

Carbonate versus silicate weathering fluxes of Sr from a High Himalayan watershed

J. D. Blum
C. A. Gazis
A. D. Jacobson
C. P. Chamberlain

Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire 03755, USA

The Himalayan uplift has been implicated as a major factor in the global climatic cooling of the past 40 m.y. because of enhanced silicate weathering and consequent atmospheric CO₂ drawdown (Raymo and Ruddiman, 1992). Supporting evidence includes the dramatic increase in marine ⁸⁷Sr/⁸⁶Sr ratios at 40 Ma, which appears to be related to Sr inputs from major rivers draining the Himalaya (Palmer and Edmond, 1992). Regional patterns of ⁸⁷Sr/⁸⁶Sr ratios in tributaries of the Ganges-Brahmaputra and Indus River systems as well as bedrock ⁸⁷Sr/⁸⁶Sr ratios suggest that the major source of the highly radiogenic Sr in Himalayan rivers is weathering of silicate minerals in the High Himalayan Crystalline Series (HHCS) (Krishnaswami *et al.*, 1992; Harris, 1995). Here we report on a geochemical investigation of the ~200 km² Raikhot watershed in the western Himalaya on the north side of the Nanga Parbat massif in northern Pakistan, with the aim of elucidating the systematics of Sr release from individual minerals in the HHCS bedrock.

The bedrock of the area is predominantly high-grade quartzofeldspathic biotite gneiss and schist with minor anatectic biotite granite and a small amount (~1%) of calc-silicate schist. The bedrock is generally representative of the HHCS, which extends over 2000 km across the length of the Himalaya and dominates the geology of the steep southern slopes that are subjected to rapid erosion during the monsoon season (Harris, 1995). Samples for analysis were taken of rainwater, snow, clear streams, Raikhot River water (which has suspended glacial flour), Raikhot riverbed sand (believed to be representative of unweathered bedrock from the watershed), bedrock from outcrops, and glacial boulders (Blum *et al.*, 1998). Rock samples containing calcite were leached for 1 h in 4 N acetic acid to dissolve carbonate, and silicate rock samples were totally digested for elemental and Sr isotope analysis. Concentrations were measured by ICP-OES and ICP-MS; ⁸⁷Sr/⁸⁶Sr ratios were measured by TIMS.

The most abundant minerals in the bedrock of the

watershed are quartz, plagioclase, K-feldspar, and biotite; calcite is present in only minor abundance but is important due to its high reactivity. Plagioclase and K-feldspar are assumed to weather to kaolinite, and biotite to vermiculite (or hydrobiotite). A mass-balance calculation was performed to quantify the proportions of each of the bedrock minerals that weathered to yield each water composition. This calculation has the following six steps based on the stoichiometry of the weathering reactions. (1) Atmospheric correction. (2) Attributing of Na to the weathering of albite to kaolinite. (3) Attributing of Ca in proportion to the Ca/Na ratio of plagioclase to the weathering of anorthite to kaolinite. (4) Attributing any remaining Si to the weathering of orthoclase to kaolinite. (5) Attributing the remaining K to the weathering of biotite to vermiculite. (6) Attributing excess Ca and Mg to carbonate dissolution.

For the Raikhot River samples, the above calculation yields an estimate of the relative amounts of weathering of minerals as follows: 14% plagioclase, 2% orthoclase, 11% biotite, and 73% carbonate. This estimate corresponds to a riverine HCO₃⁻ flux that is 18% derived from silicate and 82% derived from carbonate weathering reactions. Analyses of the carbonate and silicate fractions of the riverbed sand indicate that only 1.0 wt.% of the sediment load is carbonate. The calculated percentages of weathering of bedrock minerals for the average quartzofeldspathic gneiss and granite bedrock stream-waters were: 24% plagioclase, <1% orthoclase, 12% biotite, and 64% carbonate. High proportions of HCO₃⁻ are also derived from carbonate (68–78%) in the stream waters known to drain exclusively quartzofeldspathic gneiss and granite bedrock.

The Ca/(1000Sr) ratios of silicate rocks (gneiss and granite) range from 0.07 to 0.4, whereas marble layers range from 1 to 2. ⁸⁷Sr/⁸⁶Sr ratios of the silicate rocks (and all their constituent minerals) range between 0.82 and 0.89, whereas marble layers

range from 0.71 to 0.73. In a plot of $\text{Ca}/(1000\text{Sr})$ vs $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 1), river and streamwater samples from the watershed do not plot on a mixing line between the average silicates and marbles. Instead they plot within a triangle defined by silicate, marble, and an additional weathering end member, which must have a $\text{Ca}/(1000\text{Sr})$ ratio over 4.5 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio over 0.82 to satisfy mixing relationships in Fig 1, and must be calcite to satisfy the normative calculations.

Leachates of marble bands and the carbonate fraction of calc-silicate gneisses containing calcite range from $\text{Ca}/(1000\text{Sr})$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values similar to the average defined by the riverbed sand up to values approaching those appropriate for the additional end member (Fig. 1). Traces of finely disseminated calcite veins and blebs are found commonly in thin sections of quartzofeldspathic gneiss and granite and associated with quartz veins in the watershed. Although we have not measured it directly, we infer that this vein calcite end member has a $\text{Ca}/(1000\text{Sr})$ of >4.5 (Fig. 1), which is within the range observed in some other studies of vein calcites in granites and gneisses. We infer that this finely disseminated calcite has equilibrated isotopically with the silicates and thus has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ~ 0.86 (Fig. 1). We hypothesize that the pervasive young metamorphism and hydrothermal fluid flow in this region caused partial equilibration of marble bands with quartzofeldspathic gneisses, resulting in progressive increases in the Ca/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of metasedimentary carbonates and precipitation of disseminated calcite. We conclude that the gneiss and granite-draining streams with the highest Ca/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios represent dissolution of $\sim 75\%$ vein calcite and $\sim 25\%$ silicate minerals, which when mixed with the weathering products of marble defines the composition of all the waters in the watershed.

Thus, even in the predominantly silicate Raikhot watershed of the HHCS, the cation and HCO_3^- flux is predominantly derived from the dissolution of a small amount of calcite ($\sim 1\%$) found in thin layers of metasedimentary rocks and finely disseminated as

veins within quartzofeldspathic gneisses and granites. If the results from this single watershed can be extrapolated to the entire HHCS (and we think that they can, although this remains to be demonstrated), then the implication of our finding is that the flux of highly radiogenic Sr to the oceans related to the Himalayan uplift was predominantly derived from dissolution of carbonate minerals, which has no net effect on rates of atmospheric CO_2 consumption. Thus, models using the flux of radiogenic Sr from the Himalayas that assume this flux is due to mainly to silicate weathering may overestimate the amount of CO_2 consumption due to weathering in the Himalayas.

Our work supports that of Palmer and Edmond (1992) who suggested that the high Sr flux and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of major Himalayan rivers are likely controlled by carbonates with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that had reequilibrated with silicates. We find that the precipitation of disseminated calcite by hydrothermal fluids plays a much more important role than previously recognized. We support the conclusion that the geologic record of $^{87}\text{Sr}/^{86}\text{Sr}$ variation in Himalayan rivers through time (Derry and France-Lanord, 1996; Quade *et al.*, 1997) cannot be used to directly calculate the amount of CO_2 consumption by silicate weathering in the Himalaya. Instead, we find that weathering reactions releasing the high $^{87}\text{Sr}/^{86}\text{Sr}$ flux of dissolved Sr from the HHCS derive only $\sim 18\%$ of their HCO_3^- from silicate weathering.

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