# Hydrothermal source of radiogenic Sr to Himalayan rivers

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## ABSTRACT

Hot-spring waters near the Main Central thrust in the Marsyandi River of central Nepal have Sr concentrations to 115 μM with $^{87}Sr/^{86}Sr$ to 0.77. Small amounts of hydrothermal water (≤1% of total river discharge) have a significant impact on the solute chemistry and the budget of radiogenic Sr in the Marsyandi. In the upper Marsyandi, river chemistry reflects carbonate weathering, with $^{87}Sr/^{86}Sr$ ≤ 0.72. As the Marsyandi flows across the dominantly silicate High Himalayan Crystalline terrane, both $^{87}Sr/^{86}Sr$ and [Sr] increase, associated with increases in the concentration of $Na^+$, $K^+$, and $Cl^-$, all of which are high in the hydrothermal waters. Cation concentrations decrease along the Lesser Himalayan reach of the river. Hot-spring dissolved $CO_2$ has a $\delta^{13}C$ value to +5.9‰, indicating that metamorphic decarbonation reactions contribute $CO_2$ to the fluids. Hydrothermal $CO_2$ is partially neutralized in high-temperature weathering reactions, which generate alkalinity and yield abundant radiogenic Sr. Radiogenic hydrothermal carbonate can form from these solutions and later weather, releasing silicate Sr but imparting carbonate characteristics to the overall water chemistry.

Keywords: hot spring, alkalinity, Himalaya, strontium, geothermal system.

## INTRODUCTION

The Sr flux from Himalayan rivers is an important contributor to the Sr isotope mass balance of the modern oceans, and Himalayan rivers are unusual among world rivers in that they have both high concentrations of Sr and high $^{87}Sr/^{86}Sr$ (Edmond, 1992). Weathering of various silicate phases and weathering of radiogenic carbonates have been proposed as sources for the radiogenic Sr flux in Himalayan rivers (Palmer and Edmond, 1989; Krishnaswami et al., 1992; Derry and France-Lanord, 1996; Quade et al., 1997; Singh et al., 1998; Blum et al., 1998; Galy et al., 1999; English et al., 2000). Each of these sources has different implications for the interpretation of the marine Sr record. We have determined solute chemistry for the main stem, all major tributaries, and both hot and cold springs of the Marsyandi River in central Nepal. We find that hot springs contribute significant amounts of radiogenic Sr and other ions to the Marsyandi River.

## GEOLOGIC SETTING

The Marsyandi River flows over ~150 km from its headwaters north of the Annapurna range to its confluence with the Trisuli River, and has a basin area of ~4800 km² (Fig. 1). This major tributary to the Ganges River crosses the main tectonostratigraphic units that make up the Nepal Himalaya, and the shear zones that bound them. The Marsyandi flows across the Tethyan Sedimentary Series, the South Tibetan detachment system, formations III, II, and I of the High Himalayan Crystalline series, the Main Central thrust, and the Lesser Himalaya sequence (Colchen et al., 1980; Upreti, 1999). The Tethyan Sedimentary Series comprises a Cambrian to early Tertiary stable platform sequence dominated by shelf carbonates. The High Himalayan Crystalline series is high-grade metamorphic basement; formations III and II of the crystallines are composed of calcic gneisses and marbles as well as pelitic augen gneisses, and formation I contains mainly quartzo-pelitic gneisses and some migmatites. The Manaslu leucogranite is exposed in the northeastern part of the drainage. Variably metamorphosed Precambrian sedimentary rocks make up the Lesser Himalaya, pelitic schists and minor dolomitic carbonates in the upper formation and quartzites and schists in the lower formation. Numerous springs are found along the Marsyandi, particularly near the Main Central thrust and the South Tibetan detachment.

## SAMPLING AND ANALYTICAL METHODS

Main stem, tributary, and spring samples were collected in April 1997 and April 1999. All water samples were filtered and stored in acid-washed polyethylene bottles. Cation samples were acidified with concentrated $HNO_3$ in the field. Cations were determined by inductively coupled plasma–mass spectrometry or emission spectrometry (Cornell University
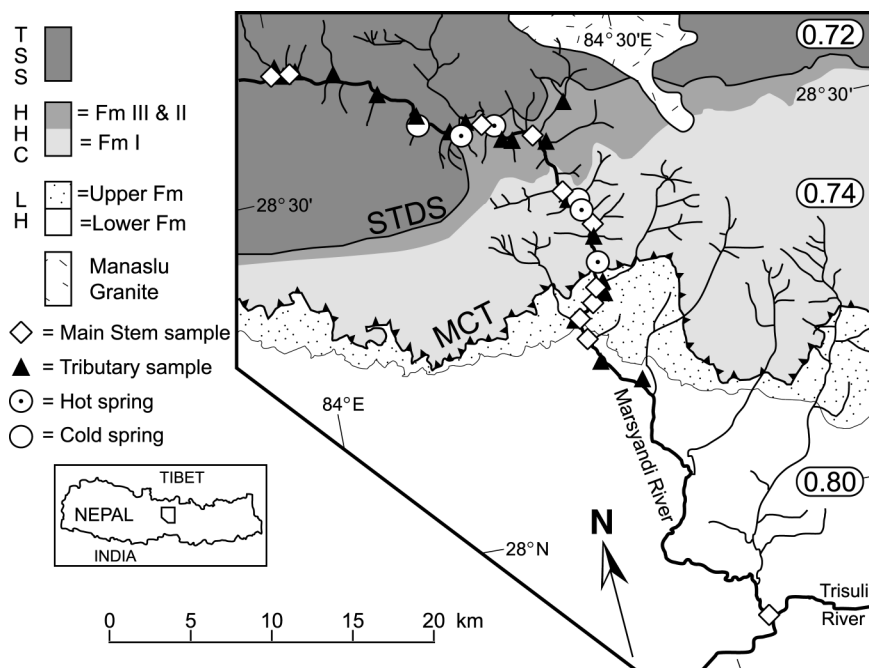


Figure 1. Tectonic sketch map of Marsyandi basin, central Nepal. TSS—Tethyan Sedimentary series; STDS—South Tibetan detachment system; HHC—High Himalayan Crystalline series; MCT—Main Central thrust; LH—Lesser Himalaya. Sampling locations are marked. Symbols and shading continue in following figures. Representative $^{87}Sr/^{86}Sr$ values for bedrock are indicated. Fm is formation.

Figure 2. Marsyandi main stem, tributary, and spring chemistry. Concentrations in micromoles/kg ($\mu$M). Note scale break on all vertical axes to accommodate high concentrations in hot-spring waters. Shading corresponds to map units in Figure 1 and symbols follow its key. Downstream distance measured from Khangsar Khola. K, Na, and Cl are particularly anomalous in hot springs and clearly affect main-stem chemistry down to its confluence with Trisuli River.
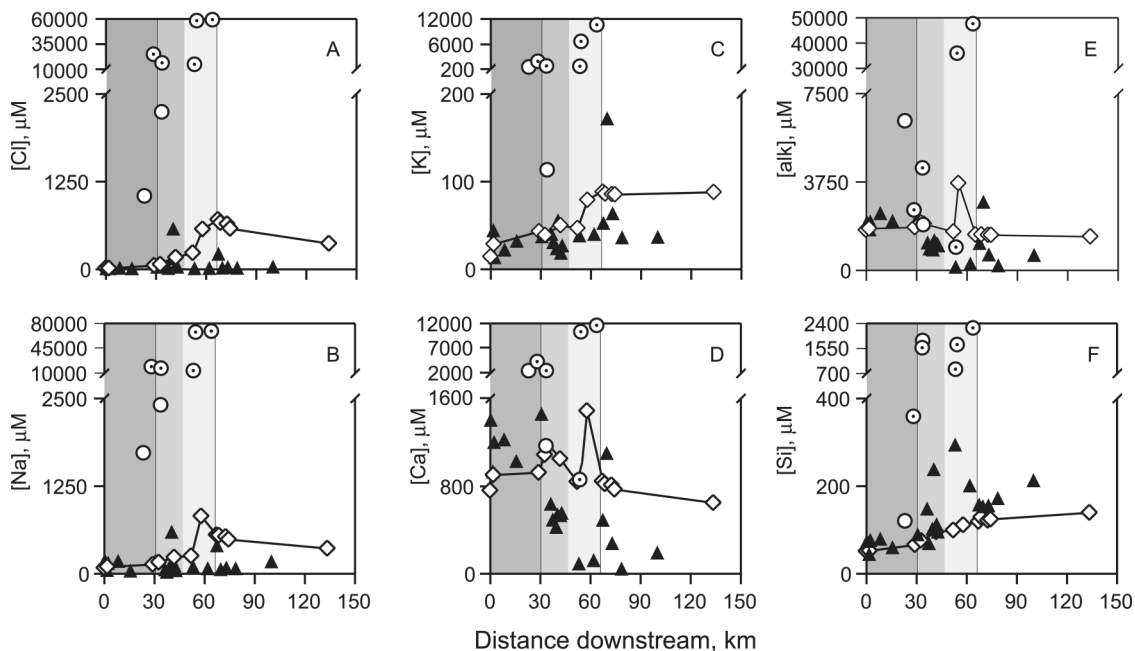
and University of California, Santa Cruz), and anions were determined by ion chromatography (Cornell and Centre des Recherches Pétrographiques et Géochimiques [CRPG]). Sr isotope ratios were analyzed on a VG Sector 54 thermal ionization mass spectrometer (Cornell). Spring waters and some river waters were spiked with an enriched [84]Sr tracer and [Sr] was determined by isotope dilution. Separate samples were reacted under vacuum with $H_3PO_4$, and the evolved $CO_2$ was measured for determination of $\delta^{13}C$ on a modified VG 602D mass spectrometer. The $\delta^{18}O$ and $\delta D$ values from $H_2O$ were determined for six spring samples by $CO_2$ equilibration and reduction over hot uranium, respectively (CRPG).

## RESULTS AND DISCUSSION
### Main Stem and Tributary Chemistry

Within the Tethyan series Ca, Mg, and Sr concentrations[1] are high in both the tributaries and main stem, reflecting carbonate weathering (Figs. 2 and 3). Within the High Himalayan Crystalline and Lesser Himalaya series these ions show overall decreases in concentration, except for main-stem [Sr], which increases in formation I. Levels of K, Na, and Cl in the Marsyandi and its tributaries are relatively low upstream of the South Tibetan detachment, but increase two to tenfold overall within the High Himalayan Crystallines. [Na], [Cl], and [K] in Lesser Himalayan tributaries are mostly relatively dilute. Measured and calculated alkalinities are similar and range from ≈1500 to 1800 $\mu$M for the main stem; the highest values are in the Tethyan series.

The $^{87}Sr/^{86}Sr$ values for the main stem of the Marsyandi increase downstream from 0.719 to 0.733 (Fig. 3) and the majority of this increase occu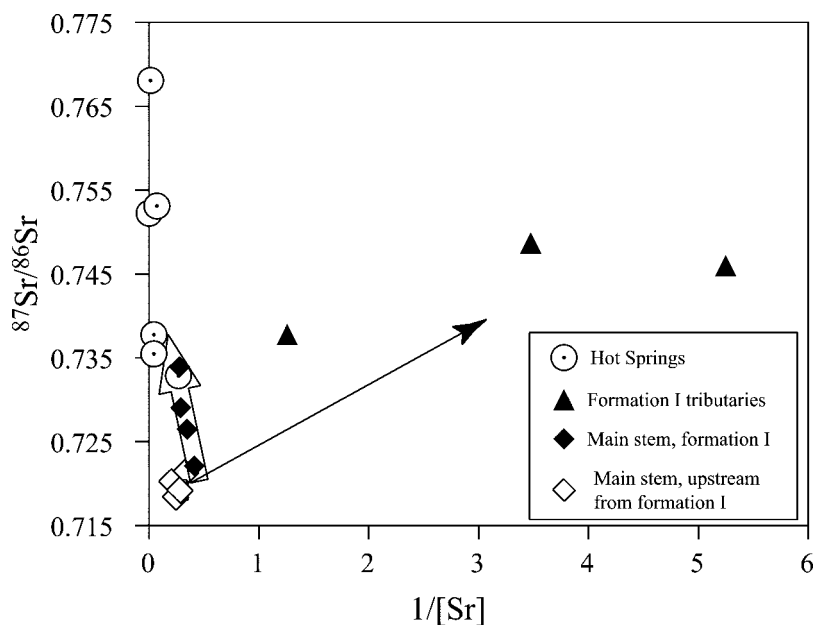rs within the High Himalayan Crystallines, concurrent with the increase in [Sr]. Each of the lithologic units in the Marsyandi basin has distinct Sr characteristics that are reflected in tributary streams from monolithologic catchments. Tethyan tributaries have high Sr concentrations (~4.5 $\mu$M) and low $^{87}Sr/^{86}Sr$, near 0.72. Tributaries from formations II and III have similar $^{87}Sr/^{86}Sr$ at 0.721, but much lower [Sr] (~0.6 $\mu$M). Formations II and III contain abundant marbles, and as in the Tethyan reach, these carbonates strongly control the riverine Sr in both the main stem and tributaries. Formation I tributaries are radiogenic ($^{87}Sr/^{86}Sr$ = 0.744) with dilute [Sr] (≈0.5$\mu$M). Lesser Himalayan streams have [Sr] of only ~0.3 $\mu$M but very high $^{87}Sr/^{86}Sr$ ratios (to 0.87).

### Spring Chemistry

Five hot (~30–55 °C) springs and two cold springs along the Marsyandi were sampled. Hot springs are Cl rich (Fig. 2) with total dissolved solid (TDS) values of 800–7000 mg/L. Cold springs have higher Ca/Na and Ca/Cl ratios but are much more dilute (TDS ≈ 300–600 mg/L) and closely resemble nearby tributaries. Sr in the hot springs is consistently more radiogenic and concentrated than in both the main stem and tributary values at the same position along the Marsyandi; the hot springs define a Sr source distinct from the tributaries, with $^{87}Sr/^{86}Sr$ ranging from 0.736 to 0.768 and [Sr] from 15 to 115 $\mu$M (Fig. 3). The two cold springs sampled near the South Tibetan detachment are much less radiogenic ($^{87}Sr/^{86}Sr$ = 0.712) and concentrated ([Sr] = 6–3 $\mu$M) than their warmer counterparts and resemble Tethyan tributaries. The $\delta^{13}C$ of dissolved inorganic carbon in the sampled
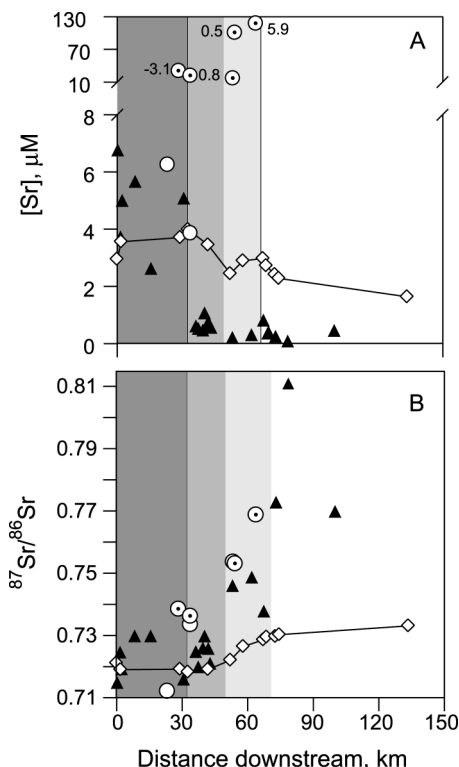


Figure 3. A: Sr concentrations in waters. Note vertical axis break for hot-spring samples. Numbers give $\delta^{13}C$ (in per mil) of dissolved $CO_2$ in hot-spring samples. B: Isotopic ratio of dissolved Sr, symbols as in Figure 1. Compared to tributaries, hot springs in formation I of High Himalayan Crystallines have ~100 times more Sr, and are more radiogenic.

**Figure 4. Mixing diagram for Marsyandi and its sources within High Himalayan Crystallines. Solid arrow shows expected mixing line between main stem and formation I tributaries. Open arrow shows expected mixing line between main stem and hot-spring source. Tributaries are radiogenic but dilute, and cannot cause increase in Sr concentration observed within formation I. Hot springs are both radiogenic and highly concentrated and drive main stem to higher [Sr] and $^{87}Sr/^{86}Sr$.**

springs ranges from $-3.1‰$ to $+5.9‰$ (Fig. 3). The springs with the highest Cl concentrations (to $\sim$57 000 $\mu M$) also have the highest [Sr] and $^{87}Sr/^{86}Sr$ values ($\sim$0.77) and tend to have positive $\delta^{13}C$. Calculated alkalinities for the highest-Cl hot springs range from 36 000 to 47 000 $\mu M$. The hot springs are supersaturated with both calcite and quartz, and travertine deposits are common near the springs. The $\delta^{18}O$ and $\delta D$ range from $-10.3$ to $-14.4$ and from $-67.5$ to $-101.9$, respectively. The $\delta^{18}O$ and $\delta D$ values are very close to the local meteoric water line (Galy, 1999) and imply that the water in the hydrothermal system is locally derived meteoric water.

### Spring Flux

Direct measurement of the overall water flux from the Marsyandi springs is difficult because they frequently do not flow from discrete point sources and diffuse flow occurs in the stream bed. Because chloride is anomalously high in the spring waters, and behaves conservatively, we can use the Cl mass balance to estimate the water flux from the springs. The average [Cl] of the tributaries is 72 $\mu M$ and that of the hot springs is 33 025 $\mu M$; thus a spring flux of slightly <1% yields the observed [Cl] of 366 $\mu M$ at the Marsyandi-Trisuli confluence. The discharge of the Marsyandi is $6.61 \times 10^9$ m³/yr (Sharma, 1997), yielding a water-flux estimate from the springs within the High Himalayan Crystallines of $\sim 6 \times 10^7$ m³/yr. The springs have a significant impact on the chemistry of the

Marsyandi despite the fact that they contribute only a small amount of the water flux.

### Hydrothermal Solutes

The high [Cl] and [Na] suggest that basinal brines or buried evaporites could be sources of solutes to the springs. Evaporites are known from possibly correlative Lesser Himalayan strata in Pakistan; however, no evaporites have been described in the Lesser Himalaya of central Nepal. We make the simplifying assumption that all Cl was originally present as NaCl. Na in excess of Cl is defined as [Na*] = [Na] $-$ [Cl]. The hot springs near the Main Central thrust have 8000–9000 $\mu M$ [Na*], 6000–10 000 $\mu M$ [K], and to 2200 $\mu M$ [Si], all of which reflect alteration of silicate minerals. Of the total alkalinity in the springs, $\sim$40% is composed of Na* and K. The balance is present as Ca and Mg, which could be derived from dolomitic carbonates in the upper Lesser Himalayan section. However, two observations suggest that a significant part of this remaining alkalinity (Ca, Mg) is also derived from silicate alteration. First, formation I gneisses are rich in biotite, and biotite alteration almost certainly provides some Mg to the hydrothermal fluids. Second, the Ca/Mg ratio of the hot-spring fluids ranges from 3 to 15, whereas streams draining Lesser Himalayan dolomites have a Ca/Mg ratio near 2. Some Ca in the hot springs is likely derived from alteration of oligoclase present in the High Himalayan Crystallines. However, at present we cannot accurately quantify the frac-

tion of hot-spring alkalinity that is derived from carbonate versus silicate sources. The fraction of hot-spring alkalinity present as Na* and K necessarily represents a minimum estimate of the silicate-derived alkalinity flux from the springs.

The positive $\delta^{13}C$ values ($+0.48‰$ to $+5.9‰$) in spring water $CO_2$ imply that some of the dissolved $CO_2$ (alkalinity) is derived from metamorphic decarbonation reactions (Shieh and Taylor, 1969; Friedman and O'Neil, 1977). Metamorphic $CO_2$ has been identified in hot springs from the nearby Mustang graben (Galy and France-Lanord, 1999). The high alkalinities of the hot springs indicate that a significant quantity of metamorphic $CO_2$ has already been neutralized by reactions with base cations.

### Source of Sr in Marsyandi River

The hot-spring flux has a significant impact on the isotopic and mass balance of Sr in the Marsyandi. Within the Tethyan series and formations II and III, the $^{87}Sr/^{86}Sr$ ratios of the Marsyandi are similar to those of its tributaries; formation II and III tributaries only serve to slightly dilute the main stem. Formation I tributaries are also dilute, and if they are the only new source of solutes to the main stem, then the Marsyandi should evolve toward more radiogenic and dilute values (Fig. 4). However, Sr in the Marsyandi River becomes both more radiogenic and concentrated in formation I of the High Himalayan Crystallines, following a mixing line toward sampled hot springs. Mixing with the radiogenic and dilute Lesser Himalayan tributaries causes a decrease in [Sr] and a slight increase in $^{87}Sr/^{86}Sr$. Approximately 30% of the Sr flux of the Marsyandi at its confluence with the Trisuli is delivered from hydrothermal sources, a figure consistent with both the Sr isotope budget and the major ion mass balances.

As in a number of other Himalayan rivers, the Marsyandi has Sr/Ca ratios higher than expected from simple carbonate dissolution. The causes of the excess Sr probably include precipitation of secondary carbonate with low Sr/Ca from supersaturated stream waters; however, the overall importance of this process is not known with certainty (Galy et al., 1999; English et al., 2000). The Marsyandi hot springs have very high Sr/Ca ratios (6.9–16.4 $\mu mol/mmol$) and can elevate Sr/Ca in the river by simple mixing. Distribution coefficients for Sr between water and calcite vary from $k_{Sr} \approx 0.03$ to 0.08 over a temperature range of 40–200 °C (Holland et al., 1964; Humphrey and Howell, 1999; Malone and Baker, 1999). With the stated $k_{Sr}$ range, Sr/Ca in calcite precipitated from these hydrothermal fluids would range from 1.31 to 0.21 $\mu mol/mmol$. The Sr/Ca in the remaining fluid would increase in

proportion to the fraction of Ca precipitated. The calculated precipitate values are very similar to Sr/Ca in hydrothermal calcite veinlets at Nanga Parbat (Jacobson and Blum, 2000), and as at Nanga Parbat, Sr in calcite formed from Marsyandi hydrothermal fluids will be radiogenic.

Silicate rocks of both the High Himalayan Crystallines and Lesser Himalaya, and Lesser Himalayan carbonates are all potential sources of radiogenic Sr in the hot springs. Silicate-derived alkalinity and high Sr/Ca ratios in the hot-spring fluids are consistent with a silicate source. Sr/Ca in formation I silicate rocks is ~11 $\mu$mol/mmol, generally similar to the hydrothermal fluids. Lesser Himalayan carbonates in central Nepal have very low Sr contents with Sr/Ca ratios ~0.1 $\mu$mol/mmol (Galy et al., 1999), making it unlikely that simple carbonate dissolution or dissolution-precipitation could be the major source for the hydrothermal Sr.

## CONCLUSIONS AND IMPLICATIONS

The hot springs along the Marsyandi are a major source of solutes and, despite composing $\leq$1% of the water budget, deliver up to 30% of the river's Sr flux. Active tectonic processes beneath the Main Central thrust provide both the heat and some of the $CO_2$ to these systems, and the hot-spring water and solute fluxes directly reflect current tectonic activity. Hydrothermal interaction is probably common in collisional orogens, driven by high uplift and denudation rates (e.g., Templeton et al., 1998).

The hydrothermal fluids contain a significant component of $CO_2$ derived from decarbonation reactions and are therefore a source of $CO_2$ in the global carbon cycle. However, the radiogenic Sr and high silicate-derived alkalinities in the spring fluids imply that hydrothermal alteration of silicate rocks have neutralized a fraction of this $CO_2$ flux. The alteration of silicates from the High Himalayan Crystallines at moderate hydrothermal temperatures is analogous to low-temperature silicate weathering reactions in that $CO_2$ is neutralized by reactions with silicate-derived base cations. Whereas much of the alkalinity in the Marsyandi is derived from carbonate weathering (Galy and France-Lanord, 1999), a significant proportion of the hot-spring alkalinity is derived from silicate sources ($\geq$40% in the hot springs near the Main Central thrust). Thus the hot springs are an important source of silicate-derived alkalinity to the river.

In developing an isotopic budget for the Sr flux in Himalayan rivers, we argue that it is important to distinguish between dissolution of sedimentary marine carbonate units and hydrothermal calcite. Weathering of altered limestones can be a significant source of radiogenic Sr (English et al., 2000) but has no net effect on the atmospheric $CO_2$ budget. However, some part of the Sr and Ca in hydrothermal calcite precipitated from the Marsyandi springs is derived from silicates. Although weathering of such precipitates will yield the solute signature of carbonate weathering, it is actually just an intermediate step in introducing the products of silicate alteration by $CO_2$ into the river system. In terms of the global cycles of Ca, Sr, and $CO_2$, hydrothermal alteration in the Marsyandi springs can be viewed as high-temperature silicate weathering. Geothermal activity is common along the Himalayan front, and a better understanding of hot-spring fluxes should help resolve some of the current ambiguities in the solute and isotopic budgets of Himalayan rivers, and clarify the ways in which the process of orogenesis interacts with the carbon cycle.

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