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Fluvial geochemistry of rivers draining karst terrain in Southwest China

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ABSTRACT

Samples of water from rivers draining karst areas within Guizhou Province, China (the Wujiang, Qingshuijiang, and Wuyanghe rivers), were analyzed for dissolved major element concentrations (HCO_3^-, NO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, K^+, Na^+), Sr^{2+}, and $^{87}Sr/^{86}Sr$ to quantify the rates of chemical weathering of rocks and associated atmospheric CO_2 consumption in a typical karst area. The analyzed water samples in rivers draining karst areas typically show a dominance of Ca^{2+}, Mg^{2+}, and HCO_3^-, and are rich in SO_4^{2-}.

The waters of the Wujiang River contain high Sr^{2+} concentrations (0.61–7.19 μmol/l) and low $^{87}Sr/^{86}Sr$ values (0.7074–0.7115), while the waters of the Qingshuijiang River, which drains silicate strata, yield high Sr isotopic ratios (0.7088–0.7155) and low Sr^{2+} concentrations (0.18–1.45 μmol/l). The chemical and isotopic compositions of these waters are largely controlled by the lithology of the basin. Stoichiometric analyses show that the water chemistry is controlled by carbonate dissolution under the influence of carbonic and sulfuric acid.

The rates of chemical weathering of rocks within the studied basin were estimated based on the chemical budget calculated for each of the three analyzed rivers. The weathering rates estimated for silicate rocks were 6.7–10.7 t/km^2/yr, while those for carbonate rocks were 67–116 t/km^2/yr. We also calculated the rates of chemical weathering of carbonate rock and related rate of CO_2 consumption by carbonic and sulfuric acid combined, and by carbonic acid alone. The results show that the involvement of sulfuric acid in weathering processes strongly enhances the rate of carbonate weathering but lowers the rate of CO_2 consumption. The catchment of the Wujiang River is dominated by a coal-bearing formation, and a coal mine is operated within the catchment. The consumption of CO_2 shows a marked decrease from 844×10^3 mol/km^2/yr in the case of carbonate weathering by carbonic acid alone to 546×10^3 mol/km^2/yr in the case of carbonate weathering by both sulfuric and carbonic acid. No atmospheric CO_2 is consumed during weathering of the carbonate rocks by sulfuric acid; consequently, this form of weathering represents a net source of CO_2 to the atmosphere in the Guizhou karst area.

1. Introduction

The decrease in atmospheric CO_2 associated with the chemical weathering of silicates is recognized as a major process in terms of controlling the evolution of the Earth's climate over periods of thousands to millions of years (Gaillardet et al., 1997, 1999; Huh et al., 1998; Roy et al., 1999; Jacobson et al., 2003; Millot et al., 2003; Wu et al., 2005, 2008), whereas the reactions involved in the weathering of carbonate rocks are thought to be ineffective in this regard. However, many studies have shown that carbonate weathering by sulfuric acid is important in models of global CO_2 flux (Hercod et al., 1998; Galy and France-Lanord, 1999; Yoshimura et al., 2001; Han and Liu, 2004; Spence and Telmer, 2005; Calmels et al., 2007; Xu and Liu, 2007; Li et al., 2008). Sulfur emissions to the atmosphere and the acidification of rain water may also play a significant role in terms of increasing weathering rates. Guizhou Province, China, is affected by intense sulfuric acid rain that occurs because of the mining and combustion of coal in the region (Lei et al., 1997; Larssen et al., 2006). In this context, the Guizhou karst basin represents an ideal setting in which to investigate the rates of chemical weathering of carbonate by sulfuric acid and associated CO_2 consumption.

In this study, we carried out a systematic investigation of the hydrogeochemistry of rivers within the Guizhou karst area. Although previous studies have presented a large amount of geochemical data for this area (e.g., Han and Liu, 2004), the chemical load and variations in river flux in the Guizhou karst areas have

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not been discussed in detail due to a lack of samples collected over longer periods of time. In the present study, we analyze temporal variations in major ion chemistry, Sr^{2+} concentrations, and $^{87}Sr/^{86}Sr$ values in river water during the high-flow period, and present integrated information on the natural rate of chemical weathering and CO_2 consumption at the scale of a drainage basin. The studied waters are rich in sulfate derived from anthropogenic emissions and/or sulfide oxidation; consequently, an additional aim of this study is to examine the effect of sulfuric acid on the weathering of carbonate rocks and on CO_2 consumption.

2. Geography, geology, and climate of Guizhou Province

Guizhou Province covers an area of 17.6×10^4 km^2, extending from 24°37′N to 29°13′N and from 103°36′E to 109°35′E. The province is located in the center of the Southeast Asia Karst Region, which is the largest karst area in the world. An account of the geology of Guizhou Province (as summarized in Fig. 1a) can be found in Han and Liu (2004).

Guizhou Province was chosen as a study area because carbonate rocks are widely distributed throughout the region. The Wujiang

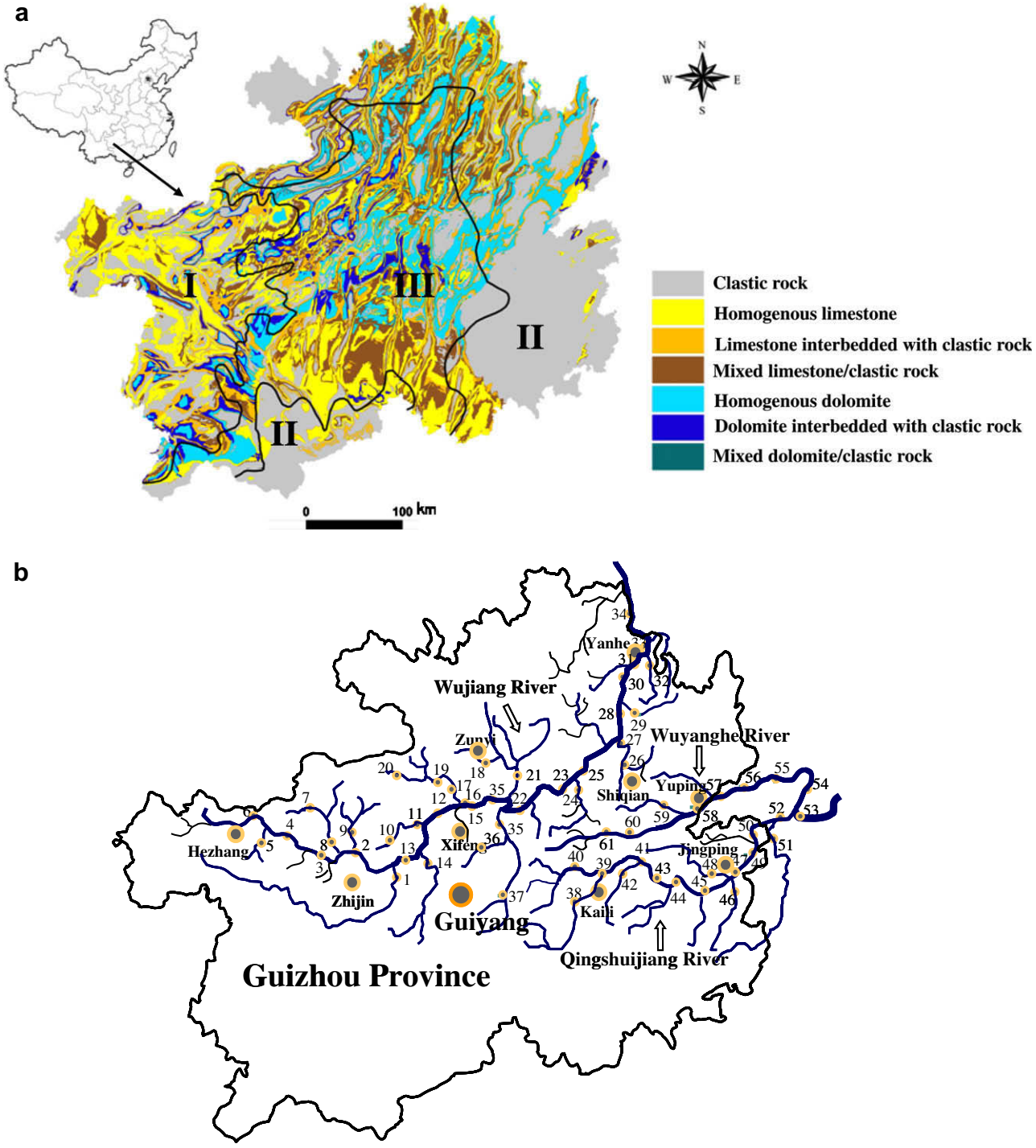

Fig. 1. (a) Sketch map showing the geology of Guizhou Province (from Wang et al. (2004)). Zones I, II, and III have average altitudes of >1500 m, <700 m, and 700–1500 m, respectively. (b) Map showing sampling locations and sample numbers.