On the interpretation of the oceanic variations in $^{87}\text{Sr}/^{86}\text{Sr}$ as recorded in marine limestones

YOUNGSOOK HUH and JOHN M EDMOND

Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139, USA

e-mail: yhuh@mit.edu

The present published inventory of fluvial Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ data, combined with new information from the big rivers of Eastern Siberia (a combined total of ~1,000 measurements), is used to investigate the probable origin of the large rise in the marine isotopic ratio, recorded in limestones, over the last ~20 million years. With the exception of the data from the Ganga-Brahmaputra all measurements fall on what is proposed to be called the “Wickman trend”, essentially a mixing line between the limestone sink for Sr, with the integrated marine ratio, and the flux from the weathering of average continental crust. However, time-variations along this trend, i.e. changes in relative weathering intensity, cannot explain the observations from limestones. They can only be caused by very high and radiogenic fluxes of Sr as are occurring from the present Himalayan orogeny, lying far above the Wickman trend and caused by metamorphic remobilization of radiogenic Sr during underthrusting and subsequent unroofing associated with the collision of India with Eurasia. In general the variations in the ratio are therefore caused by specific tectonic events, not by general climatic variations in the intensity of aluminosilicate weathering.

1. Introduction

1.1 The record

In a classic early paper Wickman (1948) proposed that since $^{87}\text{Rb}$ is strongly enriched relative to Sr in continental igneous rocks as compared to mantle basalts, i.e., is what is now called an incompatible element, the fluvial weathering yield of the resulting radiogenic daughter ($t_{1/2} = 47 \times 10^9$ year), $^{87}\text{Sr}$, should determine the oceanic $^{87}\text{Sr}/^{86}\text{Sr}$ value. Therefore this should increase monotonically with time, assuming early formation of the continental crust. This ratio could then be used as a dating tool for “soft” rocks formed in the marine environment that incorporate Sr into their lattice sites and exclude Rb, i.e., limestones, evaporites, etc. While it was soon shown that Wickman's estimate of the crustal Rb enrichment was much too high the dating potential, even with a time resolution greatly reduced from the original estimate, attracted some interest. The first test of the hypothesis was made by Gast (1955) who found that continental limestone values were constant within (considerable) measurement error over the past ~500 Ma as was the contemporary seawater value. The important result was that marine limestones sample the “whole ocean value” of the ratio. This has been confirmed by many subsequent studies. The oceanic residence time of Sr is ~2.5 Ma (90$\mu$M and 0.7091 in the oceans; 0.89$\mu$M and 0.7119 flow-weighted average in rivers; Palmer and Edmond 1989), biological effects are minimal and non-fractionating and hence the oceans are isotopically homogeneous.

Peterman et al (1970) extended this work with significantly increased precision and developed a catenary relationship with high $^{87}\text{Sr}/^{86}\text{Sr}$ values in the latest Precambrian and the Recent (~0.7090) and oscillations about lower values in the interim with pronounced minima in the mid-Permian and
the Late Jurassic (~0.7068), i.e. completely contrary to Wickman’s original suggestion (figure 1a). Veizer and Compston (1974, 1976) greatly developed this record back to the Archean (figure 1b, c). However, since the “half life” of shallow water limestones with respect to weathering is ~150 Ma, the availability of samples drops off very steeply with time. In addition, secondary diagenetic effects can disturb the record due to addition of Sr from other sources with distinctive Rb/Sr ratios, different ages and hence widely differing $^{87}\text{Sr}/^{86}\text{Sr}$ values. Thus the older part of the record showed a very broad spread (~0.0015) at a given time interval and aliasing, i.e. features determined by the sporadic sampling of a continuously varying signal.

The situation changed dramatically with the development of a very high resolution record for the Phanerozoic (Burke et al. 1982; figure 1d) derived mainly from core samples that could be “stacked” to give a synthetic, continuous stratigraphic column of limestones over the past 550 Ma. This approach showed in detail the oscillations hinted at previously. Thus the use of the ratio in chrono-stratigraphy became a possibility, the resolution depending on its time-rate of change. At a more fundamental level the question of the interpretation of the oscillations in terms of geologic and environmental processes came to the fore. As a result of this break-through, with its stratigraphic and geochemical implications, a large effort has gone into further refining the record. Initially work was directed at the continuous carbonate sections recovered by the Deep Sea Drilling Programs from the last ~50 Ma. Extension has depended on shallow water macro-fossils from various localities and has resulted in a detailed description of the evolution of the oceanic ratio over the past ~900 Ma (figure 2).

Figure 1(a–b). (Continued)
Figure 1(a–d). Illustrative summary of the evolution of the basic information on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater as recorded in marine limestones. (a) The original curve from Peterman et al (1970; error bars are purely instrumental); (b, c) from Veizer and Compston (1974, 1976; error ellipses encompass the range in measurements for a given age with the least radiogenic values used to define the curves); (d) the "Burke curve" from Burke et al (1982; again, within the measurement envelope, the least radiogenic values are generally assumed to be the best estimates).
Figure 2. Some examples of high-resolution Sr isotopic data for the past 750 Ma. (a) Hodell et al. (1990); (b) Rea (1992); (c) Jones (1994); (d) Burns et al. (1994).
A synthesis of all the data back to the Early Jurassic has been made (Jones 1994) correcting for inter-laboratory measurement bias, uncertainties in the stratigraphic ages and suspected diagenetic effects. A formal statistical analysis of the record back to 450 Ma has been made by Smalley et al (1994) in order to constrain its use in dating. Thus the validity of the original “Burke curve” is now secure and has been refined to what is probably the maximum extent feasible given the difficulties of carbonate preservation.

1.2 Interpretation

Since the publication of the Burke curve the case has consistently been made that the variations in the marine $^{87}$Sr/$^{86}$Sr ratio reflect changes in the intensity of weathering of continental aluminosilicate rocks, i.e. a revival of Wickman’s original hypothesis (Berner and Rye 1992 and references therein). This was given support by the observation that the flux of Sr and its isotopic composition ($\sim 125\mu M$, 0.7035) associated with deep sea hydrothermal activity (unknown to Wickman) is quite constant in the contemporary ocean with a contribution of $\sim$ one third to the overall total oceanic isotopic budget (Palmer and Edmond 1989). The memory of past changes in the oceanic ratio, whatever the cause, is dampened since the fluvial flux from the weathering of continental limestone deposits and the diagenetic flux from marine sediments act to integrate past variations (the time averaged value is $\sim$ 0.708) and are together responsible for at least another one third of the flux to the ocean (Brass 1976). These two sources, hydrothermal activity and limestone weathering, result in a combined, relatively stable, base-line input with a net ratio of $\sim$ 0.7065, as is seen in the Permian and Jurassic minima. The memory of past changes in the oceanic ratio, whatever the cause, is dampened since the fluvial flux from the weathering of continental limestone deposits and the diagenetic flux from marine sediments act to integrate past variations (the time averaged value is $\sim$ 0.708) and are together responsible for at least another one third of the flux to the ocean (Brass 1976). These two sources, hydrothermal activity and limestone weathering, result in a combined, relatively stable, base-line input with a net ratio of $\sim$ 0.7065, as is seen in the Permian and Jurassic minima. This leaves the dissolution of ancient Rb-rich aluminosilicate rocks as the “master variable” in determining the observed rapid changes in the marine isotopic record. The validity of this interpretation underpins all recent discussions of the evolution of the Earth surface environment since the $^{87}$Sr/$^{86}$Sr record is the only existing, well-defined potential index of changes in weathering processes associated with long term global climatic and tectonic variations.

The argument for climatic stability is quite straightforward (Walker et al 1981). Solar radiation is deposited on the Earth in two major ways: absorption of the UV, predominantly in the stratosphere by O$_3$, and deposition of the energy in the visible range on the surface there to be re-radiated in the IR, directly or as latent heat release from evaporated H$_2$O, with ultimate return to space. The major atmospheric absorber in the IR is water vapor, the dominant “greenhouse” gas. The partial vapor pressure of water, p$_{H_2O}$, is strongly constrained by thermal equilibration with the oceanic reservoir through the Clausius-Clapeyron relationship:

$$\frac{d\ln P}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2}$$

where $T$ is temperature and $\Delta H_{\text{vap}}$ is the latent heat of vaporization. This is completely validated by the meteorological observations between 0° and 75° latitude and in all seasons (Webster 1994). Since this function has an approximately exponential relationship to sea surface temperature, the system is very sensitive to the atmospheric variations in other IR-absorbing molecules, the suite of polyatomic greenhouse gases. While contemporary anthropogenic activities are adding a plethora of these species to the atmosphere, over geologic time scales CO$_2$ is the only one for which the variations can be of any significance. This becomes clear from an examination of the weathering-tectonic cycle. Atmospheric CO$_2$ reacts with water vapor to form carbonic acid:

$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$$

This reaction series constitutes the predominant source of protons for weathering reactions save for minor contributions from volcanically derived H$_2$SO$_4$ and HCl. Weathering of the simple evaporitic salts, NaCl and CaSO$_4$, is by congruent dissolution reactions that do not involve external reactants save for water as the passive medium. Dissolution of limestones, dolomites and other carbonate-containing rocks, involves protons: e.g.

$$\text{CaCO}_3 + \text{H}_2\text{CO}_3 \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^{-}.$$

However, this reaction is rapidly reversible on geologic time-scales because of inorganic precipitation, usually of the soluble phase aragonite, from seawater as it becomes supersaturated due to the accumulation of the fluvial inputs. This process is observed over all of geologic time, although at different scales, from Archean carbonate platforms (Grotzinger 1989) to the contemporary Bahaman Banks. Over the last 600 Ma biogenic formation of calcitic and aragonitic shells and other structural components has been the dominant removal mechanism. Dolomites (CaMg(CO$_3$)$_2$) are formed by secondary diagenetic processes acting on marine platform carbonates in hypersaline lagoonal environments (Sun 1994). The only other significant carbonate phase is siderite, FeCO$_3$, which forms in anoxic environments that generate Fe$^{2+}$ and thus is usually associated with black shales.

For aluminosilicate weathering the overall reaction cycle is more problematic. Using albite as a simple
example:

\[ 7\text{NaAlSi}_3\text{O}_8 + 6\text{H}_2\text{CO}_3 + 20\text{H}_2\text{O} \]

albite

\[ \rightarrow 6\text{Na}^+ + 6\text{HCO}_3^- + 10\text{Si(OH)}_4 \]

dissolved silica

\[ + 3\text{Na}_{0.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10} (\text{OH})_2 \]

montmorillonite clay.

\[ 6\text{montmorillonite} + 2\text{H}_2\text{CO}_3 + 23\text{H}_2\text{O} \]

\[ \rightarrow 2\text{Na}^+ + 2\text{HCO}_3^- + 6\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \]

kaolinite.

\[ \text{kaolinite} + 10\text{H}_2\text{O} \]

\[ \rightarrow 2\text{Al} (\text{OH})_3 + 2\text{Si(OH)}_4 \]

gibbsite.

These reactions can be viewed, very simply, as a progressive cation exchange of protons produced by carbonic acid dissociation for ions contained in the quenched, disequilibrium, high temperature igneous and metamorphic phases to produce minerals such as clays much closer to thermodynamic stability under earth-surface conditions. Structural re-arrangements result in the additional loss of Si to solution. Thus, in the absence of carbonates and evaporites, the fluvial ratios of cations (in equivalents) to bicarbonate and silica are diagnostic of weathering processes (Edmond et al 1995). The regeneration mechanism that closes this aluminosilicate weathering cycle is the “Urey reaction”:

\[ \text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{CO}_2. \]

This formulation, while thermodynamically favored, is in effect a shorthand statement of the fact that any cation-poor aluminosilicate phase, i.e. a weathered clay, will react with carbonates at intermediate to elevated temperatures to give a calc-silicate plus free CO2. Ironically, the reaction proceeds in a water-saturated environment in the same thermal regime as the “oil maturation window” 120–150°C, with the result that many super-giant gas fields identified seismically as “bright spots” have turned out, upon drilling, to be dominantly composed of CO2 (Hunt 1979). Thus the return flux of CO2 necessary to sustain weathering is from metamorphic processes in orogenically active zones with a smaller, primary mantle input from seafloor hydrothermal systems, hot-spot volcanism and andesitic volcanoes on active margins.

The control on atmospheric pCO2 and hence on global temperature is then through the Clausius-Clapeyron relationship and the Arrhenius rate law:

\[ k = \text{Ae}^{-\Delta H/RT}. \]

Increased CO2 leads to warming; this increases pH2O (at ~ 6% °C^{-1} at tropical temperatures) and hence water vapor transport and precipitation and therefore weathering rates through the increase in the availability of the reaction flux medium, H2O, and the rising ambient temperature. A contemporary example of this effect is the El Niño phenomenon. The resulting accelerated consumption of the excess CO2 brings the system back into balance through the negative feedback effect; the pCO2–pH2O interaction acts as a global thermostat preventing “runaway”. Much emphasis has been placed on the apparent necessity for a rather exact balance in this overall cycle given that the observed fluvial flux of bicarbonate “fixed” by aluminosilicate weathering is sufficient to completely deplete the inventory of atmospheric CO2 on time scales much less than 1 Ma (Berner and Caldeira 1997). Thus the average silicate weathering index assumed to be provided by the 87Sr/86Sr ratio is crucial to an understanding of the means by which the Earth has remained a habitable (oceanic) environment over geologic time escaping the “icehouse” and “greenhouse” fates of Mars and Venus, respectively.

Validating this index can only be done based on the one natural “experiment” available, the fluvial weathering rate of the contemporary continents as a function of climate. Terrains representative of most of geologic time in terms of geology, elevation, relief and climate are presently active in all latitude zones on the Earth’s surface. Yet the interpretation of the fluvial flux of Sr and the associated isotopic ratio is complicated by several factors. Even in basins mapped as entirely composed of basement or metamorphic rocks, residual outliers of the original platform cover, carbonates, evaporites and detrital sediments, can dominate the fluvial signal since the simple salts and the massive carbonates and carbonate cements are usually high in Sr, with the integrated marine isotopic ratio, making it difficult to extract the primary signal of the net sink for CO2 in these circumstances. The detrital sediments, in the absence of their reactive cements (calcite, dolomite, siderite, organics), do not contribute significantly to the dissolved load by weathering at outcrop because they are mechanically incompetent. However they do weather, sometimes intensively, during subsequent storage in flood plains; the magnitude of this contribution to the net fluvial flux is difficult to quantify although the effect on the mineralogy and 818O isotopic composition of the residual components is clear (France-Lanord et al 1996, Johnsson et al 1988). The crystalline aluminosilicate minerals themselves weather at greatly differing rates in the general order, quartz << mica < K-feldspar << Ca/Na-feldspar << Mg/Fe-minerals. Oxidative weathering of reduced facies containing Fe2+, e.g. basalts and sulfides, or organic carbon, provides an alternative source of protons and can accelerate dissolution; however this is usually a local process associated with sulfide mineralisation or with accessory minerals such as biotite and with black shales.
\[ \text{C(H}_2\text{O)} + \text{O}_2 \Rightarrow \text{H}_2\text{CO}_3. \]

organics

\[ \text{Fe}_2\text{SiO}_4 + 4\text{H}_2\text{CO}_3 \Rightarrow 2\text{Fe}^{2+} + \text{Si(OH)}_4 + 4\text{HCO}_3^- \]

(reduced Fe)

\[ 4\text{Fe}^{2+} + \text{O}_2 + 10\text{H}_2\text{O} \Rightarrow 4\text{Fe(OH)}_3 + 8\text{H}^+ \]

(oxidized Fe)

\[ 4\text{FeS}_2 + 17\text{O}_2 + 14\text{H}_2\text{O} \Rightarrow 4\text{Fe(OH)}_3 + 4\text{H}_2\text{SO}_4 \]

(pyrite sulfuric acid.

This reaction complex is of much greater importance in the weathering of shales and of ultramafic as opposed to granitic terrains since the former are dominated by Fe/Mg-silicates and hydrothermal sulfide ore deposits; while these are areally quite specific and easily identified geologically, e.g. black shales, flood basalt provinces, accreted island arcs, active margin volcanics, where present they can dominate the fluvial chemistry of large basins due to their reactivity.

The very strong contrast in weathering rates (several orders of magnitude) between the Na/Ca and K-containing minerals leads to an effective fractionation of the Sr isotopes during dissolution reactions since Sr follows Na/Ca and Rb substitutes for K in igneous and metamorphic processes. In rocks of mantle origin, basalts, ultramafics and most granites, the initial non-radiogenic isotopic ratio (~0.703) is preserved in the rapidly weathering Na/Ca phases since they effectively exclude the large-radius, radioactive, parent ion Rb from their structures during primary crystallization. River sands produced in more differentiated terrains are usually composed of quartz and K-mica, i.e. a large proportion of the radiogenic Sr is exported from the drainage in the mechanical load since Rb is accommodated in the K-sites. The average crustal ratio is ~0.725 but with a very wide range, depending on rock type and age, from ~0.704 for ultramafics to >0.9 for old potassic granites.

The net fluxes from basaltic hydrothermal systems and from carbonates are likely to be quite stable, or continuously varying, in time; they are high but with relatively constant isotopic ratios. The aluminosilicate source from continental weathering spans the isotopic range from mantle values to extremely radiogenic ratios, generally with an Sr flux inversely proportional to \(^{87}\text{Sr}/^{86}\text{Sr}\) (Palmer and Edmond 1989).

2. The fluvial flux and isotopic ratio

2.1 The data set

The published data sets usable for analysis consist of \(^{87}\text{Sr}/^{86}\text{Sr}\) measurements on rivers world-wide, in all environments and at all basin scales (figure 3); the number of analyses at hand, including recent reports from the Himalaya and the new data presented here for eastern Siberia, is ~1,000. These data have been accumulated over the last ~20 years and so their quality increases dramatically with time. However, since the few time series available (Palmer and Edmond 1989; Edmond et al 1995) show that the...
There are several features that are immediately presented in figure 3 at various levels of resolution. Preceding this Sr-STSr/S6Sr global data set which can be interpreted, at least qualitatively. However, broad trends emerge in the Sr concentrations and isotopic compositions to the dissolved load (Na, K, Mg, Ca, C1, SOn, alkalinity, Si) analysis presented here. In addition the data for the concentrations; these cannot be used in the type of reported isotopic data without the associated Sr ratio can change in the third place seasonally, data quality is not a serious limitation. Generally, the river discharge is not included with the published measurements; however, fluxes can be calculated using compilations of average runoff in the particular basins since these, in fact, are regional contour maps of actual long-term hydrologic measurement series not easily available in the literature (UNESCO 1979). The combination of point determinations, in time, of the elemental and isotopic values with decadal averages of the basin runoff results in uncertainties in net transport that are difficult to quantify; optimistically, the fluvial flux of Sr to the ocean is known to about 25% and the ratio to ~ 0.0005.

Unfortunately there exists a substantial body of reported isotopic data without the associated Sr concentrations; these cannot be used in the type of analysis presented here. In addition the data for the dissolved load (Na, K, Mg, Ca, Cl, SO4, alkalinity, Si) are often incomplete making the relationship between the Sr concentrations and isotopic compositions to the geology, topography and climate of the various basins difficult to establish. However, broad trends emerge in this Sr-87Sr/86Sr global data set which can be interpreted, at least qualitatively.

The entire published fluvial data set (as of 1998) is presented in figure 3 at various levels of resolution. There are several features that are immediately apparent.

1. The overwhelming proportion of the data (≥70%) plots in the domain of marine limestones, i.e. high Sr, ratios ~ 0.7085.
2. There is a positive “main linear trend” from this nexus to more radiogenic values at progressively lower concentrations; the scatter in this trend increases markedly at very low Sr. It can be regarded as a mixing line between continental basement, with all its heterogeneity, and the much more homogeneous limestones.
3. There is a subsidiary, undersampled, negative trend to less radiogenic values; this represents mafic rocks in their various manifestations.
4. There is a striking, strongly positive trend to very radiogenic values with high Sr concentrations; all these samples are from the Himalayan orogen, with no important exceptions.

Thus the factors required to explain the marine isotopic record reside in (2) and (4), since features (1) and (3) are probably quite constant in time. Feature (2) can be regarded as the “normal Wickman trend”, the variable contribution of aluminosilicate weathering to the limestone “buffer” flux. Note that the Sr concentrations fall off very rapidly with increase in the ratio. Feature (4) is unique to the Himalayas, the transport of radiogenic Sr in high concentrations.

The Wickman trend encompasses all the data from “normal” terrains, i.e. excluding flood basalt provinces, occluded island arcs, greenstone belts and the Himalaya, but including at least 75% of the continental area presently undergoing active weathering. Therefore, at the present state of knowledge, it can be assumed as the datum line over at least the period of the Phanerozoic limestone record and is the basis for the argument that the Sr isotopic ratio in limestones is an index of the severity of continental weathering.

Beginning with the brief suggestion by Armstrong (1971) that the oscillations are correlated with continental-scale glaciations it has been assumed that glacial processes increase the weathering rates of aluminosilicate rocks and therefore the fluvial flux of radiogenic Sr. Recent data from Eastern Siberia demonstrate that, at least in a periglacial environment dominated by ice action at all scales, this is not the case. An extensive survey has been carried out of all the significant rivers east of Lake Baikal and their tributaries (~ 300 samples; figure 3a). The data fall into three distinct groupings; a steeply rising relationship to relatively radiogenic values, > 0.720, a horizontal trend at ~ 0.7085 and a decreasing trend to ~ 0.7045. The first relationship is from the basement
rocks of the Aldan Shield and Trans-Baikal Highlands that constitute the southern rim of the Lena basin; it is not comparable in scale to the Himalayan feature but demonstrates an insignificant contribution from carbonates. There is also a component from the extensive exposures of detrital sediments to the east, in particular the Verkhoyansk and Cherskiy Ranges. The second is from the undeformed platform cover of marine Cambrian to Tertiary age found in many of the basins and is consistent with the observed dominance of marine limestones and evaporites in these sequences. The third is from the basaltic terrains found throughout the region as greenstone belts, occluded arc volcanics and extinct active margins associated with old collision zones to the east.

When compared to the global data set it can be seen that the Siberian data are not remarkable (figure 3a). In addition there are no striking features in the calculated denudation rates (figure 4); these are comparable to those from similar regimes in lower latitudes (Huh and Edmond, in press; Huh et al 1998a, b).

The important observation is that there is no obvious climatic influence on weathering rates in any of the diverse environments for which data are available, from the Tropics to the high Arctic (figure 4). The fluxes of Sr and its isotopes are not affected by climatic influences on the weathering regimes.

By a process of elimination, based as it is on a global data set, the only currently active environment producing radiogenic Sr in sufficient flux to generate the Tertiary rise in the marine ratio is the Himalayan orogeny, specifically the Ganga-Brahmaputra basins. However the mechanisms by which this flux is maintained are rather controversial. This unique feature of the Himalayan weathering regime was first identified in pioneering work by Krishnaswami et al (1992). Given the strong signal in the major ion data characteristic of carbonate dissolution it was proposed initially that hydrothermally altered limestones in the Tethyan sedimentary sequence were responsible for the flux (Palmer and Edmond 1989). There is abundant evidence for fluid alteration in these rocks. The ancient Archean Indian plate is being underthrust to great depths beneath the south Asian margin in the collision zone. Heated formation waters could extract highly radiogenic Sr from unstable Rb-sites in these rocks and emplace it in recrystallized limestones higher in the section producing a source labile to weathering. However, there are two flaws in this argument: from thermodynamic considerations the Sr concentrations in these altered rocks should be low; it also seems unlikely that such alteration should be ubiquitous in the range as is required by the fluvial measurements.

An alternative hypothesis, based on geochronological work using Rb/Sr summarized by Harris (1995; figure 3b), is that during the partial melting of the underthrust crust which produces the Central Crys-
talline Zone, characteristic of the entire Himalayan range, there was large-scale remobilization of radiogenic Sr from the refractory K-minerals into the labile Na/Ca-phases. Rapid weathering of these rocks following back-thrusting to very great elevations and subsequent erosional unroofing would then produce the observed Sr concentration and isotopic signatures.

Discrimination between these two conflicting end-member interpretations depends entirely on the field observations, geological and fluvial. Evidence for the metamorphic redistribution of radiogenic Sr within the crystalline rocks is abundant throughout the range and can be considered secure. A comparable prevalence of meta-carbonates with high concentrations of radiogenic Sr has not been demonstrated. The most comprehensive survey is that reported by Singh et al (1998). They analyzed over 30 limestones from a variety of formations outcropping in the headwaters of the Ganga, Ghaghara and Indus rivers in the Lesser Himalaya. The isotope ratios cluster around ~0.714 with a few outliers with very high values, ~0.88. In all cases the Sr concentrations are low. The associated fluvial ratios, mean ~0.75, lie in the range reported for the crystalline rocks and are significantly more...
radiogenic than the carbonate values. Assuming that all the Ca in the rivers is from carbonates then their contribution of Sr to the Ganga headwaters, based on the concentration-isotopic balance, is between 6 and 40% depending on the tributary. Clearly these are maximum values. By contrast Harris et al (1998), based on a few river samples from the BhoTe Kosi, a minor tributary of the Ganga to the east of Nepal, calculated that the contribution of radiogenic Sr from carbonates is dominant. Their fluvial values (n = 7) fall in the range 0.7123–0.7920 with a non-flow weighted average of ~ 0.720, normal for the range as a whole. Leachates from the bedload, presumed to represent carbonates, give a range of 0.7123–0.7920, average ~ 0.720. Thus their values are comparable to those from the much larger data set analyzed by Singh et al (1998). Their leachate values are generally much lower than parallel measurements of the total bulk samples suggesting the possibility of “contamination” by the partial dissolution of the aluminosilicates.

In a different approach to the problem Richter et al (1992) combined the data from the Himalaya proper, but also the Tibetan Plateau, with estimates of the historical Sr fluxes based on measurements of the rates of accumulation of detrital sediments. The latter come from seismic and drilling data from the various foreland basins and deep sea fans. They assumed that 25% of the Sr associated with bulk mechanical erosion is released to solution. The impression of a relationship between mechanical and chemical denudation rates, while common, is not borne out by observation (Rea 1992; Summerfield and Hulton 1994; figure 5). In fact the chemical denudation rate of the Himalaya is at least a factor of 50 less than the mechanical. Reconstruction of the solute flux from the preserved detrital load is not possible with present understanding. In addition the Tibetan Plateau, the source of many of the rivers included in this particular study, Yangtze, Mekong, Irrawadi, Salween, is an elevated, ~ 0.710, 2μM. All of these values fall on the Wickman trend and, hence, are not capable of markedly influencing the oceanic ratio.

Intensive investigations of the sediments of the Bengal Fan (summarized in France-Lanord et al 1996 and Derry and France-Lanord 1997) demonstrate that the detrital flux has been predominantly from the Central Crystalline Belt for at least the last 20 m.y. The measured isotopic composition of Sr in the minerals of this huge sedimentary pile is consistent with this interpretation. Relating these observations to contemporary observations of the river fluxes is complicated by the fact that much of the chemical, as opposed to mechanical, weathering appears to occur during sediment storage in the subsiding foredeep (Sarin et al 1989; France-Lanord et al 1996). The widespread occurrence of saline and alkaline soils in the Gangetic plain attests to this. This process probably leads to a sequestration of silica. However, comparing the available fluvial data for the Himalayan range at face value with those of the active margins of the Western Americas (Amazon, Orinoco, Frazer, Mackenzie, Yukon), it is clear that the chemical flux, per length of arc, is not remarkable (figure 4; Edmond and Huh 1997; Huh and Edmond 1998a, b; Huh and Edmond, in press). The dissolved load transport and CO2 consumption rates calculated for the Himalayan rivers (Ganga, Brahmaputra, Indus) are comparable to those of the Americas (Edmond and Huh 1997). What is very distinctive is the flux of radiogenic Sr (figure 3), especially from the Ganga-Brahmaputra, for the reasons argued here.

3. Conclusions

This review of all the available data for fluvial Sr and its isotopic ratio (~ 1,000 determinations) shows that there are two trends, the “normal” Wickman relation, essentially a mixing line, and the much more accentuated trend developed for the Himalayan rivers that drain the Central Crystalline Belt, not the Central Asian uplift as a whole. It therefore appears that, given the slow variation in time of the oceanic hydrothermal flux from the mantle and of the erosion/deposition of carbonates and evaporites, the major swings in the $^{87}$Sr/$^{86}$Sr ratio of seawater must be the result of discrete geologic events. In the contemporary world only the crustal “subduction” of the ancient Indian Plate and the resulting remobilization of the radiogenic Sr developed in the refractory K-minerals into more labile Ca/Na aluminosilicate phases can explain the enormous rise in the isotopic ratio over the last 20 Ma. Determination of the “initial ratio” in the Ca/Na-feldspars in the roots of ancient collision zones, e.g. the Pan-African (figure 2), would help to substantiate this conclusion. In any case there is no such thing as “average crustal weathering” any more than there is “average continental crust”. Particular rocks weather, with their individual properties and in their changing environments. The marine $^{87}$Sr/$^{86}$Sr evolution, and perhaps the $^{187}$Os/$^{186}$Os record (Peucker-Ehrenbrink et al 1995), are the only tools presently available to unravel this profound problem.

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