

# Effects of atmospheric CO<sub>2</sub> consumption on rock weathering in the Pearl River basin, China

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**Abstract:** Atmospheric CO<sub>2</sub> is absorbed and dissolved in water via karst processes not only in carbonate rock areas, but in all rock areas of the earth. The chemical and isotopic analysis results, particularly of strontium, for water samples collected from eleven stations along the Pearl River, four times over the course of one year, showed that due to weathering by carbonate or silicate rocks, HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> have become the main ions in the river water. Through river ion stoichiometric and flux calculations, the carbonate rock weathering rate and atmospheric CO<sub>2</sub> consumption were found to be 27.6 mm/ka and 540 × 10<sup>3</sup> mol/km<sup>2</sup>.a, which are 10.8 and 6.7 times the corresponding values for silicate rock. With the beneficial climatic conditions for rock erosion and large areas of carbonate rock in the Pearl River Basin, the atmospheric CO<sub>2</sub> consumption value is about 2.6 times the average value for the 60 major rivers in the world.

## 1 Introduction

Rock weathering is a universal, and one of the most influential, geological processes that occurs on the earth's surface. Atmospheric CO<sub>2</sub> is an important driving force for the karst geological processes [1]. Atmospheric CO<sub>2</sub> can be removed by chemical weathering of rocks and produce huge carbon sinks, thereby reducing atmospheric CO<sub>2</sub>. Atmospheric CO<sub>2</sub> consumption caused by rock weathering can be evaluated by the main ion flux of the river [2, 3]. Each year, approximately 0.7×10<sup>9</sup> t of atmospheric CO<sub>2</sub> is transferred from the atmosphere-biosphere to the ocean through terrestrial weathering [4]. However, disagreements of the contribution of silicate and carbonate rock weathering for global carbon sinks are still remain [5]. Therefore, it is necessary to conduct an in-depth comparative study on the rate and carbon sink effect of carbonate rocks and silicate rocks for a typical basin.

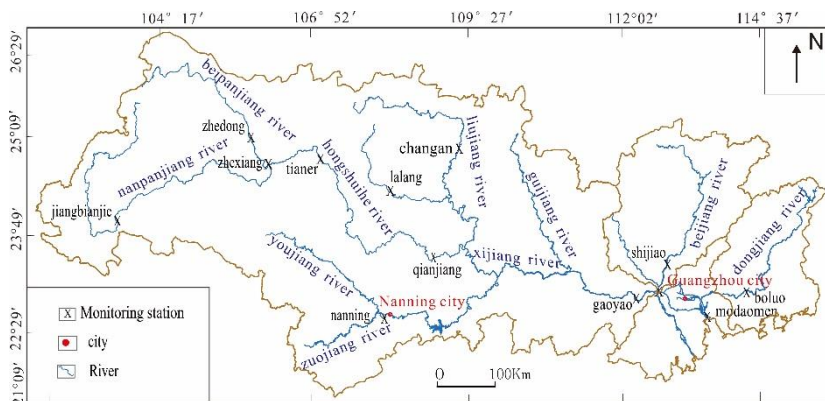
For this work, the Pearl River basin was selected to estimate the weathering rate of carbonate rocks and silicate rocks and the carbon sink effect in the basin. Inorganic carbon content in the river, carbon isotope composition, and changes in the hydro-chemical composition were used to promote research on the geological processes and global carbon cycle of the main river basins in China.

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## 2 Research area overview and research methods

The Pearl River Basin is located in the transition slope from the Yunnan-Guizhou Plateau to the Guangxi Basin and the hilly plains of Guangdong (Fig. 1). It is a typical karst basin with the most concentrated karst distribution area in China, and a drainage area of 441,000 km<sup>2</sup>. The climate of the Pearl River Basin is tropical to subtropical monsoonal climate. There is abundant rainfall in the basin, but the annual distribution is uneven. The rainfall also increases from 800 mm in the upstream southern Yunnan to 2000 mm in the Pearl River Delta to the east. High temperatures and precipitation during the same period as well as high humidity levels are very conducive to the chemical weathering of rocks and the dissolution of carbonate rocks.



**Fig. 1.** Location map of the Pearl River Basin showing the monitoring stations.

The lithology of the Pearl River basin is shown in Fig. 1. The silicate rocks are mainly sandstone, shale, volcanic rock, metamorphic rock, and basalt. The carbonate rocks are mainly limestone and dolomite, accounting for 39.6% of the total area of the basin.

In 2012-13, a special survey of karst carbon sinks in the Pearl River Basin was carried out. The water samples were collected from 11 major stations in the Pearl River in the spring, summer, fall, and winter, from April 2012 to January 2013.

## 3 Results and discussion

### 3.1 Chemical composition of river water of the Pearl River basin

Table 1 shows the average main ion contents and isotope detection results, for the samples of April 2012, July 2012, October 2012, and January 2013 from the main stations in the Pearl River Basin.

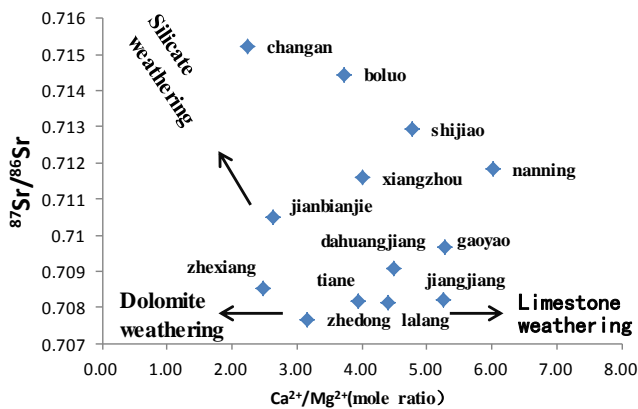
### 3.2 Strontium and its isotopic characteristics

The basic geochemical properties of strontium determine its two advantages as a tracer element: ①The strontium content in different rocks is significantly different. ②The strontium element has stable chemical properties and the strontium isotope content is not

affected by mass fractionation. Thus, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio characteristics of water can reflect the characteristics of the corresponding aquifer [6]. [7]. The characteristic molar ratios of river water endmembers are shown in Fig.2. Relatively speaking, limestone has relatively low Mg/Ca, Ca/Sr, and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is approximately 0.7075 of limestone. Dolomite has high Mg/Ca and Mg/Sr ratios. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is approximately 0.7110 of dolomite. Silicate rock has the lowest Ca/Sr ratio, but a high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (generally larger than 0.7150). This is because silicate rocks have high Rb and low Sr concentrations. Carbonate rocks however, have low Rb and high Sr concentrations. Therefore, Sr isotopic ratios are often used to identify endmember components and to study the weathering rate of the basin. Fig. 2 shows the relationship between  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\text{Ca}^{2+}/\text{Mg}^{2+}$  in the river water at each station in the Pearl River Basin.

**Table 1.** The chemical composition of major ions in water of the Pearl River Basin (mmol/L).

stations	K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	SiO <sub>2</sub>	TDS (mg/L)
Modaomen	0.180	5.070	1.020	0.800	5.710	0.550	1.830	0.120	501
Boluo	0.107	0.352	0.283	0.083	0.267	0.147	0.508	0.179	75.4
Shijiao	0.057	0.184	0.681	0.141	0.112	0.180	1.35	0.143	108
Gaoyao	0.074	0.188	1.01	0.216	0.201	0.227	1.94	0.111	148
Changan	0.023	0.117	0.221	0.095	0.059	0.081	0.615	0.139	51.7
Dahuangjiang	0.056	0.169	1.13	0.251	0.148	0.226	2.30	0.100	160
Xiangzhou	0.039	0.133	0.654	0.183	0.109	0.146	1.37	0.109	101
Nanning	0.052	0.152	1.25	0.194	0.143	0.150	2.68	0.109	168
Lalong	0.040	0.127	1.45	0.304	0.129	0.348	2.88	0.067	200
Qianjiang	0.029	0.145	1.43	0.301	0.140	0.228	2.80	0.102	187
Tiane	0.035	0.167	1.36	0.354	0.143	0.244	2.73	0.107	186
Zhexiang	0.039	0.209	1.17	0.438	0.167	0.314	2.45	0.080	178
Zhedong	0.043	0.234	1.48	0.428	0.113	0.578	2.63	0.083	222
Jiangbianjie	0.108	0.390	1.71	0.736	0.441	0.506	3.81	0.097	286

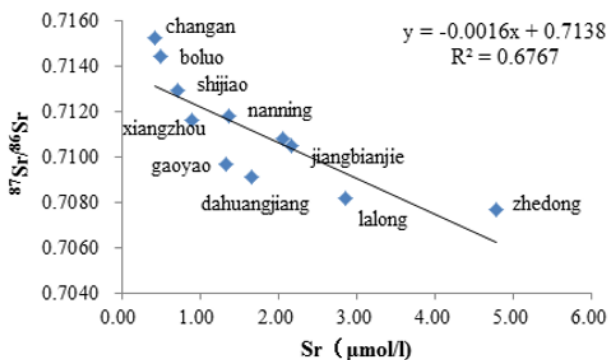


**Fig. 2.** Variation of Sr isotopic ratios with  $\text{Ca}^{2+}/\text{Mg}^{2+}$  molar ratios (in July 2012).

The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic composition of the river water in the Pearl River Basin varies from 0.70768 to 0.71583; the average is 0.7105, which is lower than that of the world's

largest rivers of 0.7119 [8]. The variation in the Sr content in the river water of the Pearl River Basin ranges from 0.42 to 4.79  $\mu\text{mol/L}$ ; the average is 1.78  $\mu\text{mol/L}$ , which is significantly higher than that of the world's largest rivers (0.89  $\mu\text{mol/L}$ ).

It can be seen from Fig. 3 that the  $^{87}\text{Sr}/^{86}\text{Sr}$  values are inversely proportional to the Sr concentrations. The river water of the Dulu River (Chang'an station), which flows through a silicate rock formation, has a relatively high radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (0.71523) and a relatively low Sr concentration (0.422  $\mu\text{mol/L}$ ). On the other hand, the river water of the Beipan River (Zhedong), which flows through a limestone formation, has a relatively low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (0.70768) and a high Sr concentration (4.79  $\mu\text{mol/L}$ ). The Nanpan River (Jiangbianjie) has a low Ca/Mg ratio, indicating that a certain portion of water has passed through a dolomite formation.



**Fig. 3.** Variation of Sr isotopic ratios with Sr concentrations of the river water.

### 3.3 Calculation and results analysis

Based on the relationships between isotopic and elemental ratios of the river water, the chemical compositions of the Pearl River water are mainly from the weathering of limestone, dolomite, and silicate rocks. In contrast, the Beipan (Zhedong), Nanpan (Jiangbian Street), Longjiang (Lalang), and Yu (Nanning) rivers are dominated by limestone weathering. The Dong (Bolu station) and Dulu (Chang'an) rivers flow through a silicate rock formation, and their isotopic ratios show silicate rock weathering.

The contribution of various endmember weathering to river water solutes was estimated in this study using a method developed by Galy and France-Lanord (1999) [2]. River sampling data and runoff data from 11 stations in the Pearl River Basin in the four seasons of spring, autumn, fall, and winter (see Table 1) are used in the calculations. From Zhedong station, Jiangbianjie station, and Zhexiang station, the equivalent ratios of  $[\text{Ca}^{2+} + \text{Mg}^{2+}] / [\text{HCO}_3^-]$  are 1.452, 1.316, and 1.325, respectively, and the equivalent ratios of  $[\text{SO}_4^{2-}] / [\text{HCO}_3^-]$  are 0.439, 0.297, and 0.255, respectively. This indicates that  $\text{SO}_2$  from the atmospheric input or  $\text{H}_2\text{SO}_4$  formed from the oxidation of sulfides is involved in the dissolution of carbonate minerals. Therefore, the case wherein both sulfuric acid and carbonic acid participate in the reaction and the case wherein only carbonic acid participates in the reaction are considered in the calculation. The calculation results are shown in Table 2.

**Table 2.** Chemical weathering rate and CO<sub>2</sub> consumption by rock weathering in Pearl River basin<sup>a</sup>.

station name	Basin area km <sup>2</sup>	Carbonate rock ratio %	Silicate weathering by carbonic acid		Carbonate weathering by carbonic acid			
			t/km <sup>2</sup> .a	mm/ka	CO <sub>2</sub> 10 <sup>3</sup> mol/km <sup>2</sup> .a	t/km <sup>2</sup> .a	mm/ka	CO <sub>2</sub> 10 <sup>3</sup> mol/km <sup>2</sup> .a
Boluo	25300	5.4	17.7	6.5	272	29.3	10.9	57.6
Shijiao	38400	25.0	20.7	7.7	297	111	41.4	739
Gaoyao	352000	47.2	7.2	2.7	74.8	70.7	26.2	533
Changan	21600	43.3	10.6	3.9	99.8	28.7	10.6	238
Dahuangjiang	289000	46.6	6.5	2.4	76.1	81.9	30.3	654
Nanning	73728	38.4	5.0	1.9	49.7	70.4	26.1	605
Lalong	9340	75.7	5.7	2.1	49.0	144	53.4	1140
Qianjiang	129000	72.2	3.5	1.3	37.2	63.1	23.4	495
Carbonate weathering by both sulfuric and carbonic acids								
Zhexiang	82300	71.9	4.3	1.6	53.2	75.1	27.8	362
Zhedong	20100	80.0	7.0	2.6	141.4	134	49.7	341
Jiangbianjie	25100	55.5	3.1	1.2	22.3	71.6	26.5	337
On average			6.9	2.6	80.2	74.5	27.6	540

<sup>a</sup> The average density of silicate rock and carbonate rock is 2.7 and 2.0, respectively.

## 4 Conclusions

(1) Isotope data can be used to show that the HCO<sub>3</sub><sup>-</sup> ions in some rivers are from the weathering of silicate rocks. Therefore, rock weathering and carbon sink effects have covered the entire Pearl River Basin.

(2) In the Pearl River Basin, the weathering of carbonate rocks is dominant. The weathering erosion rate of carbonate rocks and the atmospheric CO<sub>2</sub> consumption caused by weathering and dissolution of carbonate rocks are 10.8 and 6.7 times of the silicate rock weathering rate and the atmospheric CO<sub>2</sub> consumption caused by silicate rock weathering, respectively.

(3) Due to the hydrothermal conditions in the Pearl River Basin, the exposed area of carbonate rocks is large. The atmospheric CO<sub>2</sub> consumption caused by rock weathering is 620.4×10<sup>3</sup> mol/km<sup>2</sup>.a, which is 2.6 times the average of 60 rivers in the world.

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## References

1. ZC Jiang, DX Yuan, JH Cao, XQ Qin, SY He, C Zhang. *Acta Geoscient. Sin.*, **33**, 129-134 (2012)
2. A Galy, C France-Lanord. *Chem. Geol.*, **159**, 31-60 (1999)
3. PA Suchet, JL Probst. *Tellus*, **47B**, 273-280 (1995)
4. JY Li, J Zhang. *Adv. Earth Sci.* **17**, 411-419 (2002)

5. ZH Liu. *Chin. Sci. Bull.*, **57**, 95-1029 (2012)
6. ZY Wang, J Liu, T Wang, YS Wang, JW Hu. *Geol. Sci. Tech. Info.*, **22**, 91-95 ( 2003)
7. ZH Xu, CQ Liu. *Chem. Geol.*, **239**, 83-95 (2007)
8. J Gaillardet, B Dupre, P Louvat. *Chem. Geol.*, **159**, 3-30 (1999)