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Tracing silicate weathering in the Himalaya using the ^{40}K-^{40}Ca system: A reconnaissance study

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Abstract

This study investigates the potential of the ^{40}K-^{40}Ca decay scheme as a tracer of silicate vs. carbonate weathering in the Himalayan erosional system. To this end, we present high precision ^{40}Ca data on river sediments, dissolved river loads and whole-rock carbonates representative of the main tectonic units of the Himalayas. Our results show that metamorphosed dolomites from the Lesser Himalaya (LH) exhibit no radiogenic ^{40}Ca excess despite highly variable $^{87}Sr/^{86}Sr$ signatures (0.73-0.85). In contrast, silicate material is radiogenic, with $\varepsilon^{40}Ca$ ranging between +1 in the TSS to +4 ε-units in the LH. Preliminary results obtained from a series of 27 Himalayan rivers show that $\varepsilon^{40}Ca$ in the dissolved load is significantly influenced by silicate lithologies, with $\varepsilon^{40}Ca$ ranging from +0.1 to +1.6 ε-units. Our results suggest that the ^{40}Ca signature of Himalayan rivers primarily reflects the lithological nature of their erosional source, and highlights the potential of the ^{40}K-^{40}Ca decay scheme as a tracer of silicate weathering.

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Keywords: weathering; silicate; carbonate; Himalaya; calcium cycle; ^{40}K-^{40}Ca system

1. Introduction

The uplift and erosion of the Himalayan-Tibetan Plateau (HTP) has long been thought to play a key role in controlling the $^{87}Sr/^{86}Sr$ evolution of seawater throughout the geologic past [1-6]. Understanding the relative contribution of silicate versus carbonate weathering in the Himalaya is important for understanding the evolution of the CO_2 cycle and seawater chemistry [7]. However, Himalayan rivers have distinct characteristics, i.e. high Sr

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concentrations and radiogenic $^{87}Sr/^{86}Sr$, that exclude a simple mixing relationship between silicate and carbonate lithologies [8-10]. The use of $^{87}Sr/^{86}Sr$ signatures as a tracer of Himalayan weathering is not straightforward because (1) the formations of the Himalaya have different crustal aging, hence contrasted bulk $^{87}Sr/^{86}Sr$, and (2) the recent metamorphism redistributed radiogenic ^{87}Sr towards weatherable minerals such as feldspars and carbonates [5, 8-11].

This study investigates the potential use of the ^{40}K-^{40}Ca system as a tracer to better quantify the contributions of silicate and carbonate lithologies in the dissolved load of major Himalayan rivers [13-15]. Previous work showed that the ^{40}Ca budget of seawater is dominated by mantle inputs [15], so that marine carbonates display a homogeneous $\varepsilon^{40}Ca$ signature indistinguishable from the mantle value (i.e. $\varepsilon^{40}Ca=0$). In contrast, the silicate upper crust, with a K/Ca ratio of 1, is expected to have developed a radiogenic $\varepsilon^{40}Ca$ of ca. +2 ε -units. It was therefore anticipated that the ^{40}K-^{40}Ca system could yield robust constraints on the relative contribution of silicate vs. carbonate lithologies in dissolved river loads. Here, we present the first extensive investigation of ^{40}K-^{40}Ca systematics in the Himalayan erosional system. We show that during the collision of India with Asia, ^{40}Ca, unlike ^{87}Sr, remained remarkably resistant to metamorphism/dolomitization, allowing us to distinguish carbonate and silicate sources in the dissolved load of the major Himalayan rivers.

2. Samples

Three types of samples were investigated in this study. First, bedload sediments (Figure 1) were selected from rivers draining the main lithological and tectonic units of the Himalaya. These include the Marsyandi in the TSS, the Chepe in the HHC and the Isul in the LH, as well as sediments from the Ganga and Brahmaputra rivers. The silicate fractions of these sediments have $^{87}Sr/^{86}Sr$ compositions ranging from 0.72 (in the TSS) to 0.86 (in the LH) and εNd between -16 and -25.6 [9]. Based on Sr-Nd provenance work in [8], these samples fall into

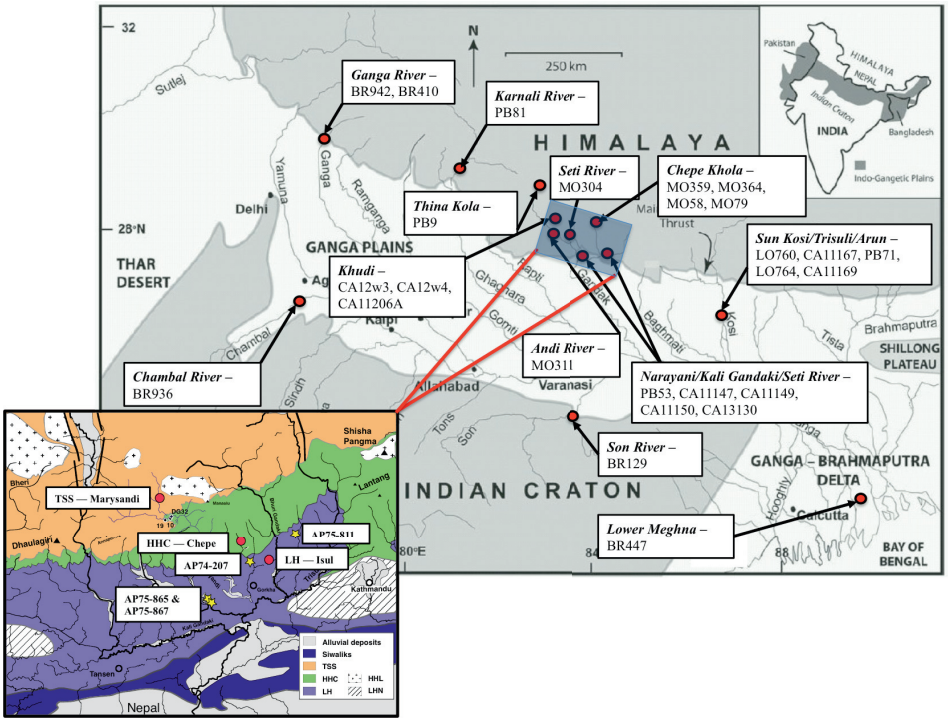


Figure 1. Map of the Ganges and Brahmaputra basin and major tributaries. Location of river samples is denoted by a red dot with the specific river and sample number also identified. The Main Frontal Thrust (MFT) is also denoted on the larger map. The MFT places Siwalik foreland basin sediments over the modern Gangetic plain, while the MCT places the HHC over the LH. The inset image shows an enhanced geological map view of the Narayani watershed and the location of bedload (red dots) and carbonate samples (yellow stars) analysed in this study.

compositional fields representative of the main tectonic units of the Himalayas and should therefore provide a general overview of $^{40}Ca/^{44}Ca$ variability in the Himalayan system.

Second, a suite of 27 river water samples (Figure 1) was selected to gain a clearer understanding of the contribution from main litho-tectonic units to the ^{40}Ca dissolved flux. The selected samples include the major tributaries of the Ganga (Upper Ganga, Narayani, Karnali, Kosi) as well as small rivers draining single lithologies (Khudi, Chepe). While this study is more strongly focused on the Narayani watershed, these samples cover most of the Sr isotope and major element variability observed in Himalayan rivers.

Lastly, a series of variably dolomitized impure marbles from the Lesser Himalaya were analyzed to assess the sensitivity of ^{40}Ca to post-depositional effects (dolomitization, metasomatism, metamorphism) (Figure 1, inset image). The marbles are characterized by a carbonate content of 60-80 wt% and a Mg/Ca ratio from 0.1 to 0.55 [9]. Their $^{87}Sr/^{86}Sr$ varies between 0.72 (for massive beds) and 0.86, reflecting extensive redistribution of ^{87}Sr between carbonates and the surrounding calc-silicate shists.

3. Methods

Relatively little work has been completed so far on the ^{40}K-^{40}Ca system due to the difficulty of measuring small radiogenic effects on the large ^{40}Ca isotope. Work in the 1980s using the Finnigan-MAT 262 reported external precisions of ±0.6-1.5 ε-units (2σ) [16-17]. More recently, using a Thermo-Finnigan Triton Thermal Ionization Mass Spectrometer (TIMS) to analyze samples from Archean cratons, Kreissig and Eliott [18] obtained a reproducibility of ±0.5 ε-units (2σ) and Caro et al. [15] reported $^{40}Ca/^{44}Ca$ data in marine carbonates with external precision of ±0.35 ε-units. This improvement was made possible by i) the measurement of larger ion beams on the Triton (<50V, against <10V using the MAT262), and ii) the implementation of multidynamic acquisition schemes using the "Zoom" optical system of the Triton. Thus, problems with the requisite sensitivity to analyze small variations in the abundant ^{40}Ca isotope (96.9%) can now be resolved using the Triton TIMS [15].

The mass spectrometric method implemented here is a multidynamic approach modified from [15]. Prior to analysis, ca.10 µg of Ca is loaded in concentrated HNO_3 onto the evaporation filament of a double rhenium filament assembly. Heating the ionization filament to about 3000 mA generates a stable signal during approximately 2-4 hours of analysis (15V on ^{40}Ca, 100 mV on ^{42}Ca). The multidynamic scheme involves the acquisition of ^{40}Ca, ^{42}Ca ^{43}Ca and ^{44}Ca on line 1 (L1) followed by ^{42}Ca and ^{44}Ca on line 2 (L2). The $^{40}Ca/^{42}Ca_{(L1)}$ ratio is corrected from instrumental mass fractionation using the exponential law with $^{42}Ca/^{44}Ca_{(L2)}=0.31221$ as a normalization ratio. Sample analyses were interspersed with measurements of the NIST SRM915a standard, whose $^{40}Ca/^{42}Ca$ value is identical within errors to both seawater and MORBs [15]. $^{40}Ca/^{42}Ca$ variations are normalized to the NIST value and expressed using the conventional $\varepsilon^{40}Ca$ notation. In-run internal precision is typically ±0.2-0.3 ε-units ($2\sigma_m$) and external precision in multi-dynamic mode is ±0.2-0.4 ε-units (2σ).

4. Results

Calcium and strontium isotopic results for bedrock, bedload sediments and rivers are presented in Figure 2. A major result of this study is the remarkably homogeneous $\varepsilon^{40}Ca$ signatures measured in both bedrock and bedload carbonates, which contrasts with their heterogeneous $^{87}Sr/^{86}Sr$ compositions (from ≈0.72 to ≈0.86). It is certainly plausible that despite isotopic exchange associated with Himalayan metamorphism, the high Ca content of carbonate rocks prevented any significant modification of their original signature (at $\varepsilon^{40}Ca=0$). In contrast, the silicate fractions in bedload sediments show significant ^{40}Ca excesses on the order of +0.9 ε-units in the TSS to +3.8 ε-units in the LH (±0.3 ε-units, 2σ), correlating with their $^{87}Sr/^{86}Sr$ ratios. In the Brahmaputra and Ganga sediments, $\varepsilon^{40}Ca$ average ca. +2 ε -units, similar to those measured in HHC bedloads. These $\varepsilon^{40}Ca$ values are consistent with the K/Ca and Nd model ages for their respective Himalayan formations. Therefore, the ^{40}K-^{40}Ca system offers a simple means of distinguishing carbonate vs. silicate sources in the dissolved river flux.

As shown in Figure 2, Himalayan rivers display a wide range of $\varepsilon^{40}Ca$ compositions, from +0.1 in rivers draining carbonate dominated catchments to +1.6 in HHC rivers draining predominantly silicate catchments. Given the limited magnitude of $\varepsilon^{40}Ca$ excesses measured in silicate rocks, this result implies that silicate weathering makes a significant contribution to the dissolved calcium budget of Himalayan rivers. Interestingly, rivers with the most radiogenic $^{87}Sr/^{86}Sr$ ratios are not necessarily associated with the highest $\varepsilon^{40}Ca$ values. For example, the Andi River,

which drains Lesser Himalayan lithologies, exhibits one of the highest $^{87}Sr/^{86}Sr$ signatures at 0.7720 and has a relatively low $\varepsilon^{40}Ca$ at +0.64 (±0.30 ε-units, 2σ). In contrast, the Khudi, which drains a HHC silicate catchment, has a lower $^{87}Sr/^{86}Sr$ of 0.74 but an $\varepsilon^{40}Ca$ signature that is far more radiogenic at +1.6 (±0.3 ε-units, 2σ). As mentioned above, such decoupling is expected from the presence in the LH of metamorphosed carbonates with high $^{87}Sr/^{86}Sr$ ratios but non-radiogenic $^{40}Ca/^{44}Ca$. Overall, the positive $\varepsilon^{40}Ca$ observed in Himalayan rivers seem to originate primarily from silicate catchments of the HHC, while their radiogenic ^{87}Sr budget is more strongly influenced by carbonates of the Lesser Himalaya. Since calcium is a major constituent in water and sediment, compared to strontium — a trace element, the calcium isotopic system might better represent the overall weathering budget and fluxes. This suggests that, with a more extensive knowledge of ^{40}Ca distribution in silicate catchments, the ^{40}K-^{40}Ca system could become a powerful tool to quantify silicate weathering in the Himalayan system.

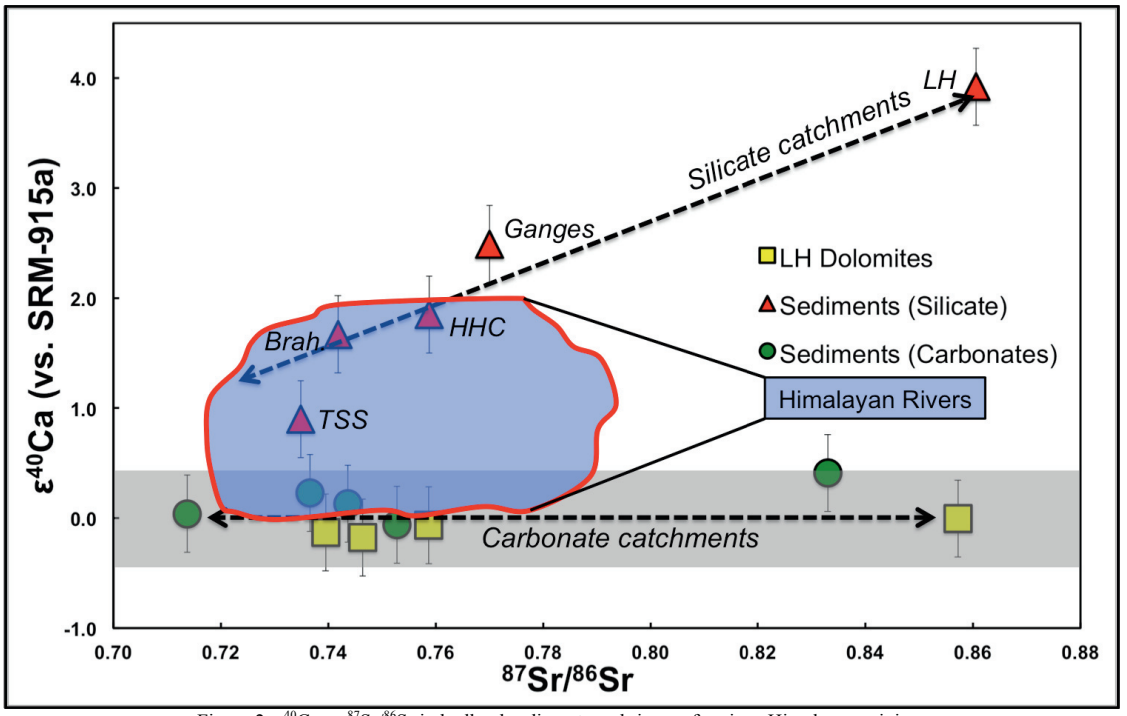


Figure 2. $\varepsilon^{40}Ca$ vs $^{87}Sr/^{86}Sr$ in bedload sediments and rivers of various Himalayan origins.

5. Conclusions

High precision ^{40}Ca analyses using the Triton TIMS enable the use of ^{40}K-^{40}Ca as a tracer of silicate weathering in the Himalaya as well as other complex erosional systems. To the contrary, unlike with strontium, calcium isotopic compositions in carbonates appear to be remarkably resistant to metamorphism and thus no radiogenic effect was found in carbonates from the main Himalayan formations. In contrast, radiogenic ^{40}Ca excesses are found in dissolved river loads with a composition intermediate between non-radiogenic carbonate and radiogenic silicate HHC sources. These results suggests that silicate catchments make a major contribution to the dissolved Ca budget of major Himalayan rivers.

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