

Himalayan Tectonics, Weathering Processes, and the Strontium Isotope Record in Marine Limestones

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The time evolution of the isotopic composition of seawater strontium (the ratio of strontium-87 to strontium-86) over the last 500 million years has the form of an asymmetric trough. The values are highest in the Cambrian and Recent (0.7091) and lowest in the Jurassic (0.7067). Superimposed on this trend are a number of smaller oscillations. Consideration of the geochemical cycle of strontium and the dynamics of weathering shows that only Himalayan-style continental collisions can influence the isotope ratio on the scale observed. The contemporary Himalayan orogeny is by far the largest since the late Precambrian Pan-African event that produced the high in the Cambrian.

Variations in the isotopic composition of strontium in seawater, recorded in marine limestones, are a proxy of the interplay of mantle processes and crustal weathering. Wickman originally proposed that Rb (the radioactive parent of ^{87}Sr , half-life ~ 48 billion years), as an incompatible element, should be progressively enriched in continental crustal rocks over geologic time relative to Sr (1). Hence, Sr from fluvial inputs to the ocean should become increasingly radiogenic, leading to a monotonic increase in the isotopic composition of Sr in seawater. Wickman was the first to recognize that the record of this increase, preserved in marine sediments, could be used for dating, particularly of limestones and evaporites (1). This latter idea has recently been revived and applied with some success (2) (Fig. 1). However, the isotopic systematics are much more complex than Wickman could have realized.

The isotopic composition of Sr in seawater at any time is determined by the balance between the deep-sea hydrothermal input of nonradiogenic Sr of mantle origin (~ 0.7035) and the more radiogenic fluvial flux derived from continental weathering (~ 0.712) (3). The major sink for Sr is marine carbonate rocks; incorporation in the carbonates involves no isotopic fractionation. The residence time of Sr in this limestone reservoir is on the order of 150 million years (and in seawater ~ 3 million years) (3). Variations in the continental signal, caused by the dissolution of igneous and metamorphic rocks, are therefore damped by the weathering of these carbonates after exposure caused by changes in eustatic sea level or by tectonic uplift. Because of the weathering of carbonates, the fluvial flux retains a "memory" of isotopic fluctuations in the geologic

past (4). Observations indicate that the fluvial flux is dominated by the weathering of platform carbonates and evaporites of marine origin. There is only a minor contribution from the primary weathering of the refractory igneous and metamorphic basement rocks (5). Hence, the memory effect is dominant.

A synthetic stratigraphic column composed of marine limestones has been assembled that is continuous over the past 500 million years (6). The Sr isotopic record of seawater derived from this column is characterized by large oscillations on a variety of time scales (Fig. 2). Values of the ^{87}Sr to ^{86}Sr ratio were high in the Cambrian (~ 0.7091) but declined irregularly until the late Jurassic (~ 0.7067). Several intermediate-scale fluctuations are superimposed on this trend. The continuation of these oscillations in the Cretaceous and Tertiary was interrupted in the mid-Tertiary by a steep rise that has continued until the present time (Fig. 1). The contemporary seawater ratio (0.7091) is the same as that at the height of the Cambrian and is substantially higher than at any intervening time. These observations are completely at variance with the original linear evolution model (1).

In attempts to explain the features in the isotope curve, correlations have been claimed with many events contained in or inferred from the geologic record (2, 7). Changes in the fluvial inputs have been attributed to variations in continental glaciation, eustatic sea level, atmospheric CO_2 levels, climate, vegetation, and mountain building, individually or in combination. For time periods before about 100 million years ago where the paleomagnetic record provides little constraint, changes have been claimed because of substantial variations in the oceanic hydrothermal flux and hence the sea floor spreading rate. Because many of

these variables are causally related, it has not proved possible to develop an unambiguous and specific interpretation of the isotope record in terms of explicit mechanisms. The consensus is that variations in the intensity of continental weathering are important, although this notion has not been developed in any detail.

The average isotope ratio of Sr in the fluvial flux from the weathering of limestones and evaporites over the period of record varied between about 0.7075 and 0.7080, a quite narrow range (4). The long residence time of Sr in the limestone reservoir acts strongly to damp the signal from the relatively high-frequency marine isotopic oscillations (~ 50 million years). Contemporary oceanic hot springs have a uniform ratio of about 0.7035, which probably has not varied over the last 500 million years (3). On the basis of the sea floor spreading record of the last 150 million years, the hydrothermal flux has changed slowly and continuously but probably less than $\pm 30\%$ (8), an amount insufficient to result in any marked change in the isotopic record. Hence, strong features in the record most likely reflect continental processes. Given that the average Sr flux from limestones has isotopic ratios between the extrema of the oscilla-

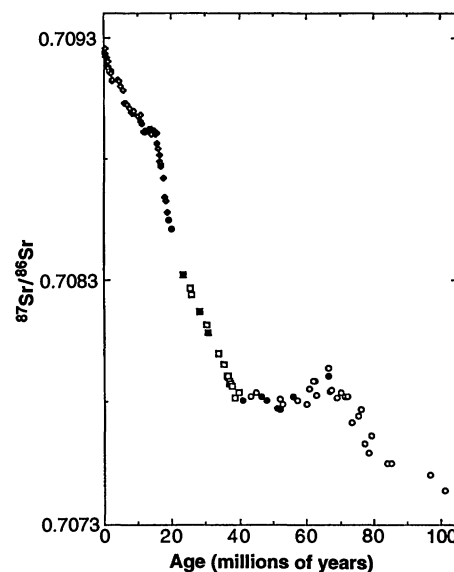


Fig. 1. High-resolution isotope ratio curve for abyssal carbonates over the past 100 million years based on drill core samples [modified from (2)]. The chronometric potential is clear.

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tions and that deviations, such as the recent one, extend well above this range, the fundamental variable is the weathering yield of radiogenic Sr from old basement rocks. To the first order, the problem is reduced to the identification of distinct processes that produce a high fluvial flux of radiogenic Sr and operate repeatedly over discrete intervals of geologic time.

Strontium in Rivers

A large amount of data exists on the Sr systematics in rivers that characterize the relations among the Sr flux, the Sr isotope ratio of the rivers and oceans, the geologic events, and weathering environments where Sr is released for transport. A number of local studies are available (9), along with some regional ones (10, 11) and one

global reconnaissance (3, 12). The fundamental result is that exposed igneous basement terrains, in continental shields, do not yield radiogenic Sr in high flux, even when the rocks are highly alkalic and of great age. This is true of both deeply weathered, lateritic soils from basement in the Tropics, such as that found in the Guyana, Brazilian, and southern African shields (3, 12), and recently glaciated terrains, as found in eastern Canada (10). Of the other siliceous rocks (12), black shales can give a high dissolved yield as a result of acid weathering associated with sulfide oxidation; basic rocks also weather rapidly because of the oxidative breakdown of mafic minerals. However, the Sr that is released is not radiogenic because of the usual admixture of carbonate rocks in black shales and the mantle affinities of volcanic rocks. The only observed exception to this generalization is the metamorphic core complex from the central Himalaya, which influences the Ganges and Brahmaputra rivers (3, 11, 12). Data from a wide variety of geologic environments (Fig. 3, A and B) define a uniform shallow increase in the isotopic composition as Sr concentration decreases. Only the data from the Himalaya fall markedly off this trend; the main relation is geologically normal. The modeling studies (7) have shown, in effect, that this trend does not support the observed changes in the isotope curve if the hydrothermal input

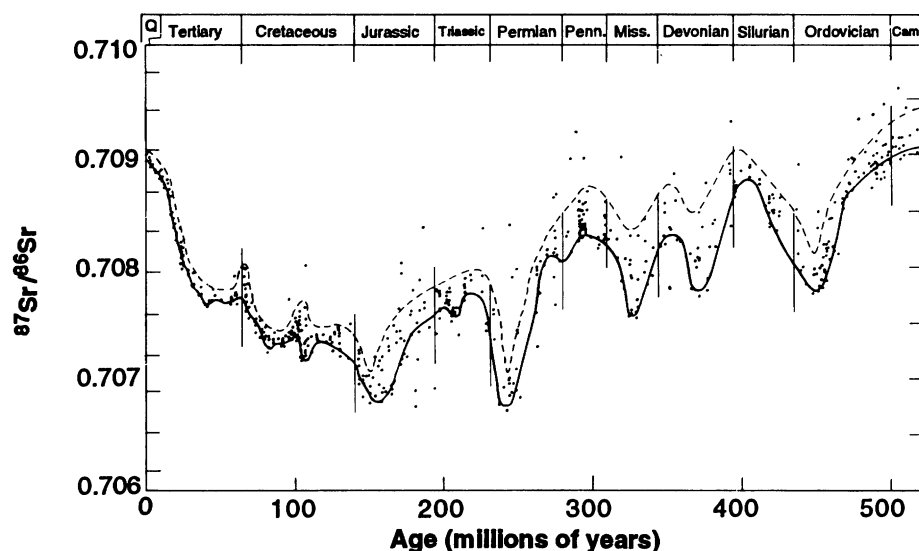


Fig. 2. The variations in the ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ in marine limestones over the past 500 million years [modified from (6)].

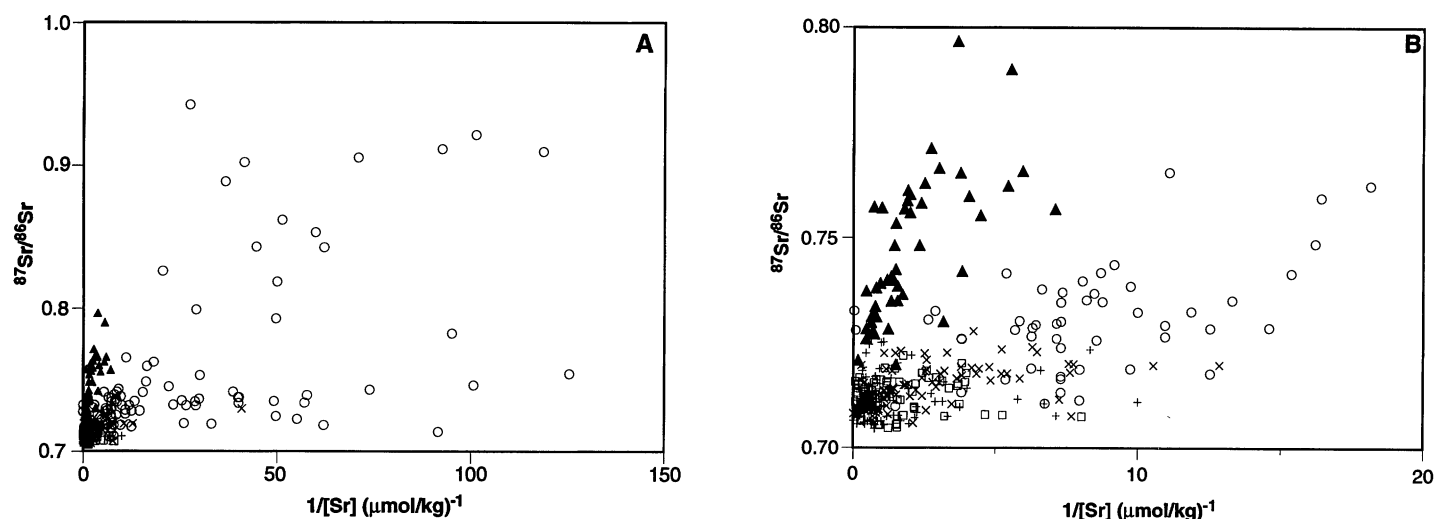


Fig. 3. (A) Summary plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/[\text{Sr}]$ (concentration in micromoles per kilogram) in river water using all the available data (~425 points) for which both isotopic composition and concentration were reported (3, 4, 9–12). The data form several groups: (○) Shields (Guyana, Brazilian, southeastern Canada, east Greenland, western Australia). These are generally highly radiogenic with very low concentrations. (□) North America (with the exception of southeastern Canada). The geographical coverage is essentially complete. (▲) Himalayan streams (Ganges left bank; Brahmaputra in Assam). (×) The Andean arc in the drainages of the Amazon and Orinoco (southern Bolivia to northwestern Venezuela). (+) Other point samples collected in reconnaissance efforts (the Amazon flood plain, western and central Europe, east Africa, central India, eastern Australia, southeast Asia, China, Philippines, and Japan).

There are several data sets for which no concentrations are reported. For the Canadian Shield (mollusks), southern Africa (elephant tusk and bone), central Europe (Rhine drainage), and the Baltic Shield (Gulf of Bothnia drainage), the data are consistent with complete data sets from the rivers of the regions as displayed here. (B) The flow-weighted mean concentration of fluvial Sr is $\sim 1 \mu\text{mol/kg}$, so the global plot (A) is truncated at $0.05 \mu\text{mol/kg}$ ($1/[\text{Sr}] = 20$) to show in more detail the relations for rivers carrying significant flux. The separation of the Himalayan streams from the others is clear. The positive, shallow isotope-concentration gradient is followed by all non-Himalayan rivers, regardless of geologic setting and weathering environment, for reasons discussed in the text. Data defining the lower envelope of this trend are from basaltic terrains at convergent margins. The upper envelope is defined by the data from the shields.

is fairly constant. Excluding the Himalayan rivers, the average isotopic composition of fluvial Sr is about 0.710, a value that probably does not (and from the above discussion cannot) vary appreciably with time.

Several factors contribute to this behavior. Carbonate rocks and evaporites weather much more rapidly than massive basement rocks, and shales rarely have the mechanical competence to sustain significant chemical weathering at outcrop in the face of rapid physical erosion and transport. In addition, these three rock types dominate shelf sequences and are thus preferentially exposed to weathering during eustatic sea-level lowering or after tectonic transition from passive to active margin regimes. The constituent minerals of basement rocks weather chemically at greatly different rates (13). In particular, sodic and calcic aluminosilicates are much more reactive than K-containing minerals. Because Sr is partitioned into Na- and Ca-rich minerals, whereas Rb is in resistant K-rich minerals, the dissolved yield during partial chemical weathering is predominantly nonradiogenic Sr with an isotopic composition between the whole-rock value and the initial ratio at the time of emplacement, before the onset of in situ Rb decay. Because the Na- and Ca-rich minerals are abundant in silicic rocks, their preferential dissolution destabilizes the rock surface mechanically, enhancing the removal of the resistant K-rich minerals and quartz by physical processes. In areas of subdued local relief, where hydrologic transport is very low, complete weathering of basement rocks does occur and results in a residual mantle of kaolinite, gibbsite, quartz, and iron oxyhydroxides—a laterite. However, the dissolution rates of the K minerals are sufficiently slow that, although very radiogenic Sr is released, ratios >0.9 in some cases (Fig. 3A), the flux is extremely low (12). Partial weathering of even highly radiogenic basement rocks tends to give isotope values not significantly greater than those from limestones; hence, the data from shield and platform carbonate terrains are superposed on the isotope-concentration diagram (Fig. 3A). The observational data and the mechanistic understanding of weathering processes are both sufficiently good to allow one to conclude that, under normal circumstances, it is difficult to sustain a high flux of radiogenic Sr, regardless of the intensity of the weathering process. The cause of the large deviations from the isotope curve must be sought elsewhere.

Effects of the Himalayan Orogeny

The Ganges-Brahmaputra is the only major river system to show a significant departure

from the Sr isotope-concentration relation (Fig. 3B). On a global basis, the fluvial isotope ratio increases slowly with decreasing concentration from the marine range at high concentration (limestones, partial weathering of silicates) to more radiogenic values at low concentration (progressive weathering of more refractory aluminosilicates) (3). In the Ganges-Brahmaputra, the rise is much steeper. Extensive sampling of Himalayan headwater tributaries in the Indian sector of the chain demonstrates that this anomalous behavior is driven by the weathering yield from the unroofed metamorphic core complex of the collision zone (3, 11, 12) and not from diagenetically altered carbonates, as recently proposed (12). Streams with Sr concentrations characteristic of limestone terrains ($>2 \mu\text{mol/kg}$) display isotope ratios of 0.8 and greater. Modeling studies by various workers using these data from the Himalaya (7) identify the weathering yield from this orogen as the driver of the dramatic rise in the marine isotope ratio over the last 20 to 40 million years. The cause of this distinct source of radiogenic Sr in high flux has not been clear.

The metamorphic core complex extends along the axis of the mountain belt, from Assam to Pakistan (14). It consists of amphibolite-grade gneiss and associated large leucogranite masses (15). The complex is thought to represent thermally remobilized basement of the Indian plate, possibly of Archean and Early Precambrian age, that was buried to great depth early in the collision and then tectonically exhumed to high altitude and rapidly unroofed (16). The age of the complex, in particular the time of emplacement of the leucogranites, is quite uncertain but appears to be ~ 20 million years (17). The thermal remobilization of the basement rocks during deep burial was sufficient to disrupt the Rb-Sr systematics but not to reset the system by homogenization throughout the rock masses (17).

The complex is exposed over a huge elevation range in an area of intense glacial erosion. Earlier interpretations have ascribed the high flux of radiogenic Sr to this weathering environment (7); however, observations from other glaciated regions do not support this inference. Data from streams draining the essentially continuous fluvio-glacial cover of the stable shields in eastern Canada (10) and the Baltic region (18) give low concentrations ($<0.2 \mu\text{mol/kg}$ for eastern Canada; data from Baltic Shield not reported) and an isotope ratio around 0.73, both much lower than in the streams from the complex. Recent data (19) for streams draining the Early Archean Aldan Plateau, in the drainage of the Upper Lena River in the Russian Far East,

range between 0.710 and 0.713. This semi-arid terrain has not been glaciated, despite regional elevations of between 1 and 2 km, but has all the features of a periglacial regime, including extensive frost shattering, frozen and patterned ground, and so forth. The rivers are boulder torrents that transport large amounts of immature sand but negligible quantities of fine-grained material. Weathering yields are quite high (Sr values up to $3 \mu\text{mol/kg}$), comparable to those of the Himalaya, but the intensity, as reflected in the isotopes, is very low.

The key to the high radiogenic yields from the rocks of the complex lies in the disturbed Sr-Rb systematics (17). High-grade metamorphism and partial melting of the rocks during the recent Tertiary collision of India with Asia have been sufficient to mobilize radiogenic Sr out of the K-rich minerals into phases that weather more rapidly. With reported initial isotope ratios as high as 0.769 in both the leucogranites and the gneisses (20), the Na- and Ca-rich minerals have been transformed into a source of radiogenic Sr. In striking contrast, the Aldan Shield has been tectonically quiescent for at least the last 2 billion years. Rapid erosion does sustain the flux in both regions but only by accelerating the production of fresh surfaces. The intense mechanical action associated with glacial and periglacial processes means that, while the total erosion rate is increased, the intensity of chemical weathering is not; it may even decrease. Rock flour, the dominant particulate product from glaciated igneous and metamorphic terrains, is much more immature than the suspended material derived from rocks of similar composition in nonglaciated terrains. The result is Sr isotopic values in the flux that are close to the initial ratio in the rock masses and characteristic of the most labile minerals.

Implications for Past Variations

The major oscillations in the Sr isotope record in marine limestones can be caused only by continental collisions of the Himalayan type. This is the sole mechanism by which ancient basement rocks are down-thrust to great depth, thermally remobilized, heated, even partially melted such that radiogenic Sr is redistributed into the Na- and Ca-rich phases, and rapidly exhumed and eroded. Orogenic collapse (21) determines the relatively uniform time scale of discrete events in the record and, in particular, the steepness of the decline in the signal. Recent work has extended the isotope record, discontinuously, back to about 950 million years ago (22). The record shows a rise in the late Precambrian, which resulted in the Cambrian high, that

is comparable to the rise being produced by the Himalayan event (Fig. 2). It is almost certainly associated with the Pan-African orogeny (22). If the magnitude and steepness of the isotope shift are indicative of the scale of a particular collision, then, from Fig. 2, it can be concluded that nothing comparable in size with these two events has occurred in the intervening 600 million years. Similarly, the time span of the Cambrian high implies that the Himalayan orogenic cycle of basement reactivation, unroofing, and erosion should continue for tens of millions of years, sufficient to rework much of the Indian Shield.

In the absence of constraints on the sea floor spreading rate before ~100 million years ago, the primary information that can be extracted from the isotope curve is the timing and relative scale of previous collision events. Because the total weathering flux from the Himalayan chain, and the major element composition of this flux, is similar to that from an Andean-type margin of an equivalent length, there is no necessary correlation of the Sr isotope curve with other geochemical proxy records (7). Himalayan-style events also may not necessarily cause large-scale perturbations of the preexisting CO₂ cycle, such as would be caused by a globally significant increase in the rate of chemical weathering (23). However, these events, because they generate enormous areas of extreme elevation located in the interior of the newly composited continent, may have effects on climate markedly different from those of the narrow, peripheral, Andean-type orogenies (23). If this is the case, then global perturbations in climate, and hence in the geochemical cycle, may be induced by large-scale continental collisions. Postulated increases in the subduction-related CO₂ flux at the time of the collision, caused by the shift from shelf to pelagic accumulation of carbonate (24) due to the associated sea level drop, merely move the Sr isotope-concentration relation along the shallow global trend (Fig. 3). Dramatic increases in

the fluvial Sr isotopic value cannot be expected because the normal weathering yield of radiogenic Sr is transport-limited (3, 12).

This interpretation of the record of the isotopic composition of marine Sr illustrates the difficulties in developing and interpreting geochemical proxy records in the absence of a complete understanding of all of the processes affecting the behavior of the elements and isotopes in question. The best developed proxy records are those used for radiometric age dating. All unknowns in the behavior of the chronometer contaminate the derived age. The obvious problem is the uncertainty in the half-life. However, changes in the source function, for example, for the cosmogenic isotopes, initial disequilibrium, postformation mobilization, and so forth, all lead to spurious ages if not accounted for quantitatively (25). In principle, the same and other difficulties attend the proxy records for geological events in general. The ultimate utility of environmental paleorecords is that they constrain models of processes of climatic and geological change (7). The validity of these constraints can only be established by comprehensive field observation.

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