Isotopic compositions of strontium in river water of Guizhou karst areas, China

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Abstract We have carried out a study on the variation of strontium isotope composition of river waters, Wujiang and Yuangjiang River, in karst areas of Guizhou Province, China. The results obtained permit us to characterize the geochemistry of the river draining karst terrain and obtain a better understanding of main controls of catchment geology, chemical weathering of different rocks, and evaluate impact of human activities on the environment. The isotopic ratios of dissolved Sr in all rivers are between $^{87}Sr/^{86}Sr$ =0.7077 and 0.7110, totally lower than the weighted average of $^{87}Sr/^{86}Sr$ =0.7119 for the world large rivers. The Wujiang River waters have Sr concentrations from 1.0 to 6.1 μmol/L, while the Yuanjiang River waters have much lower Sr concentrations ranging from 0.28 to 1.3 μmol/L. Most of the river waters from the Wujiang river are characterized by low Ca/Sr and Mg/Sr, and $^{87}Sr/^{86}Sr$ ratios, in which a majority of river waters are of $^{87}Sr/^{86}Sr$ ratios lower than the average Sr isotope ratio ($^{87}Sr/^{86}Sr$ =0.709) of present seawater. The higher $^{87}Sr/^{86}Sr$ ratios are observed in the river waters in the lower reach of the Wujiang River, where the lithology is dominated by detrital rocks and dolomite. The water from Yuanjiang River show higher Ca/Sr, Mg/Sr and $^{87}Sr/^{86}Sr$ ratios due to weathering of silicates, as compared to the river waters from Wujiang river.

Keywords: karst river, strontium isotope, hydrogeochemistry.

1 Introduction

Geochemical study of river water allows us to obtain important information on chemical weathering of catchments, climate, chemical and isotopic compositions of upper continental crust (UCC) and the elements cycling in the continent-river-ocean system[1—5]. A number of studies[6—8] on chemical compositions and the strontium isotope system of river waters have shown that the geochemical compositions of river water can be described by mixing of two end members: one is derived from weathering of silicates (silicate end-member) and another from weathering of carbonate rocks (carbonate end-member). The carbonate end-member is characterized by high strontium concentrations (up to 11.4 mmol/kg) and low $^{87}Sr/^{86}Sr$ ratios (0.706—0.709), and the silicate end-member by lower strontium contents and higher $^{87}Sr/^{86}Sr$ ratios (>0.710). Recent researches show that the fluvial chemistry of world rivers in both tectonically stable and active regimes is dominated by the rapid weathering of biogenic and inorganic carbonates and slower dissolution of sedimentary aluminosilicate rock, with relatively minor contributions from primary basement

formations[9]. Because carbonate weathering has significant control on the geochemical composition of river water, it is important to get better understanding of the relationships between chemical weathering of carbonate rocks and hydrogeochemistry of river water through systematic studies on geochemical compositions of river waters draining carbonate-dominated terrain.

This work is focused on the strontium isotopic compositions of river waters in Guizhou karst areas of southwestern China, with a main purpose to understand main controls of catchment geology, chemical weathering of different rocks, biogeochemical processes in the typical karst terrain and to evaluate the impact of human activities on the environment.

2 Lithology of drainage catchment

Guizhou Province is located in the center of the Southeast Asian Karst Region where karstification is most developed, with various types of karst physiognomy and the largest distribution in area in the world. The Wujiang River, the largest river in Guizhou Province, rises in the Wumeng Ranges on the Yunnan-Guizhou Plateau. It is the largest tributary of the Changjiang River in the upper reaches and winds through four provinces including Yunnan, Guizhou, Sichuan and Hubei. The Wujiang River drainage system is located in karst areas of Guizhou Province. The catchment is characterized by many different and complicated lithologies. The strata exposed in the Wujiang River catchment consists mostly of the Pre-Jurassic system, in which carbonate rocks are widely spread. The upper reaches of the Wujiang River catchment are dominated by Permian and Triassic carbonate rocks, coal-bearing formations and basalts. In the middle reaches are widely distributed Permian and Triassic limestones, dolomitic limestones and dolomites; while in the lower reaches are mainly carbonate rocks, as well as shales, sand shales and siltstones. The Yuanjiang River drainage system is located in the northeast of Guizhou Province, which includes the upper reach of Yuanjiang River, Qingshuihe River and Wuyanghe River. The strata exposed in the Yuanjiang River catchment is composed mainly of detrital and metamorphic rocks.

3 Sampling and analytical procedures

The river water samples were collected from Jan. 7 to Feb. 11, 1999. During the sampling period, the Wujiang River and Yuanjiang River had minimum discharge in winter. Water temperature, dissolved oxygen, pH and conductivity were measured at sampling sites with a portable pH and salt conductivity meter. HCO_3^- was titrated by HCl on the spot. The river water samples were collected by way of placing an acid-cleaned linear polyethylene bottle in a plastic holder. Immediately after collection, all the samples were filtered through 0.22 μm membrane filters (Millipore) and a small aliquot of these samples was stored in darkness, while another aliquot was acidified with ultra-purified hydrochloric acid to pH<2. Major cations were determined by AAS and anions by chromatography. Filtered water samples were directly passed through an AG50W-50 resin column in HCl media to separate strontium from major elements. The isotopic compositions of Sr were determined on a VG354 mass spectrometer with five Faraday collectors

in the Institute of Geology, Chinese Academy of Sciences, Beijing. The value $^{87}Sr/^{86}Sr$ for the NBS987 strontium standard was 0.710238±0.000021 (2σ, n = 11) during the measurement period of these samples.

4 Results and discussion

The characteristics of major ion composition and their geochemical implication are discussed elsewhere[10]. This paper is concerned mainly with the strontium concentrations and isotope compositions of the waters of the Wujiang River catchment and Yuanjiang River catchment.

The isotopic ratios of dissolved Sr in all rivers are between $^{87}Sr/^{86}Sr$ =0.7077 and 0.7110, totally lower than the weighted average of $^{87}Sr/^{86}Sr$ =0.7119 for the world large rivers[9]. Although there is no significant difference of Sr isotopic composition between the Wujiang River and the Yuanjiang River, clear difference in Sr concentration of these rivers exists. The Wujiang River waters have Sr concentrations from 1.0 to 6.1 μmol/L, while the Yuanjiang River waters have much lower Sr concentrations of from 0.28 to 1.3 μmol/L.

It has been well documented by studies on hydrogeochemistry of rivers in the world that a wide range of $^{87}Sr/^{86}Sr$ ratios from 0.703 to 0.943 is observed in river waters, and waters draining different lithological terrains show various Sr isotopic compositions. Water draining silicate terrain has more radiogenic ^{87}Sr and higher $^{87}Sr/^{86}Sr$ ratios, while water draining carbonates shows lower ^{87}Sr and $^{87}Sr/^{86}Sr$ ratios. This is because the silicates normally contain high Rb and low Sr concentrations, while carbonates contain low Rb and high Sr concentrations [6—8]. For these reasons, Sr isotopes are often used to identify weathering end-members in a watershed and to study the crustal weathering rates of certain drainage basins.

Most of the river waters from the Wujiang river are characterized by low Ca/Sr and Mg/Sr, and $^{87}Sr/^{86}Sr$ ratios, in which a majority of river waters are of $^{87}Sr/^{86}Sr$ ratios lower than the average Sr isotope ratio ($^{87}Sr/^{86}Sr$ =0.709) of present seawater. The higher $^{87}Sr/^{86}Sr$ ratios are observed in the river waters in the lower reach of the Wujiang River, where the lithology is dominated by detrital rocks and dolomite. Although only a few of samples from the Yuanjiang River have been analyzed for their $^{87}Sr/^{86}Sr$ ratios, the data obtained indicate that these river waters show higher Ca/Sr, Mg/Sr and $^{87}Sr/^{86}Sr$ ratios due to weathering of silicates, as compared to the river waters from Wujiang river. From the correlations of the elemental and Sr isotopic ratios, existence of three weathering components is clear. The carbonate end-member is speculated to have a Ca/Sr ratio of around 150, and a Mg/Sr ratio of less than 100, and $^{87}Sr/^{86}Sr$ ratio of 0.7075. The dolomite end-member seems to have slightly higher $^{87}Sr/^{86}Sr$ ratio, but distinctively high Mg/Sr and Ca/Sr ratios. The third one, silicate end-member, has Mg/Sr and Ca/Sr ratios between those of the limestone and dolomite, and high $^{87}Sr/^{86}Sr$ ratio around 0.7115. As a first approximation, it can be concluded that most of river waters from Wujiang River are mainly dominated by chemistry of the water draining limestone, while the river waters from Yuanjiang River are mainly of chemistry of water draining silicate detrital rocks together with some dolomite.

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