Applied Geochemistry 85 (2017) 61–72

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Isotopic study of the source and cycle of sulfur in the Yamdrok Tso basin, Southern Tibet, China

Jin-Liang Feng [a, *], Feng Chen [a, b], Hai-Ping Hu [a, b]

[a] Key Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100101, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 7 July 2016
Received in revised form
31 May 2017
Accepted 4 September 2017
Available online 7 September 2017

Handling Editor: Prof. M. Kersten.

Keywords:
Sulfur source
Sulfur isotope
Oxygen isotope
Pyrite oxidation
Lake sediment
Sulfur isotope fractionation

ABSTRACT

This study focuses on the inland drainage basin of Yamdrok Tso (Tso means ‘lake’ in the Tibetan language), which lies at altitudes between 4394 and 4989 m, in southern Tibet. The basin is located in the Tethys Himalayan zone, and consists of seven lakes with different hydrological characteristics. The main purpose of the study was to investigate the source of dissolved SO_4^{2-} and the sulfur cycle in the groundwater-river-lake system. We measured the hydrogeochemical composition, $\delta^{18}O_{H2O}$, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ of sulfate in river, spring and lake water; the total sulfur content (S_{Total}) and $\delta^{34}S_{Total}$ of total sulfur in a lake sediment core; and the $\delta^{34}S_{pyrite}$ of pyrite in the bedrock. The results indicate that most of the rivers in the study area are characterized by a high sulfate content with values of up to 270 mg/L. In addition, the $\delta^{34}S_{pyrite}$ of pyrite in the bedrock ranges between −4.31‰ and −5.77‰, while the sulfate in river and spring waters has mainly negative values of $\delta^{34}S_{SO4}$ (−7.14‰ to −2.02‰) and $\delta^{18}O_{SO4}$ (−13.2‰ to −4.04‰). In contrast, the waters of closed lakes in the study basin have high values of $\delta^{34}S_{SO4}$ (3.44‰ −8.58‰) and $\delta^{18}O_{SO4}$ (7.26‰−10.3‰). The negative $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ dual-isotopic composition of sulfate indicates that pyrite weathering controls the dissolved sulfate and other solutes in rivers and spring water, while the anthropogenic pollutant sulfur flux is negligible. Water is the main oxygen source for sulfate derived from the oxidation of pyrite, while Fe^{3+} is the main direct agent of pyrite S oxidation. The lake water and sediments in the study basin are important sinks/stores of sulfur. The $\delta^{34}S_{Total}$ values of total sulfur in a sediment core from a closed and holomictic lake ranges between −8.5‰ and −44.9‰. As evidenced by the strong ^{34}S and ^{18}O enrichment in the residual pool of SO_4^{2-} in the lake waters, and the marked depletion of ^{34}S in the sediment core, the dissimilatory microbial sulfate reduction (MSR) in the lake sediments generally results in the preferential sequestration of sulfur enriched in ^{32}S. In addition, the magnitude of $^{34}S/^{32}S$ fractionation between sulfate in the lake water and sedimentary total sulfur can reach up to 48.3‰. This abnormally high fractionation value can be explained mainly by the reoxidation of reduced inorganic sulfur compounds, together with the dispropotionation pathway in the sediments, caused by lake level fluctuations. The changes in S_{Total} and $\delta^{34}S_{Total}$ values with depth in the sediment core can also be explained by the same mechanism.

1. Introduction

The sulfur cycle is important for hydrological, sedimentary and living systems, and even the atmospheric system (Spence and Telmer, 2005; Meyer et al., 2009; Ono et al., 2014; Hoefs, 2015). Sulfide oxidation and sulfate reduction play an important role in the sulfur cycle. Through the oxidation of reduced sulfur to sulfate, the concomitant chemical weathering of rocks releases sulfur, CO_2, and other major dissolved ions to rivers, lakes and/or the ocean (Strauss, 2003; Calmels et al., 2007; Meyer et al., 2009). Thus, the sulfuric acid derived from sulfide oxidation is potentially the most important weathering agent, except for carbonic acid, in earth surface processes. However, there is still debate about the role of pyrite and other types of sulfide weathering in the global carbon cycle (Spence and Telmer, 2005; Calmels et al., 2007; Torres et al., 2014). In addition, the contribution of sulfuric acid as a

* Corresponding author. Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Building 3, 16th Lincui Road, Chaoyang District, Beijing, 100101, China.
E-mail address: fengjl@itpcas.ac.cn (J.-L. Feng).

http://dx.doi.org/10.1016/j.apgeochem.2017.09.005

weathering agent remains poorly quantified (Calmels et al., 2007; Meyer et al., 2009).

The process of microbial sulfate reduction (MSR) leads to the formation of reduced sulfur. Pyrite is the end-product of this process and once again becomes a stable solid phase of sulfur in sedimentary systems. The process is characterized by the accumulation of sulfur and by significant sulfur isotope fractionation. The MSR process is also an important pathway of organic carbon mineralization in freshwater sediments (Holmer and Storkholm, 2001).

In general, both processes are involved in the geochemical cycles of carbon, sulfur, oxygen, and iron (Berner, 1982; Garrels and Lerman, 1984; Canfield, 2001; Torres et al., 2014). The characterization and quantification of the sulfur cycle could potentially improve our understanding of the history of atmospheric oxygen and CO_2, the evolution of ocean chemistry and climate, and the relationship between the operation of the relevant biogeochemical processes in both the distant geological past and at present (Strauss, 2003).

The Tibetan Plateau is one of the major regions of alpine inland lakes in the world. The lakes of the plateau are important in terms of biodiversity, the hydrological cycle, ecosystem functioning, local climate and human survival. In the Tibetan Autonomous Region, the total area of the inland drainage basins is 612.2×10^3 km^2 (Guan and Chen, 1984). The Tibetan Plateau is also the source of many of the great rivers of Asia, including the Yarlung Tsangpo, Yangtze, Yellow, Indus and Ganges rivers.

In the adjacent mountain ranges around the Tibetan Plateau, the $\delta^{34}S_{SO4}$ of sulfate in the outflow rivers has been reported (Karim and Veizer, 2000; Chakrapani and Veizer, 2006; Turchyn et al., 2013; Li et al., 2014). The major ionic composition of the waters of the rivers and lakes of the Tibetan Plateau has also been investigated (Hu et al., 1982; Hren et al., 2007; Huang et al., 2009; Zheng, 1997; Zheng and Liu, 2009; Lei et al., 2012). In the Yamdrok Tso basin of southern Tibet, the hydrogeochemical components and $\delta^{18}O_{H2O}$ of river and lakes have been reported (Guan and Chen, 1984; Shi, 1995; Ju et al., 2008; Tian et al., 2008; Gao et al., 2009; Zhang et al., 2012; Shi et al., 2014; Chen et al., 2016.). In addition, Ju et al. (2008) speculated that pyrite oxidation may influence the hydrogeochemical components in the Phuma Yutso catchment. However, no direct evidence is currently available to test this hypothesis.

Information about the weathering agents, sulfur isotope systematics and sulfur source in the rivers and lakes of the Tibetan Plateau is limited (Zheng et al., 1983), and in particular the sulfur source and sulfur cycle in several inland drainage basins are unknown. Moreover, the aquatic environments of the Tibetan Plateau are characterized by low-temperature, hypoxia, oligotrophy and significant glacial meltwater inputs. Under these extreme conditions, however, our knowledge of the processes of sulfide oxidation and sulfate reduction in the sulfur cycle is meagre.

Here, we focus on the sulfur cycle of the Yamdrok Tso basin, southern Tibet (Fig. 1). The aims of the study are (1) investigate the dual isotopic characteristics of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ of dissolved sulfate in river and lake waters; (2) identify the origins of riverine sulfate; (3) determine the pathway of pyrite oxidation; and (4) elucidate the biogeochemistry of the sulfur cycle within the lake system. Overall, it was hoped that the study would improve our understanding of the sulfur cycle in alpine aquatic environments.

2. Geological setting

The Yamdrok Tso basin is an inland basin in southern Tibet (Fig. 1). The summit elevation in the area reaches 7191 m above sea level (a.s.l.) and the lake surfaces range between 4394 and 4989 m a.s.l. (Fig. 1). Currently the region experiences a monsoon-influenced, semi-arid climate; and annual temperature and precipitation are 2.4 °C and 372.8 mm, respectively. The basin is surrounded by many glacier-capped mountains, and the area occupied by glaciers is about 218 km^2. The rivers and lakes are partly fed by glacial meltwater.

The Yamdrok Tso basin consists of seven lakes. Gongmo Tso and the small Nongzhen Tso are through-flow lakes, and both are connected to the Yamdrok Tso via a narrow channel (Figs. 1 and 2A). Phuma Yutso is a semi-closed lake with a maximum water depth of 65 m, with an outlet stream at its far northeastern end (Fig. 2B). The water of Phuma Yutso is occasionally discharged into the Yidam Chu River, and subsequently flows into Yamdrok Tso (Zhang and Chen, 1981, Figs. 1 and 2B). Yamdrok Tso, Drem Tso (Chen Co) and Pagyu Tso are closed lakes. Yamdrok Tso has a maximum water depth of 59 m and is characterized by a very irregular lakeshore geometry. Drem Tso with a maximum water depth of 34.6 m is a holomictic lake at present (Jian-Ting Ju, unpublished data). The depth of Gongmo Tso is more than 17.8 m. The Gotse Tso has not yet been investigated. In general, these rivers and lakes are minimally disturbed by human activity.

Drem Tso and Gongmo Tso are believed to have been isolated from Yamdrok Tso by falling lake level in the neoglacial period some 2000 years ago (Chen, 2016). At present, Drem Tso, Gongmo Tso and Yamdrok Tso are separated by paleo-lacustrine deltaic sediments and glaciofluvial fan deposits. The paleo-lacustrine, lacustrine delta, and alluvial fan sediments are exposed as lake terraces around Yamdrok Tso, Gongmo Tso, Drem Tso and Pagyu Tso (Fig. 2C, D, E) and these sediment terraces have recorded the history of lake level fluctuation.

The study area is located in the Tethys Himalayan zone. It is surrounded by the Khamba La Mountains to the north and by the crystalline Himalayan zone to the south (TBGMR, 1993, Fig. 1). Mesozoic flysch and marine sedimentary strata and their respective low-grade metamorphic rocks are widely exposed. The outcropping rocks are limestone, shale, sandstones, siliceous rock, marl, slate and a few volcanic rocks. It is noteworthy that pyrites often occur in limestone, black slate and sandstone (Wang et al., 1983; TBGMR, 1993). The pyrites near ground surface have undergone intense chemical weathering, and have frequently been transformed to iron oxide and/or hydroxide with a pyrite pseudomorph (Fig. 2F, G, H, I). In addition, many of the river valleys filled with extensive glaciofluvial deposits.

3. Materials and methods

3.1. Field sampling

Most of the river, lake and spring water samples were taken during June 29-July 3, 2013. All the river water samples were collected from the main river (Fig. 1). The lake water samples were collected from the lake surface near the lake shore (Fig. 1). Spring water with a temperature 9.5 °C was collected near the Yamdrok Tso shore (Fig. 1). All samples were filtered using 0.45 μm pore-sized membrane filters (Anpel) *in situ*. The filtrate was stored in clean, previously-unused HDPE bottles. The bottles were cleaned by rinsing several times with filtrated water. The samples for cation analyses were acidified with ultrapure HNO_3. Samples of incompletely weathered pyrite were collected from the Jurassic limestone (P1-1, P1-2) and Triassic black slate (P-2). The locations of the sampling sites are shown in Fig. 1.

On 5 July, 2013, a short gravity core (CC13-1; length: 57 cm) was obtained from the central part of Drem Tso (28°58′30.836″N, 90°30′45.811″E; water depth: 27.6 m; Fig. 1). The core was sectioned into 1-cm intervals throughout. Based on the ^{210}Pb and