



Isotope evidence for secondary sulfide precipitation along the Marsyandi River, Nepal, Himalayas



Alexandra V. Turchyn^{a,*}, Edward T. Tipper^b, Albert Galy^a, Jun-Kai Lo^a, Mike J. Bickle^a

^a University of Cambridge, Earth Sciences, Downing Street, Cambridge, United Kingdom

^b University of St Andrews, Department of Earth and Environmental Sciences, United Kingdom

ARTICLE INFO

Article history:

Received 23 October 2012

Received in revised form

20 April 2013

Accepted 22 April 2013

Editor: T.M. Harrison

Available online 3 June 2013

Keywords:

sulfate
sulfur isotopes
oxygen isotopes
Marsyandi River
Nepal
sulfide

ABSTRACT

We present sulfur and oxygen isotope data from 41 samples of dissolved riverine sulfate from along 65 km of the Marsyandi River in the Northern Himalayas. Coupled sulfur and oxygen isotopic composition of riverine sulfate ($\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ respectively) yield unique constraints on the source of sulfur to the river system. The headwaters of the Marsyandi River have light $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$, which requires that the source of sulfate to the river is through the anoxic weathering of pyrite (likely via Fe^{3+}). The $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ of sulfate in tributaries to the Marsyandi increase downstream, which could result either from inputs from evaporites or bacterial sulfate reduction with subsequent sulfide precipitation in warmer and wetter catchments; either of these processes could result in heavy $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ of the residual river sulfate. Elemental ratios such as Sr/Ca and Ca/SO₄ suggest, as previous studies have also concluded, that evaporite weathering is not important in the Marsyandi River. We conclude that the isotope data is most consistent with the onset of bacterial sulfate reduction and secondary sulfide precipitation in the soils in the warmer and wetter downstream catchments. Our results have implications for understanding the source of sulfate to the ocean as well as the redox and acidity budget within rapidly eroding catchments.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Global river systems provide the largest source of sulfate to the ocean and thus are critical in the marine biogeochemical sulfur cycle (Meybeck, 1979). Riverine sulfate is sourced from the weathering of sulfide bearing minerals in terrestrial environments, the dominant minerals being sulfide minerals (largely pyrite, FeS_2) and evaporite minerals (largely gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, or anhydrite, CaSO_4 , Berner and Berner, 1996). The oxidative weathering of pyrite can proceed directly through reduction of atmospheric oxygen or indirectly through reduction of iron bearing minerals. The latter oxidative process is responsible for the extreme acidity seen in acid mine drainage (AMD) environments (e.g. Druschel et al., 2004).

Resolving the source of sulfate to river systems is important for understanding the importance of sulfuric acid in silicate weathering reactions in terrestrial environments; if the primary source of sulfate is the oxidative weathering of pyrite then the pathway by which this occurs can exert control on the acidity generated or consumed (e.g. Calmels et al., 2007). The standard assumption is that carbonic acid dissolved in rainwater (from atmospheric CO_2) provides critical silicate weathering acidity and alkalinity

generation within a river system; this plays a major role in the feedbacks within the long-term carbon cycle (Walker et al., 1981). However, the role of the oxidative weathering of pyrite in terrestrial weathering remains ambiguous. Resolving the source of sulfate to river systems, and thus to the global ocean, is further important because the role that sulfide weathering plays in the long-term regulation of atmospheric oxygen (Petsch and Berner, 1998). The oxidative weathering of pyrite has the potential to consume atmospheric O_2 either directly or indirectly, yet it is held that evaporite weathering dominates the source of sulfate to river systems (Chakrapani and Veizer, 2006).

Sulfur and oxygen isotopes are a powerful tool for resolving the source of sulfate to river or groundwater systems (Karim and Veizer, 2000; Pawellek et al., 2006; Calmels et al., 2007; Otero et al., 2008; Tuttle et al., 2009; Yuan and Mayer, 2012). Evaporite minerals such as gypsum and anhydrite are typically more enriched in the heavy sulfur and oxygen isotopes (^{34}S and ^{18}O), while pyrite is more enriched in the light sulfur isotope (^{32}S). Oxygen isotopes in sulfate ($\delta^{18}\text{O}_{\text{SO}_4}$), on the other hand, are set when the aqueous sulfate molecule is formed and do not subsequently exchange oxygen isotopes with water (Lloyd, 1968). During gypsum dissolution, the $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ of the original gypsum mineral are preserved in the aqueous sulfate produced; thus gypsum-derived riverine sulfate reflects the $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ of ambient seawater at the time of original gypsum

* Corresponding author. Tel.: +44 1223 333479.

E-mail address: avt25@cam.ac.uk (A.V. Turchyn).

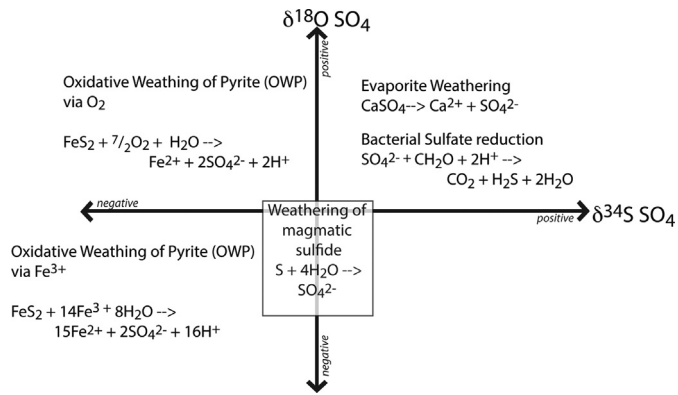


Fig. 1. A diagram of sulfur–oxygen isotope space showing how mineral weathering sources of riverine sulfate produce isotopically distinct sulfate. The combination of sulfur and oxygen isotopes measured in riverine sulfate thus has unique potential to resolve the source of sulfate to a weathering catchment.

deposition. These values range from $\sim 10\text{‰}$ to $\sim 35\text{‰}$ for Phanerozoic evaporites (Claypool et al., 1980). During the oxidative weathering of pyrite, there is minimal sulfur isotope fractionation, mostly between 0‰ and 1‰ , between the original pyrite and the resulting aqueous sulfate; pyrite-derived riverine sulfate largely reflects the $\delta^{34}\text{S}_{\text{SO}_4}$ of the host-rock pyrite (Balci et al., 2007; Heidel and Tichomirowa, 2011). The $\delta^{34}\text{S}$ of pyrite can range from 0‰ to -100‰ for $\delta^{34}\text{S}$. On the other hand, during the oxidative weathering of pyrite, the oxygen atoms in the resulting aqueous sulfate are derived either from atmospheric oxygen ($+23.5\text{‰}$) or from meteoric water (-15‰ to -2‰ in mid-latitude mountain ranges) or a combination of the two. The variability of $\delta^{18}\text{O}_{\text{SO}_4}$ in riverine sulfate separates the anoxic versus oxic pyrite oxidation pathways. When atmospheric oxygen acts as the oxidant, the aqueous sulfate gets oxygen atoms from both atmospheric oxygen and water (Balci et al., 2007; Calmels et al., 2007). In anoxic sulfide oxidation, when the oxidation is typically coupled to the reduction of iron minerals, the aqueous sulfate gets oxygen atoms only from water. The coupled analysis of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ in sulfate combined with the analysis of the $\delta^{18}\text{O}_{\text{SO}_4}$ in water thus constrains the pathway of sulfide oxidation (iron versus oxygen—Calmels et al., 2007). These various sources of riverine sulfate and where they plot in sulfur–oxygen isotope space are shown in Fig. 1.

In this study we analyzed 36 tributaries to the Marsyandi, spanning 65 km of its catchment in the Nepalese Himalayas, for their sulfate–sulfur and sulfate–oxygen isotope composition, as well as four samples from the river's mainstem. The study area is an ideal area in which to attempt to model and constrain the source of sulfate in river water because of the known range of rock types drained with published data on their strontium isotope ratio (e.g. Bickle et al., 2005) and Ca and Mg isotope ratios and major element data (Tipper et al., 2006a, 2008). In addition, the riverine chemistry and its seasonal variation in the basin is relatively well constrained (Tipper et al., 2006b). Finally, the Marsyandi has unusually high sulfate concentrations for a terrestrial environment, but the source of the sulfate remains debated.

2. Site location

A range of sample of large and small tributaries were analyzed (Fig. 2). The region has been sampled and studied previously by Galy et al. (1999), Evans et al. (2001), Bickle et al. (2005), Tipper et al. (2006a, 2006b, 2008), Becker et al. (2008), and Gabet et al. (2008, 2010). The specific samples we worked on were previously presented in Tipper et al. (2006b, 2008) and Becker et al. (2008). The Marsyandi basin has a catchment area of approximately

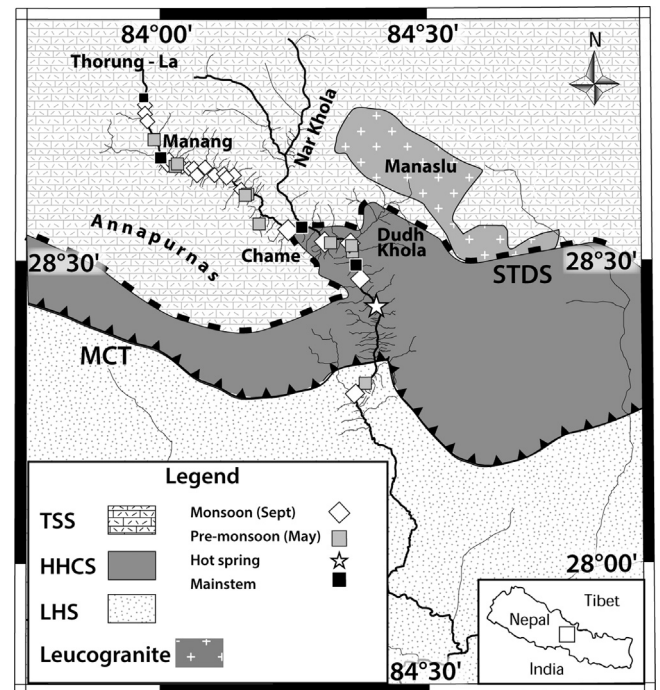


Fig. 2. Map of the Marsyandi with sample locations, local names, and lithologies marked.

4750 km². It is one of the tributaries of the Narayani River, which itself is a major tributary of the Ganges River; the Marsyandi flows approximately 150 km from headwaters in the Tethyan Sedimentary Series (TSS) with arid and glacial conditions through the High Himalayan Crystalline Series (HHCS) to the confluence with the Trisuli in the sub-tropical Lesser Himalayan Series (LHS—Fig. 2). Glacial water contributes significantly to the total water flux in certain tributaries. Small-scale agricultural activities are cultivated in terraces at flanks of mountain ranges concentrating on the wetter slopes of HHCS and LHS. The Marsyandi has a downstream chemical profile typical of many Himalayan rivers where the tectonically controlled changes in bedrock geology which coincide with strongly zoned changes in climate and vegetation exert strong control on river chemistry (e.g. Bickle et al., 2003, 2005; Galy and France-Lanord, 1999; Evans et al., 2001; Tipper et al., 2006b).

Precipitation in the Nepal Himalaya is markedly concentrated during the summer monsoon season ($\sim 80\%$ between May and October), where a low-pressure cell forms on the Tibetan plateau and humid air masses generated in Bay of Bengal deliver heavy rainfall to the southern Himalayan front (Lang and Barros, 2003). There is strong topographic control on precipitation in the Marsyandi catchment (Burbank et al., 2003). Consequently, river discharge and solute fluxes are at their highest during the monsoon period (Tipper et al., 2006b).

The portion of the Marsyandi studied in this project flows mostly through the TSS and partially through the HHCS with two samples in the LHS. The TSS consists of continental margin sequence of variable metamorphosed impure limestone and siliclastic rocks including pyrite rich black shale interbedded at all scales (Bordet et al., 1971) delimited by the Southern Tibetan detachment System. Rivers draining the TSS are characterized by high total dissolved solids (Galy and France-Lanord, 1999; Bickle et al., 2005). The altitude of the mainstem Marsyandi decreases from 5099 m at its source, 2800 m at the contact between the TSS and HHCS to 786 m where the lowest sample was collected, and which is at the contact between the HHCS and LHS (Fig. 2). The change in altitude coincides with marked changes in temperature,

Download English Version:

<https://daneshyari.com/en/article/6430129>

Download Persian Version:

<https://daneshyari.com/article/6430129>

[Daneshyari.com](https://daneshyari.com)