¹ and the low TDS implied that the anthropogenic origins of major ions could be ignored in the study. However, the Beijiang River is characterized as a typical region suffered from severe acid deposition (Larssen et al., 2006) and active mining area (Li et al., 2019). The acid deposition and acid mining discharge contribute to the highest concentration of SO₄²⁻.

(2) Natural origin of SO₄²⁻ is the dissolution of evaporite, such as gypsum, while no evaporite was

found in the study area. If SO_4^{2-} comes from the gypsum dissolution, the ratios of Ca^{2+} and SO_4^{2-} should be close to 1:1. The stoichiometric analysis showed that the ratio of Ca^{2+} and SO_4^{2-} deviated from 1:1 and also proved this point (Fig.11 in the manuscript and also showed below). The two reasons have been added in the lines 141-152.

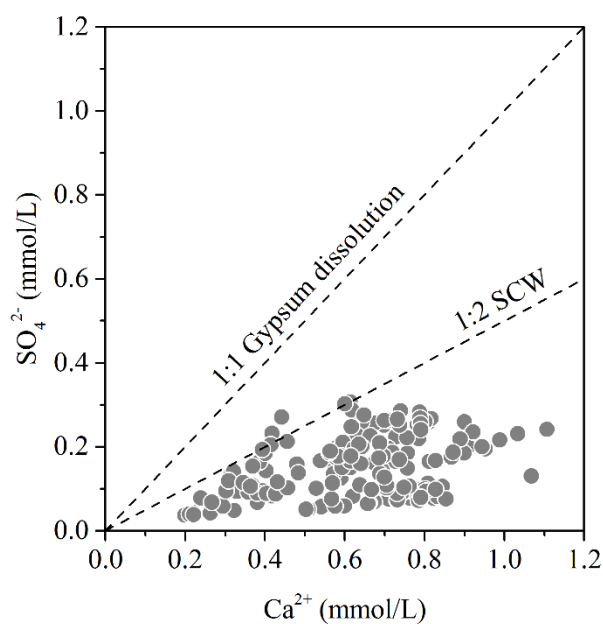


Fig.11 Stoichiometric relationship between Ca^{2+} and SO_4^{2-}

Question 2: Part 5.1 is too long, may be it is a good idea to separate it into two parts.

Answer 2: Thank you for your suggestion. The part 5.1 has been separated into two parts: 5.1.1 Chemical weathering rates and 5.1.2 Factors affecting chemical weathering. The modified part was showed in lines 327 and 371.

Question 3: Unify the reference format throughout the paper

Answer 3: Thank you for your suggestion. The format of reference has been modified throughout the paper.

Responses to the specific comments:

Comment 1: Lines 36-37, “regulating the atmosphere-land-ocean fluxes and earth’s climate”

should be “regulating the atmosphere-land-ocean carbon fluxes and earth’s climate”

Answer 1: Thanks a lot. It has been modified in the lines 37-39.

Comment 2: Lines 38-39, delete the “A profound case in point”

Answer 2: Thanks a lot. It has been modified in the lines 41-44.

Comment 3: Lines 54, delete “because”

Answer 3: Thanks a lot. It has been modified in the lines 56-57.

Comment 4: Lines 56, delete “(sulfide oxidation)”

Answer 4: Thanks a lot. It has been modified in the lines 58-59.

Comment 5: Lines 93, change into “it covers an area of 52068 km²”

Answer 5: Thanks a lot. It has been modified in the lines 95-96.

Comment 6: Lines 129 delete “According to the principle of the mass balance”

Answer 6: Thanks a lot. It has been modified in the line 134.

Comment 7: Lines 245 change into “chemical compositions”

Answer 7: Thanks a lot. It has been modified in the lines 264.

Comment 8: Lines 282-284, “Nov”, “Jun” and “Feb” should give full names.

Answer 8: Thanks a lot. It has been modified in the lines 304-307.

Comment 9: Line 289, “It is” should be “It was”.

Answer 9: Thanks a lot. It has been modified in the lines 312-313.

Comment 10: Lines 450-451, Equations are not labeled a Eq. number.

Answer 10: Thanks a lot. It has been modified in the lines 469-470.

Comment 11: Lines 466, “SCW” should give a explain in the Fig. 11

Answer 11: Thanks a lot. It has been modified in the lines 485-486.

Comment 12: Line 485, “The result of CCR_{Total} , CCR_{CCW} , CCR_{CSW} and CCR_{NET} were summarized in Table 4” should be “The results of CCR_{Total} , CCR_{CCW} , CCR_{CSW} and CCR_{NET} are summarized in Table 4”.

Answer 12: Thanks a lot. It has been modified in the lines 505.

Comment 13: Line 514, “significant influence” should be “significant influences”.

Answer 13: Thanks a lot. It has been modified in the lines 540-541.

Comment 14: Line 518, “Runoff manly controlled” should be “Runoff mainly controlled”.

Answer 14: Thanks a lot. It has been modified in the lines 545-546.

Comment 15: Lines 530-531, How human activities induced sulfur acid deposition altered the CO₂ sinks, increased or decreased?

Answer 15: Thank you for your question. In addition to the chemical weathering induced by H₂CO₃, sulfuric acid (H₂SO₄) of anthropogenic origins produced by sulfide oxidation such as acid deposition caused by fossil fuel burning and acid mining discharge (AMD) also becomes an important chemical weathering agent in the catchment scale. Many studies have shown the importance of sulfide oxidation and subsequent dissolution of other minerals by the resulting sulfuric acid at catchment scale (Hercod et al., 1998; Spence and Telmer, 2005). Depending on the fate of sulfate in the oceans, sulfide oxidation coupled with carbonate dissolution could facilitate a release of CO₂ to the atmosphere (Spence and Telmer, 2005), the carbonate weathering by H₂SO₄ plays a very important role in quantifying and validating the ultimate CO₂ consumption rate.

Responses to Anonymous Referee #2:

Thank you for your time and sincere evaluation for our manuscript. Thank you very much for your constructive comments, and they are very useful for improving our manuscript. We have revised the manuscript according to the suggestions and comments, and the responses to questions one by one are as follows.

Question 1: I understand that the authors have collected abundant data in different sampling stations

and seasons. However, I have serious concerns over the description of the data and calculation methods. For example, the mass and chemical parameters of rainwater are not provided, and I couldn't assess the results.

Answer 1: Thank you very much for your suggestion about data of rainwater. We attach the major ions concentrations of rainwater in Table S1 in the supplementary material. We also refer this point in the lines 139-140 in the manuscript. We also present the data of rainwater here.

Table S1 The major ions concentrations of rain water samples at 5 hydrological stations in the Beijiang River (mean±SD).

Hydrological stations	Na ⁺ (μmol/L)	K ⁺ (μmol/L)	Ca ²⁺ (μmol/L)	Mg ²⁺ (μmol/L)	Cl ⁻ (μmol/L)	SO ₄ ²⁻ (μmol/L)	NO ₃ ⁻ (μmol/L)
XGLs	12.8±9.7	21.0±16.8	22.2±20.5	10.9±10.3	25.9±22.6	320.2±370.7	83.3±85.2
XSs	20.4±11.8	7.8±4.5	86.9±30.4	10.1±5.2	10.0±0.0	606.5±511.5	36.3±23.4
Yds	16.3±9.5	10.1±10.8	161.1±56.5	9.0±7.8	23.9±12.4	136.9±169.5	143.1±135.5
FLXs	18.8±12.3	3.2±2.5	31.1±17.7	4.2±2.7	23.1±16.6	45.4±27.5	77.1±70.4
SJs	12.6±9.2	12.5±16.3	22.9±13.8	15.4±18.1	25.4±16.0	79.0±79.8	156.7±206.4

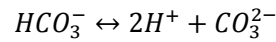
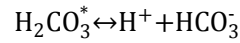
Question 2: There are no information about analytical errors.

Answer 2: Thank you very much for your suggestion. Reference, blank and replicate samples were employed to check the accuracy of all the analysis and the relative standard deviations of all the analysis were within ±5%. The ionic charge balance defined by the equation of $\frac{meq(\text{sum of cations}) - meq(\text{sum of anions})}{meq(\text{sum of cations and anions})}$ of the water samples was less than 5%. The modified part was in the lines 125-131.

Question 3: The authors seem to confuse alkalinity, DIC, and [HCO₃⁻], which have totally different definitions (although I understand that these parameters are similar at pH 8 in the river waters, HCO₃⁻ is the main topic of this paper and the authors should calculate and explain accurately).

Answer 3: Thank you very much for your question. The definitions of alkalinity, DIC, and $[\text{HCO}_3^-]$ are different. The alkalinity describes the acid neutralizing capacity. It is determined by titrating with acid down to a pH of about 4.5. Equal to the concentrations of $[\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$ (mmol/L) in most samples. DIC is the abbreviation of the dissolved inorganic carbon and is defined as the sum of $[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ in water samples. In this study the alkalinity is determined by titration in situ.

The DIC which is defined as the sum of $[\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ can be calculated by using the $[\text{HCO}_3^-]$, water temperature (T) and pH measured in the field according to the equation as follows:



$$K_1 = \frac{[\text{H}^+] \times [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]} = 10^{(-1.1 \times 10^{-4} \times T^2 - 0.012T - 6.58)}$$

$$K_2 = \frac{[\text{H}^+] \times [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{(-9 \times 10^{-5} \times T^2 + 0.0137T - 10.62)}$$

In addition, for all the samples, the pH values ranged from 7.5 to 8.5 with an average of 8.05. Under this pH conditions, the major species of DIC is HCO_3^- (Fig.C1). Based on our calculation, H_2CO_3^* and CO_3^{2-} only account for less than 5% in all sampling sites, so we use the concentrations of HCO_3^- (mmol/L) to represent the DIC in this study.

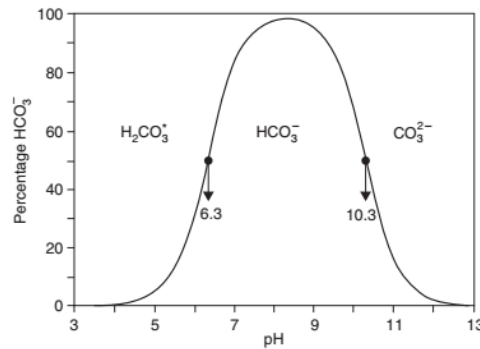


Fig.C1 Percentage of HCO_3^- of total dissolved carbonate as function of pH (Appelo and Postma,

Question 4: Are the chemical parameters of the river (and relevant calculation results) weighted average over 12 months?

Answer 4: Thank you very much for your question. In this study, the chemical parameters of river water in Table 1 in the paper were the flow-weighted average over 12 months. For every sampling station, the flow-weighted average of ion concentration can be expressed as followed equation:

$$[X]_{average} = \frac{\sum_{i=1}^{n=12} [X]_i \times Q_i}{\sum_{i=1}^{n=12} Q_i}$$

Where $[X]$ is denotes the elements of the elements of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- in $\text{mmol} \cdot \text{L}^{-1}$. Q denotes average monthly discharge in $\text{m}^3 \cdot \text{s}^{-1}$. The subscripts i denotes 12 months from January to December. Also, we add this information in the lines 267-270 in the manuscript. For the relevant calculation results, we did the calculations using month data and sum the month results to obtain the year result by equation (15), (16) and (17) in the lines 178-183 in the manuscript.

Question 5: What kind of methods do the authors use to calculate the area of silicate/carbonate outcrops or river water discharge?

Answer 5: Thank you very much for your question. The area of silicate/carbonate outcrops was calculated by hydrological module of ArcGIS based on geology map from provided by China Geological Survey. The data of river water discharge was provided by the local hydrology bureau. The information has been added in the lines 254-257.

Question 6: The background of this study is unclear, and the authors should provide more basic information. What is "hyperactive region"?

Answer 6: Thank you for your question.

(1) Explanation of background: As described in the Introduction, from the view of the global carbon cycle, the CO₂ consumption due to carbonate weathering is recognized the “temporary” sink, while the consumption of CO₂ during the chemical weathering of silicate rocks has been regard as the net sink of CO₂ and regulates the global carbon cycle. Thus in carbonate-silicate mixing catchment, it is essential to distinguish proportions of the two most important lithological groups, i.e., carbonates and silicates, and evaluate the net CO₂ sink due to chemical weathering of silicate. In addition to the chemical weathering induced by H₂CO₃, sulfuric acid (H₂SO₄) of anthropogenic origins produced by sulfide oxidation such as acid deposition caused by fossil fuel burning and acid mining discharge (AMD) also becomes an important chemical weathering agent in the catchment scale. Depending on the fate of sulfate in the oceans, sulfide oxidation coupled with carbonate dissolution could facilitate a release of CO₂ to the atmosphere, the carbonate weathering by H₂SO₄ (sulfide oxidation) plays a very important role in quantifying and validating the ultimate CO₂ consumption rate. Thus, under the influence of human activities, the combination of silicate weathering by H₂CO₃ and carbonate weathering by H₂SO₄ controlled the net sink of atmospheric CO₂.

The Pearl River includes three principal rivers: the Xijiang, Beijiang, and Dongjiang Rivers. The three river basins have distinct geological conditions. The Xijiang River is characterized as the carbonate-dominated area and the Dongjiang River has silicate as the main rock type. While the Beijiang River, which is the second largest tributary of the Pearl River, is characterized as a typical carbonate-silicate mixing basin. In addition, as the serve acid deposition and active mining area, chemical weathering induced by sulfuric acid make the temporary and net sink of atmospheric CO₂ to be reevaluated. These two points make the study area is representative.

(2) About the “hyperactive region”

According to the work of (Meybeck et al., 2006), the global coastal catchments were classified into eight classes based on the yields of riverine material by the COSCAT data set. In order to facilitate the visualization, mapping and comparison of river fluxes for any given material, the authors normalize all yields (Y_i) to their global average (Y^*). If the values of normalized yields Y_i/Y^* is between 5 and 10, the catchment is called the “hyperactive region”. Based on the calculation (Meybeck et al., 2006), the Pearl River is the “hyperactive region”.

Question 7: I recognize that Beijiang River is a major tributary of the Pearl River, but this river is relatively small compared to other world major river such as Amazon or Changjiang River. How does this river contribute the global carbon cycle?

Answer 7: Thank you very much for your question. Although the Beijiang River is not as large as Amazon or Changjiang River, the study of chemical weathering and CO₂ sink in the Beijiang River can represent the carbon source and sink of such a river basin to some extents. In addition, the information of chemical weathering and CO₂ sink in the Beijiang River can also provide scientific evidence for global carbon cycle. The reasons why we chose the Beijiang River for our study area are that (1) The Beijiang River is characterized as a typical carbonate-silicate mixing basin, however, little study investigated chemical weathering and CO₂ sink in such a mixing basin which has a different mechanism of chemical weathering compared to river basins with a simple lithology (carbonate or silicate dominant). (2) The Beijiang River is located in the subtropical area in South China, the warm and wet climatic conditions make the Beijiang River a hyperactive region in China. Water discharge and chemical weathering is highly seasonal due to the warm and humid summer

monsoon and the cool and dry winter monsoon. (3) The Beijiang River is the second largest tributary of the Pearl River, and it covers a basin of 52 068 km². The study of chemical weathering and CO₂ sink of the Beijiang River Basin is a supplement to the study of carbon cycle of the Pearl River which is the second largest river in China in terms of discharge volume.

Question 8: In addition, I have no idea why the authors compared total chemical weathering rate with latitude.

Answer 8: Thank you very much for your question. Based on the work of (Meybeck et al., 2006) and other researchers, the chemical weathering rate shows significant spatial trend. Generally it is found that the riverine output of materials is large in the low latitude area due to large runoffs (Fig.C2). So in this study, we compared total chemical weathering rate with latitude to give further evidence to support the conclusion.

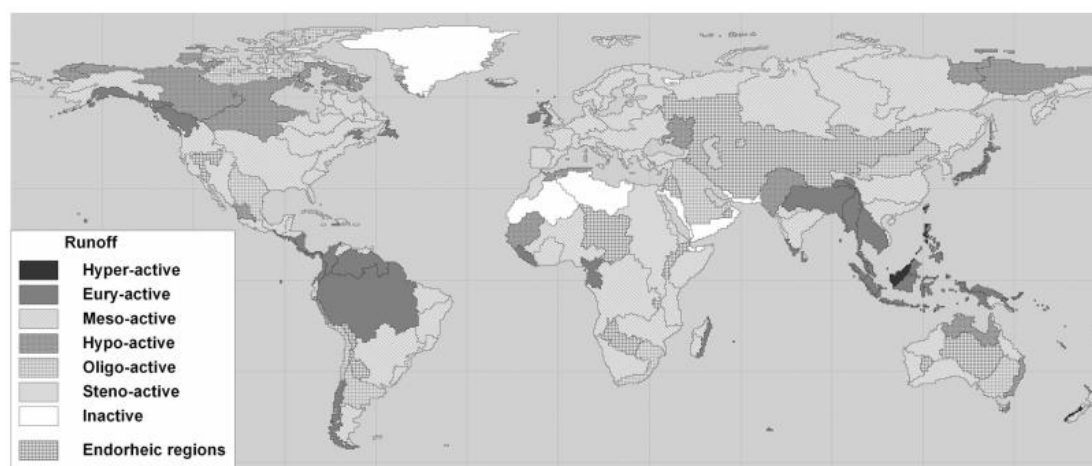


Fig.C2 Relative runoff for COSCATs related to mean annual runoff for the exorheic realm (Meybeck et al., 2006)

Question 9: Furthermore, there are also some previous studies about the Pearl River and its

tributaries, some of which have already taken into consideration anthropogenic weathering in some way. Do the author's HCO_3^- -basis calculation methods and their results make a difference?

Answer 9: Thank you very much for your question. Based on our calculation method, the results in this study have compared with other Chinese rivers, as well as the Xijiang River which is the largest tributary of the Pearl River (see Lines 486-492 in Section 5.2.2). The total of CO_2 consumption rates CCR was $823.41 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$ in the Beijiang River and was $960 \times 10^3 \text{ mol km}^{-2} \text{ a}^{-1}$ in the Xijiang River. The total of CO_2 consumption rates in our study area showed little lower than that in the Xijiang River of the previous study.

In addition, some previous studies calculated the DIC apportionment based on the carbon isotope of DIC, however, our study calculated the DIC apportionment based on mass balance and HCO_3^- concentration, the difference of these two methods will discuss in our other paper. Actually, this manuscript is focused on (1) the chemical weathering rate and the controlling factors on chemical weathering processes, and (2) the temporary sink of CO_2 and the influence of sulfide oxidation on net sink of CO_2 by DIC apportionment procedure. Thank you very much for your attention to our studies, we hope our study can provide further information for global carbon cycle studies.

Question 10: I think the last section in discussion is too descriptive. I also have a concern that temporary and net sink of CO_2 show large spatial variations, but in the discussion, the authors mentioned these values only in the SJs station (lowermost part).

Answer 10: Thank you very much for your suggestion. Actually, SJs station is the lowest station of the Beijiang River, which can represent the temporary and net sink of CO_2 of the whole river basin. In addition, the CO_2 net sink of each sub basin were also different and show large spatial variations

due to heterogeneity of geology and human activities. The geology showed weak correlation with the CO₂ net sink (Fig. 1a), while the SO₄²⁻ have negative correlation with the CO₂ net sink (Fig. 1b). It proved that human activities (sulfur acid deposition and AMD) dramatically decreased the CO₂ net sink and even make chemical weathering a CO₂ source to the atmosphere. We have added this part in the lines 517-520.

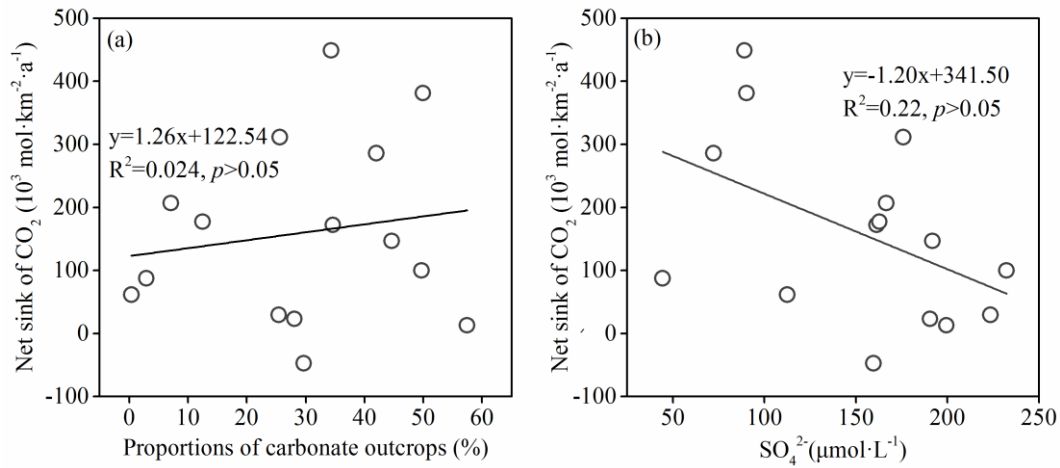
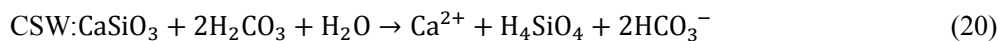
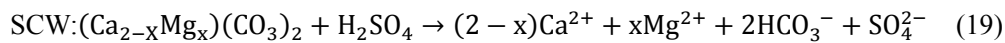
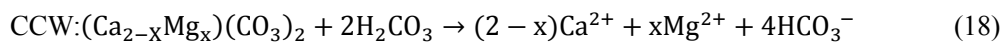
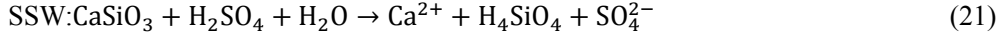


Fig. 1 Correlations between CO₂ net sinks and proportions of proportions of carbonate (a) and correlations between CO₂ net sinks and SO₄²⁻ (b)

Question 11: As shown in equation (21), silicate weathering by sulfuric acid does not affect the concentrations of HCO₃⁻ in the river. However, in equation (23) and (24), [SO₄²⁻]_{ssw} seemed to be described as $\alpha_{CSW} \times \alpha_{SCW} / \alpha_{CCW} \times [\text{HCO}_3^-]_{\text{riv}}$. Would you please explain this calculation?

Answer 11: Thank you very much for your question. Firstly, we are very sorry for that there are two equations numbered (23). We have changed numbers in the revision manuscript. In other to explain clearly for this question, we present some of equations as followed.





Where CaSiO_3 represents an arbitrary silicate.

(1) If we do not use the equation (22) and (23) as followed, just two equations (24) and (26) can get based on mass balance, however, we have three unknowns (α_{CCW} , α_{SCW} and α_{CSW}). Thus, we have a hypothesis, according to the studies of (Galy and France-Lanord, 1999) and (Spence and Telmer, 2005), carbonate and silicate weathering by carbonic acid in the same ratio as carbonate and silicate weathering by sulfuric acid, the mass balance equations are followed:

$$[\text{SO}_4^{2-}]_{\text{riv}} - [\text{SO}_4^{2-}]_{\text{pre}} = [\text{SO}_4^{2-}]_{\text{SCW}} + [\text{SO}_4^{2-}]_{\text{SSW}} \quad (22)$$

$$[\text{SO}_4^{2-}]_{\text{riv}} - [\text{SO}_4^{2-}]_{\text{pre}} = \alpha_{\text{SCW}} \times [\text{HCO}_3^-]_{\text{riv}} \times 0.5 + \frac{\alpha_{\text{CSW}} \times \alpha_{\text{SCW}}}{\alpha_{\text{CCW}}} \times [\text{HCO}_3^-]_{\text{riv}} \quad (23)$$

Where the subscripts CCW, SCW, CSW and SSW denotes the four end-members defined by carbonate weathering by carbonic acid, carbonate weathering by sulfuric acid, silicate weathering by carbonic acid and silicate weathering by sulfuric acid, respectively. The parameter α denotes the proportion of DIC derived from each end-member processes.

(2) According to the above equations (22) and (23), we can get a further equation (25) as followed.

$$[\text{Ca}^{2+}]_{\text{car}} + [\text{Mg}^{2+}]_{\text{car}} = \alpha_{\text{CCW}} \times [\text{HCO}_3^-]_{\text{riv}} \times 0.5 + \alpha_{\text{SCW}} \times [\text{HCO}_3^-]_{\text{riv}} \quad (24)$$

$$[\text{SO}_4^{2-}]_{\text{SCW}} + [\text{SO}_4^{2-}]_{\text{SSW}} = \alpha_{\text{SCW}} \times [\text{HCO}_3^-]_{\text{riv}} \times 0.5 + \frac{\alpha_{\text{CSW}} \times \alpha_{\text{SCW}}}{\alpha_{\text{CCW}}} \times [\text{HCO}_3^-]_{\text{riv}} \quad (25)$$

$$\alpha_{\text{CCW}} + \alpha_{\text{SCW}} + \alpha_{\text{CSW}} = 1 \quad (26)$$

(3) Combing the equations (24), (25) and (26), the proportions of HCO_3^- derived from three end-members (CCW, SCW and CSW) can be calculated, and the DIC (equivalent to HCO_3^-) fluxes by different chemical weathering processes are calculated by following equations.

$$\text{DIC}_{\text{CCW}} = \alpha_{\text{CCW}} \times [\text{HCO}_3^-]_{\text{riv}} \quad (27)$$

$$\text{DIC}_{\text{SCW}} = \alpha_{\text{SCW}} \times [\text{HCO}_3^-]_{\text{riv}} \quad (28)$$

$$\text{DIC}_{\text{CSW}} = \alpha_{\text{CSW}} \times [\text{HCO}_3^-]_{\text{riv}} \quad (29)$$

Reference

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