

Rock chemical weathering by sulfuric acid: pathway, method and prospect

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Abstract To investigate the role of sulfuric acid-based carbonate weathering in global CO₂ sequestration of climate changes, we systematically discussed the pathway of sulfuric acid in rock chemical weathering and its feedback mechanism for global warming. We showed the methods used to determine the accurate amount of sulfate flux, accounting for the sulfuric acid resulted from sulfide oxidation. Finally, we pointed out some prospects for further detailed work on the exact calculation of the sulfate fluxes for the CO₂ net-release.

Keywords Chemical weathering · Sulfuric acid · Global climate change · Sulfate isotope

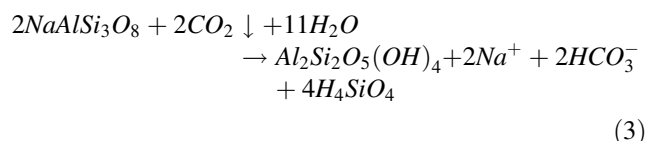
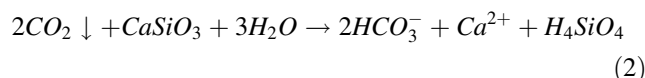
1 Pathway

The level of atmospheric CO₂ is an important issue for global warming. The atmospheric/soil CO₂ consumption by rock chemical weathering causes negative feedback (Walker et al. 1981). On geological time scales (Multimillion years, Ma), chemical weathering of silicate rocks has a key role in regulating the level of atmospheric CO₂ (Hartmann et al. 2009). Atmospheric/soil CO₂ consumption by rock weathering is

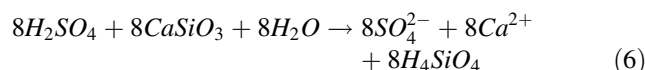
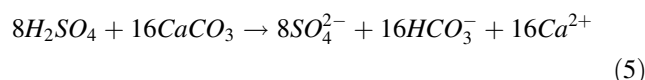
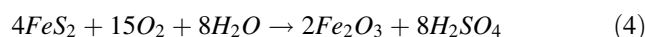
estimated to be 258–288 Mt C a⁻¹ at present day of which silicate weathering proportions range from 49% to 60% (Amiotte Suchet et al. 2003; Gaillardet et al. 1999).

There are two distinctive pathways of rock chemical weathering associated with atmospheric/soil CO₂ sequestration (Beaulieu et al. 2011; Calmels et al. 2007; Li et al. 2008; Spence and Telmer 2005).

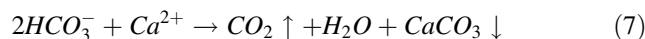
1.1 Carbonic acid-based weathering



1.2 Sulfuric acid-based weathering



When dissolved constituents of these reactions are transported to the oceans by river water, carbonate minerals will be precipitated along with the release of CO₂ as shown in Eq. 7:



Because the residence time of bicarbonate (HCO₃⁻) in the ocean is estimated to be 0.083 Ma, carbonate

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weathering and deposition must be balanced on roughly the same time scale ($\sim 10^5$ year) (Hartmann et al. 2009). Over this time scale, carbonic acid-based weathering of carbonate rocks has no net-sink of consumed atmospheric CO_2 (Eqs. 1 and 7). However, calcium feldspar and albite have nearly 50% and 100% net-sink of consumed atmospheric CO_2 (Eqs. 2, 3 and 7), respectively (Hartmann et al. 2009).

The marine residence time of SO_4^{2-} (10 Ma), (Beaulieu et al. 2011) is two orders of magnitude greater than that of HCO_3^- (0.1 Ma). Therefore, the rate of removal of SO_4^{2-} is slow compared to the rate of removal of HCO_3^- and sulfuric acid-based weathering of carbonate rocks has a net-release of CO_2 into the atmosphere (Eqs. 5 and 7) (Beaulieu et al. 2011). However, sulfuric acid-base weathering of calcium feldspar and albite has no effect on the balance of atmospheric CO_2 sequestration (Eq. 6).

Therefore, sulfuric acid-based weathering of carbonate rocks has a long-term effect on the amount of atmospheric CO_2 and has an important role in global warming. Considering this aspect, many researchers have conducted studies to illustrate the mechanism of this process by laboratory and field experiments (Beaulieu et al. 2011; Calmels et al. 2007; Han et al. 2010; Li et al. 2008, 2011).

2 Methods

To accurately define this sulfuric acid-based weathering and determine the consequence for global CO_2 sequestration, two key methods have often been used to identify the source of sulfuric acid in river water and calculate the proportion of sulfuric acid responsible for the net-release of CO_2 .

2.1 Forward modeling

The initial purpose of forward modeling is to calculate the accurate contribution of silicate weathering in atmospheric CO_2 sequestration (Gaillardet et al. 1999), but we can also use this modeling to obtain the ratio of sulfate from sulfuric acid in river water. The principle of forward modeling is that dissolved components in river water are all derived from dissolution of carbonate rocks, silicate rocks, atmospheric wet deposition, sulfide oxidation, gypsum, and anthropogenic effluents as described in Eq. (8):

$$[X]_{\text{River}} = [X]_{\text{Carbonate}} + [X]_{\text{Silicate}} + [X]_{\text{Sulfide}} + [X]_{\text{Gypsum}} + [X]_{\text{Anthropogen}} + [X]_{\text{Atmosphere}} \quad (8)$$

where $[X]$ represents the dissolved components in river water. Atmospheric wet deposition constituents should be confirmed first to calculate the other components. After we obtained the actual rainwater chemical compositions in background station, we calculated the exact ratios of

respective component concentrations in rainwater to chloride (Cl^-) concentration because of its conservative behavior. The ratios were chosen to quantify the contribution of rainwater into river water as discussed below.

It was assumed that chloride in river water was totally derived from atmospheric deposition, halite, and anthropogenic activities. The head stream of river water had less anthropogenic activities, so if there was no obvious halite existing, chloride could be assumed to only be derived from atmospheric wet deposition. Other components from atmospheric deposition in river water could be calculated by the ratios to chloride (Table 1). After calculating the contribution of atmospheric deposition, other contributions could similarly be determined by ratios within different sources (see below Table 1).

It is worth to note that atmospheric deposition has different ion ratios at different stations due to variable geology and climate (Table 1), so only the local rainwater ratios could be used to verify the contribution of rainwater to river water. Based on different ratios of dissolved sulfate compared to sodium (Na) in different sources, contributions of sulfate ions in river water from atmospheric deposition, sulfide, and gypsum could be obtained. Therefore, the net-release of CO_2 could be calculated as Eq. (9):

$$\text{CO}_2\text{-Sulf-carb} = 0.5[\text{HCO}_3]_{\text{Sulf-carb}} = [\text{SO}_4]_{\text{Sulf}} \quad (9)$$

2.2 Dual sulfate isotopes

The dual sulfate isotope method is very beneficial in identifying the sources of sulfate in river water and is valid in many rivers in the world (Brenot et al. 2007; Calmels et al. 2007; Li et al. 2011, 2013, 2015; Otero et al. 2008; Yuan and Mayer 2012). To exactly determine contributions of sulfuric acid from oxidation of sulfide minerals and SO_2 , the sulfate from dissolution of gypsum and agriculture fertilizers must be excluded. Sulfur and oxygen isotopes of gypsum usually have values from +10‰ to +30‰ and from +10‰ to +20‰, respectively (Calmels et al. 2007). Agriculture fertilizers have wide sulfur and oxygen isotope values due to the application of sulfide and gypsum minerals (Zhang et al. 2015a), so local fertilizers must be sampled to know the range of dual sulfate isotope values. Sulfide minerals also have a wide range of sulfur isotope compositions from -20‰ to +10‰ (Calmels et al. 2007) but obviously different from those of gypsum, which allows us to calculate the contribution of sulfide oxidation as in the following equations:

$$[\text{SO}_4]_{\text{River}} = a * [\text{SO}_4]_{\text{Atmosphere}} + b * [\text{SO}_4]_{\text{Sulfide}} + c * [\text{SO}_4]_{\text{Gypsum}} \quad (10)$$

$$\delta^{34}\text{S}_{\text{River}} = a * \delta^{34}\text{S}_{\text{Atmosphere}} + b * \delta^{34}\text{S}_{\text{Sulfide}} + c * \delta^{34}\text{S}_{\text{Gypsum}} \quad (11)$$

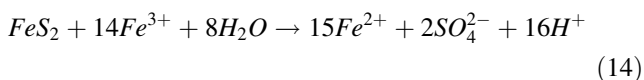
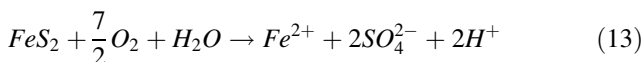
Table 1 Common used ratios for different sources during forward modeling

Ratios	Evaporites ^a	Carbonates ^a	Silicates ^a	Anthropogenic ^a	Atmospheric ^a	Atmospheric ^b
Ca/Na	0.17 ± 0.09	50 ± 20	0.35 ± 0.5	0.00	2 ± 1	4.18 ± 2.58
Mg/Na	0.02 ± 0.01	20 ± 12	0.2 ± 0.1	0.00	0.7 ± 0.3	0.69 ± 2.58
K/Na	0.00	0.00	0.17 ± 1	0.2 ± 1	0.4 ± 1	0.44 ± 0.23
Cl/Na	1.00	0.00	0.00	2 ± 2	1 ± 1	0.92 ± 0.52
NO ₃ ⁻ /Na	0.00	0.00	0.00	4 ± 1	1 ± 0.5	0.94 ± 0.43
SO ₄ ²⁻ /Ca	1.00	0.00	0.00	0.00	/	/
SO ₄ ²⁻ /Na	0.00	0.00	0.00	5.95	/	3.03 ± 2.04

^a From Li et al. (2014)^b From Zhang et al. (2015b)

$$1 = a + b + c \quad (12)$$

where a , b , c parameters are individual proportions of atmospheric, sulfide and gypsum sulfate, and the sum of a , b , c is equal to 1. The sulfate concentration and the dual isotope compositions of atmospheric deposition could be determined by annual sampling or references from nearby meteorological stations. Dual isotope compositions of gypsum often fall into a narrow range scale (e.g. +16‰ and +12‰ for sulfur and oxygen isotopic values of gypsum in Yalong River Basin, (Li et al. 2014)). It is worth noting that sulfide oxidation has two distinctive pathways illustrated as Eqs. 13 and 14 (Calmels et al. 2007; Li et al. 2014):



Sulfate derived from Eq. 13 was expected to have heavier oxygen isotope values, but those from Eq. 14 tended to have lighter oxygen isotope values due to $\delta^{18}O$ of O₂ being generally heavier than that of H₂O.

With the above equations, we could calculate the accurate proportion of sulfate from sulfide oxidation, and then the CO₂ net-release from carbonate weathering by sulfuric acid could also be obtained by Eq. 9.

3 Results

We have summarized the calculations of CO₂ net-release into atmosphere by sulfuric acid in carbonate weathering and compared it to the CO₂ consumed by carbonate and silicate weathering by carbonic acid (Table 2).

From Table 2, it was found that in some river basins the amount of CO₂ net-released from carbonate weathering by sulfuric acid exceeded the amount of CO₂ consumed by silicate weathering by carbonic acid, e.g. Qin River,

Wuyang River, Nanpan River, Jinshajiang, Lancangjiang and Nujiang. In some silicate-dominated areas, the amount of CO₂ net-released from sulfuric acid-based carbonated weathering was less than the amount of CO₂ consumed by carbonic acid-based silicate weathering due to the lack of carbonate rocks. Although most of the results in Table 2 were calculated by forward modeling and the results may have some uncertainties, it still could be believed that the amount of CO₂ net-released from carbonate weathering by sulfuric acid was considerable and should be seriously reassessed when balancing the global CO₂ sequestration.

3.1 Prospect

It is a vital step to accurately identify sulfuric acid derived from sulfide oxidation by forward modeling or dual sulfate isotope for global CO₂ sequestration. However, sulfate behaviors are very complicated in river systems, and several important aspects are not well understood yet and more attention must be paid to:

3.1.1 Spatial and temporal variations of dissolved sulfate sources in river water

Dissolved sulfate has different sources in different seasons during which the atmospheric deposition and groundwater supply appear to have significantly variable characteristics. Detailed sampling should be considered, e.g. once a month, to more accurately determine the sulfate flux derived from sulfide oxidation to the ocean.

3.1.2 Further study on the behavior of DIC during sulfuric acid-based carbonate weathering

Many studies have used the carbon isotope of DIC to determine the process of sulfuric acid in carbonate weathering. If the carbon in DIC was derived from carbonate rocks, carbon isotope values of DIC should show more positive than the average value of DIC derived from carbonic acid and carbonate. However, variations of carbon

Table 2 CO₂ sequestration by carbonic acid and sulfuric acid

River	Flow 10 ⁸ m ³ year ⁻¹	Basin 10 ⁴ km ²	CO ₂ sequestration/10 ⁹ mol C year ⁻¹			References
			Silicate–carbonic acid	Carbonate–carbonic acid	Carbonate–sulfuric acid	
Carbonate-dominated						
Qin River	5.2	1.35	0.04	1.93	0.85	Zhang et al. (2015b)
Yalong River	603.6	12.84	11.81	36.08	8.47	Li et al. (2014)
Wujiang River	376.0	6.68	6.55	45.56	6.75	Han and Liu (2004)
Wuyang River	35.7	0.65	0.70	5.71	1.31	Han and Liu (2004)
Qingshui River	111.0	1.71	2.31	10.82	2.07	Han and Liu (2004)
Nanpan River	0.78	5.7	4.10	35.00	10.03	Liu et al. (2008)
Beipan River	2.09	2.64	3.38	19.32	2.26	Liu et al. (2008)
Jinshajiang River	394.0	22.9	7.79	32.06	16.72	Tao et al. (2015)
Lancangjiang River	290.0	8.6	10.15	21.24	25.89	Tao et al. (2015)
Nujiang River	531.0	11.3	15.82	25.09	48.25	Tao et al. (2015)
Silicate-dominated						
Nenjiang River	225.0	29.70	12.18	10.10	0.89	Liu et al. (2013)
Second Songhuajiang	169.0	7.34	9.40	10.28	1.76	Liu et al. (2013)
Songhuajiang	733.0	55.70	37.32	29.52	2.79	Liu et al. (2013)
Han River-summer	625.4	26.4	430.32	300.96	49.37	Shin et al. (2011)
Han River-winter	135.2	26.4	32.47	85.27	11.09	Shin et al. (2011)

isotope values of DIC in river are very complicated and the positive changes could be induced by many factors, e.g. CO₂ outgassing from over-saturation of carbonate, CO₂ outgassing from oxidation of organic carbon, and CO₂ releasing from organic acid-based weathering. As we found in the Qin River Basin, river water mixed with much sewage water often had more positive carbon isotope values because of organic acid-based weathering not because of sulfuric acid-based carbonate weathering (see Zhang et al. 2015a, b).

3.1.3 More detailed work on sulfide oxidation pathways

As shown in Eqs. 13 and 14, two distinctive pathways happened during sulfide oxidation which resulted in different dual sulfate isotope values of produced sulfate. The variable dual sulfate isotope values from sulfide oxidation result in some difficulties in obtaining the accurate contribution of sulfide oxidation to dissolved sulfate in river water. Which pathway is dominated and what percent of this pathway accounts for the sulfate in river water? Sometimes, dual sulfate isotope values did not work well, triple oxygen isotopes of sulfate seem to be used to differentiate the mechanism of these two pathways due to the different capital oxygen-17 isotope values ($\Delta^{17}\text{O}_{-\text{SO}_4} = \delta^{18}\text{O}'_{-\text{SO}_4} - 0.5305 * \delta^{17}\text{O}'_{-\text{SO}_4}$, where $\delta^{18}\text{O}'_{-\text{SO}_4} = \text{Ln}(\delta^{18}\text{O}_{-\text{SO}_4}/1000 + 1)$, similar with $\delta^{17}\text{O}'_{-\text{SO}_4}$) in O₂ and H₂O. But in fact, the sulfur and oxygen isotope fractionations

occurred during the sulfide oxidation, making it more difficult to exactly determine the sulfate amount produced by sulfide oxidation.

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