

ISOTOPIC COMPOSITIONS OF DISSOLVED STRONTIUM AND
NEODYMIUM IN CONTINENTAL SURFACE AND
SHALLOW SUBSURFACE WATERS

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Weathering of rocks, denudation of continental surfaces, hydrodynamics of drainage basins, and estimates of fluxes of chemical elements delivered annually to the oceans by the rivers are among central themes in many geochemical studies of continental surface and shallow subsurface waters. Oxygen and H stable isotope geochemistry has long proved very useful in addressing problems in hydrologic studies. But only recently analyses of some commonly occurring natural radiogenic isotopes have become popular means of investigating hydrodynamics of surface and shallow ground waters and modes of present-day continental denudation, although these isotopes had been known as very useful natural tracers for studies of origins of rocks and minerals. Radiogenic isotopic characteristics of rocks and minerals are widely varied due to their varied

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ages and parent to daughter isotope ratios. Natural hydrologic systems evolve through complex mineral-water interactions. Hence common radiogenic isotopes may serve as tracers in defining weathering of rocks, water provenance in drainage basins and average compositions of annually delivered components to the oceans.

Recent literature on radiogenic isotopes in surface and shallow subsurface waters is heavily slanted toward Sr isotopic measurements. This bias is primarily a reflection of the commonly high abundances of Sr in natural waters. Interest in Nd isotopic compositions of waters is growing, but nearly a vacuum exists in the field of Pb isotope geochemistry. The aim of this chapter is to discuss the available isotope data of dissolved Sr and Nd in surface and shallow subsurface waters. As run-off and shallow ground waters are intimately connected, these two water types have been considered as one hydrologic unit in the discussion.

STRONTIUM ISOTOPE COMPOSITIONS OF SURFACE WATERS

Strontium contents in surface waters are widely varied between 0.02 and 2 mg/l and average about 0.06 mg/l (Alexander et al., 1954; Nichols and McNall, 1957; Faure et al., 1967; Mueller, 1969; Vernet et al., 1971; Harmeson et al., 1973; Goldstein and Jacobsen, 1987; Palmer and Edmond, 1989). Values as high as 60 mg/l of Sr are known, but these high values have been related to dissolution of Sr-enriched carbonate and sulfate minerals in the drainage basins (Feulner and Hubble, 1960; Skougstad and Horr, 1963; Carpenter and Miller, 1969). By contrast, Rb contents in surface waters are generally low, ranging between 0.0002 and 0.02 mg/l and averaging about 0.003 mg/l. Rb/Sr ratios commonly vary from 0.003 to 0.06, although values as high as 0.70 were obtained in some instances.

Isotopic Compositions of Strontium in Rivers and Lakes

The study of Faure et al. (1963), reporting on the Sr isotopic

compositions of surface waters and associated fresh-water shells from the Kenoran (2.5 Ga), Hudsonian (1.7 Ga), and Grenville (1.1 Ga) age provinces and from the Great Lakes in North America, ushered a new direction of hydrochemical research. Their study showed that the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of surface waters in the Kenoran, the Hudsonian, and the Grenville provinces were similar between 0.718 and 0.719, but that of waters in the Great Lakes were varied, the values being 0.718, 0.711, and 0.708 for Lake Superior, Lake Erie, and Lake Huron, respectively. Faure et al. interpreted these variations as broad reflections of the isotopic differences of the bedrocks in the drainage basins, the low values being related to marine chemical sedimentary rocks and the high values corresponding to very old crystalline rocks with high Rb/Sr ratios. Many subsequent studies used Sr isotopic compositions of surface waters to characterize bedrocks of drainage basins (Hart and Tilton, 1966; Eastin and Faure, 1970; Stueber et al., 1972; Curtis and Stueber, 1973; Steele and Pushkar, 1973; Stueber et al., 1975; Fisher and Stueber, 1976; Albarède and Michard, 1987; Goldstein and Jacobsen, 1987; Palmer and Edmond, 1989).

In some later studies, Faure and his colleagues explored the potential of using Sr isotopes as natural tracers for identification of the source of dissolved constituents in saline lakes in closed valleys (Jones and Faure, 1967; Jones and Faure, 1968; Jones and Faure, 1972). In their studies on the origin of salts in Lake Vanda of the Wright Valley in Antarctica, Jones and Faure (1967) found nearly identical Sr isotopic values of about 0.7146 for waters and sediments of the lake, soils in the valley, and soluble salts leached from the soils. The bedrocks in the valley of the lake consist of marble, dolerite, granite, and granite-gneiss and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these rocks range from 0.7088 to 0.7285. Based on this evidence, Jones and Faure ruled out trapped sea water and wind transported marine salts as being a major source of salinity of the lake waters. The regolith was probably the major source of the dissolved constituents in the lake, but the authors were unable to defend this assumption for lack of information on the Sr isotopic compositions of the different constituents in the soils.

The collection of studies since the pioneer works of Faure and

his associates in the late 1960s and the early 1970s has shown that the isotopic compositions of dissolved Sr in major rivers in the world range from 0.7036 to 0.9430 (Table 1). Nearly 50% of the rivers have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.710 and 0.720, about 30% have values less than 0.7100, and the remainder have values higher than 0.720 (Fig. 1). Lithologic diversity in the drainage basins is, as already mentioned, a major control on the Sr isotopic compositions of river waters. Rivers with drainage basins on young volcanic rocks, such as those in Philippine, Japan and Indonesia, have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.703 and 0.706, which constitute the low end of the spectrum of the Sr isotopic compositions for global rivers. On the other hand, rivers flowing over very old silicate rocks with high Rb/Sr ratios, as illustrated by three rivers in Greenland, have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios much higher than 0.730 (Goldstein and Jacobsen, 1987). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of most other rivers in the world reflect derivation of Sr from essentially two sources, one of which is marine chemical sedimentary rocks known to have limited range of $^{87}\text{Sr}/^{86}\text{Sr}$ values from 0.707 to about 0.709 and the other is silicate crystalline rocks and minerals whose $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are widely varied depending on age, Rb/Sr ratios, and initial isotopic compositions of the materials.

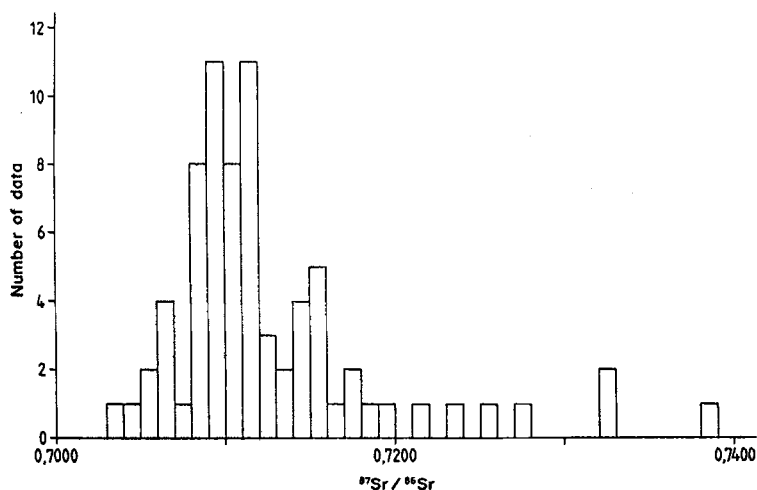


Figure 1: Histogram of Sr isotopic compositions of large rivers in the world

Table 1: Sr isotope data of waters from major rivers and lakes

Sample	Rb(1)	Sr(1)	$^{87}\text{Sr}/^{86}\text{Sr}$	
North America				
Scioto	--	12.3	0.7085	(1A)
Colorado 1	--	--	0.7086	(2A)
Colorado 2	--	1.16	0.71075	(3B)
Susquehanna 1	--	0.31	0.7090	(4A)
Susquehanna 2	--	0.63	0.7150	(4A)
Chesapeake Bay	--	0.13	0.7125	(4A)
MacKenzie	--	0.17	0.71102	(5A)
Wellson	--	0.08	0.71463	(5A)
Yukon	--	0.11	0.71616	(5A)
St Maurice	--	0.01	0.71121	(5A)
Grande Riviere	--	0.01	0.73844	(5A)
Churchill	--	0.02	0.71996	(5A)
Mississippi 1	--	0.26	0.70953	(3B)
Mississippi 2	--	0.07	0.71530	(3B)
Missouri	--	0.35	0.70998	(3B)
St Lawrence	--	0.18	0.70959	(3B)
Columbia	--	0.09	0.71210	(3B)
Ohio	--	0.20	0.71106	(3B)
Ottawa	--	0.06	0.71134	(3B)
Tennessee	--	0.05	0.71123	(3B)
Hudson	--	0.02	0.71025	(3B)
Pearl	--	0.07	0.7119	(10A)
Rio Grande	--	0.29	0.7092	(10A)
Great Salt Lake	--	--	0.7174	(6A)
Michigan Lake	--	0.13	0.70951	(3B)
Huron Lake	--	0.10	0.71002	(3B)
Superior Lake 1	--	0.02	0.71547	(3B)
Superior Lake 2	--	0.02	0.71512	(3B)
West Greenland				
Isua-B	1.73*	2.38*	0.88907	(3B)
Isua-F	0.22*	3.19*	0.94297	(3B)
Mingsik	3.30*	4.28*	0.82636	(3B)
Australia				
Murray	0.99*	0.21	0.71075	(3B)
Avon	0.02	2.94	0.73255	(3B)
Murchis	5.33*	1.08	0.72796	(3B)
Japan				
Kitikami	1.67*	0.05	0.70633	(3B)
Mogami	0.24*	0.04	0.70711	(3B)
Shinano	2.73*	0.04	0.70825	(3B)
Tone	3.19*	0.09	0.70829	(3B)
Philippines				
Abra	0.42*	0.10	0.70628	(3B)
Aqno	4.19*	0.12	0.70452	(3B)
			0.70622	(3B)
India				
Pampanga	2.55*	0.12	0.70540	(3B)
Europe				
Po	--	--	0.7097	(2A)
Rhone	--	0.52	0.70872	(7B)
Garonne	--	0.11	0.71057	(7B)
Rhine	--	0.55	0.7092	(10A)
Danube	--	0.24	0.7089	(10A)
Vistula	--	0.43	0.7094	(10A)
Weser	--	0.72	0.7089	(10A)
Elbe	--	0.57	0.7097	(10A)
Tisza	--	0.18	0.7096	(10A)
Seine	--	0.40	0.7081	(10A)
Antarctica				
Vanda Lake	--	0.25	0.7145	(8A)
Bonney Lake	--	--	0.7126	(9A)
Africa				
Nile	--	0.23	0.7061	(2A)
Victoria Nil	--	0.10	0.7114	(10A)
Blue Nile	--	0.15	0.7056	(10A)
Zaire	--	0.03	0.7155	(10A)
Niger	--	0.02	0.7140	(10A)
Orange	--	0.15	0.7146	(10A)
South America				
Amazon 1	--	--	0.7111	(2A)
Amazon 2	--	0.03	0.7109	(10A)
Orinoco	--	0.02	0.7183	(10A)
Tocantins	--	0.02	0.7170	(10A)
Xingu	--	0.01	0.7292	(10A)
Tapejos	--	0.01	0.7322	(10A)
Parana	--	0.04	0.7139	(10A)
Hawaii				
Wailuki	--	--	0.7036	(2A)
China				
Yangtze	--	0.18	0.7109	(10A)
Mekong	--	0.30	0.7102	(10A)
Red	--	0.13	0.7114	(10A)
Yellow	--	0.65	0.7111	(10A)

(1) amounts in ug/g except when * in ng/g; (2) Data A are normalized to std E & A = 0.7080, and data B to std NBS = 0.71025 ref. 1 = Stueber et al. (1972); 2 = Brass (1976); 3 = Goldstein and Jacobsen (1987); 4 = Fisher and Stueber (1976); 5 = Weddleigh et al. (1985); 6 = Jones and Faure (1972); 7 = Albareda and Michard (1987); 8 = Jones and Faure (1967); 9 = Jones and Faure (1968); 10 = Palmer and Edmond (1989)

Only in limited situations the Sr isotopic compositions of river waters might be very similar to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the bulk rocks in the drainage basin. Where bedrocks and regoliths in drainage basins consist entirely of either chemical sedimentary rocks or young volcanic rocks with constituent minerals having essentially the same Sr isotopic composition, the waters and the rocks can be isotopically closely similar. Starinsky et al. (1980) noted a close similarity in Sr isotopic values between shallow ground waters and their associated host sedimentary carbonate rocks. They concluded that the isotopic compositions of shallow ground waters may be used to estimate the average Sr isotopic composition of carbonate aquifers in which the waters occur.

The Sr isotopic relations between waters and rocks are complex in drainage basins developed over old immature siliciclastic rocks or crystalline rocks. Minerals in these old rocks are typically heterogeneous in their Sr isotopic compositions due to their varied Rb/Sr ratios, and they have different degrees of susceptibility to weathering. Consequently, surface waters in drainage basins underlain by old siliciclastic or crystalline rocks can have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios either higher than the whole rocks due to selective dissolution of the Rb-rich minerals such as biotite and K-feldspar, or lower than the rocks due to preferential dissolution of the Rb-poor minerals such as plagioclase.

Reported values in the literature about the Sr isotopic compositions of rivers often relate to a single flow stage of each river. Such a value for a river cannot be considered as its annual mean Sr isotopic value, as many rivers are known to have seasonal variations in dissolved chemical constituents, which are influenced by (a) lithology of the basin, (b) amount and annual distribution of rainfall, (c) temperature, (d) relief, and (e) vegetation. Very few studies have attempted to document the extent of seasonal isotopic variations of dissolved Sr in rivers. The first indication on seasonal isotopic variations came from the study of Eastin and Faure (1970) on dissolved Sr in the Olentangy and the Scioto rivers in Ohio. They observed that during a period of eight months the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Olentangy River ranged from 0.7086 to 0.7130 and that the isotopic changes did not correlate well with changes

either in the discharge, the pH values, or the content of dissolved Sr. By contrast, no isotopic change was apparent for the Scioto River. The drainage basin of the Olentangy River is underlain by till sediments consisting of celestite-rich clasts of sedimentary origin and silicate clasts of igneous and metamorphic origins. Faure et al. attributed the seasonal Sr isotopic variation of the Olentangy River to the relative contribution of Sr from the two types of clasts present in the till sediments in response to changes of hydrodynamic conditions in the drainage basin.

Palmer and Edmond (1989) also provided evidence for the seasonal isotopic variations of dissolved Sr. They analyzed Sr isotopic compositions of dissolved Sr in five different rivers at their low, median and high flow stages (Table 1). Unlike what Eastin and Faure (1970) observed in their study on the Olentangy River in Ohio, Palmer and Edmond found flow stages and Sr contents to be inversely related. Strontium isotopic variations occurred with changes in flow stages, but the direction of isotopic shift was not the same for all streams. Noting these irregular changes in Sr isotopic compositions of rivers, the authors suggested that a single sample may not yield the annual mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio.

Additional evidence for temporal Sr isotopic variations was presented recently by Ste Marie (1990) who noted both monthly and annual variations in Sr isotopic compositions of shallow subsurface waters around a bog located in southwestern Ohio (U.S.A.). For example, ground waters collected during April and July of 1986 from a well into ground moraine deposits differed in their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios by as much as 0.00021. On the other hand, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of waters from a well in outwash deposits changed by only 0.00013 from 0.70837 in 1987 to 0.70850 in 1989. The changes were generally small because Sr derived primarily from carbonate clasts which have a narrow range of Sr isotopic composition and make up bulk (90%) of the sedimentary deposits.

Provenance of Waters in Lakes and Rivers

Faure et al. (1967, a and b) used Sr isotopes as tracers to

investigate the dynamics of waters in Lake Huron, which receives waters from four different drainage systems. Analyzing Sr of waters from the North Channel area, they observed a positive correlation between the $^{87}\text{Sr}/^{86}\text{Sr}$ and the $1/\text{Sr}$ ratios of the waters with Sr isotopic values ranging from 0.7111 to 0.7181 and Sr contents between 0.084 and 0.022 mg/l (Fig. 2). They related this relationship to mixing in varying amounts of waters from two sources, one of which is the northern drainage system over Precambrian crystalline rocks characterized by high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and the other is the discharge from Lake Michigan which receives Sr primarily from Paleozoic marine chemical sedimentary rocks having low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The correlations between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr contents were less distinct for waters from the other areas of Lake Huron.

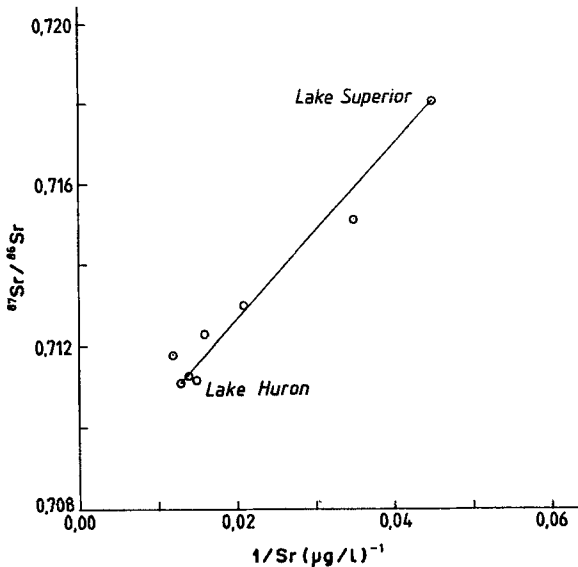


Figure 2: Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $1/\text{Sr}$ values for waters of the North Channel area of the Lake Huron (Faure et al., 1967)

To assess whether Sr isotopes can be used to characterize hydrologic properties of a major river, Stueber et al. (1975) analyzed the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters from the Scioto River basin in Ohio, where two contrasting lithologies influence the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ground waters and tributary streams in the drainage basin. In the upper and central reaches of the drainage basin, Pleistocene glacial deposits with abundant locally-derived dolomite

clasts overlie Silurian dolomite. Ground waters and tributary streams to the Scioto River in this part of the basin were found to have low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.708 and 0.709 with Sr contents from 0.1 to 43 mg/l. The high Sr contents and low Sr isotopic values were believed to be a consequence of dissolution of celestite minerals in the bedrocks and glacial-derived sediments. By contrast, ground waters and streams in the lower part of the Scioto River basin, which is non-glaciated and underlain primarily by Carboniferous shale-sandstone sequences, had high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.710 and 0.713 with Sr contents of less than 0.4 mg/l. While ground waters and tributary streams in the drainage basin could be differentiated into two groups based on the Sr isotopic criteria, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were nearly uniform at about 0.7086 for waters along the entire length of the Scioto River within the basin.

The Sr isotopic composition of any system of mixed waters is a function of the amount of water, the Sr content and the Sr isotopic composition of each component in the system. When the input of total Sr from any one component is significantly much higher than the inputs from others and the isotopic compositions of Sr for different components are not greatly different, the Sr isotopic composition of the mixed system is essentially the same as that of the component with relatively very high amounts of Sr. As Stueber et al. (1975) noted, the low input of Sr from tributary streams can explain why the Scioto waters in the lower part of the basin experienced no noticeable change in their Sr isotopic compositions relative to waters in the upper reaches, although ground waters and tributary rivers in the lower part of the basin had measurably higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than ground waters and tributary rivers in upper and central parts of the basin. The study of Stueber et al. has demonstrated that balancing the fluxes of different sources of Sr in a major river might be difficult to achieve by means of Sr isotopic data when the Sr input from the main river far exceeds the Sr inputs from tributaries.

Analyzing waters from a 150 km course of the Susquehanna River and from several of its tributary streams, Fisher and Stueber (1976) noted a scatter in the Sr isotopic compositions of waters

from main river and its tributary streams. A wide variety of igneous, metamorphic and sedimentary rocks underlie this part of the Susquehanna drainage basin, but single lithologic types exist in several sub-drainage basins defined by the tributaries. Figure 3 illustrates the distribution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters at the mouths of different tributaries to the Susquehanna River and of the types of bedrocks in the drainage basins. As expected, tributaries with dominance of carbonate bedrocks in their basin have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of about 0.709 and relatively high Sr concentrations, whereas those with shale or metamorphic bedrocks have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.716 and 0.719 and low Sr concentrations. Tributaries with mixed bedrocks have Sr isotopic values between 0.709 and 0.716. As figure 4 indicates, the $^{87}\text{Sr}/^{86}\text{Sr}$ and the $1/\text{Sr}$

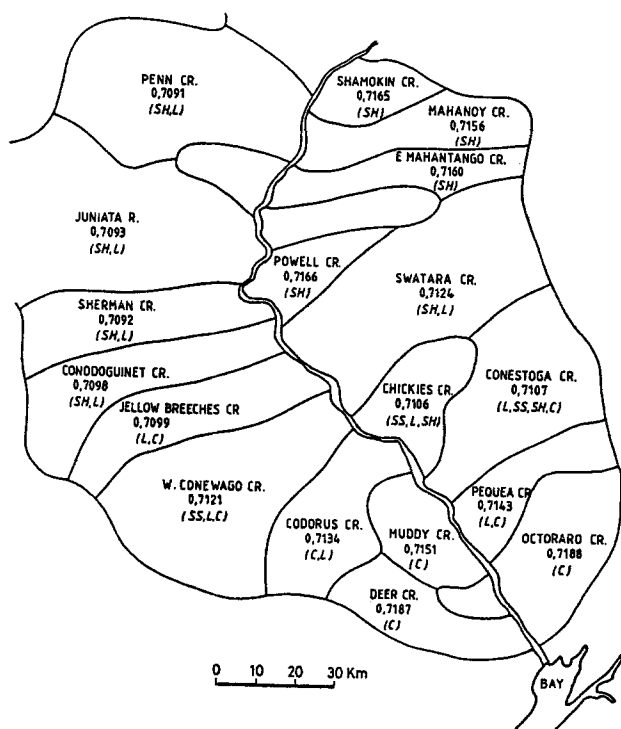


Figure 3: The mineral compositions of the bedrocks (SH=shales; L=limestones; SS=sandstones; C=crystalline rocks) and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of waters in the drainage basins of the tributary streams of the Susquehanna River (Fisher and Stueber, 1976)

ratios for the tributary streams on mixed bedrocks in their basins bear an approximately positive linear relationship, which suggests

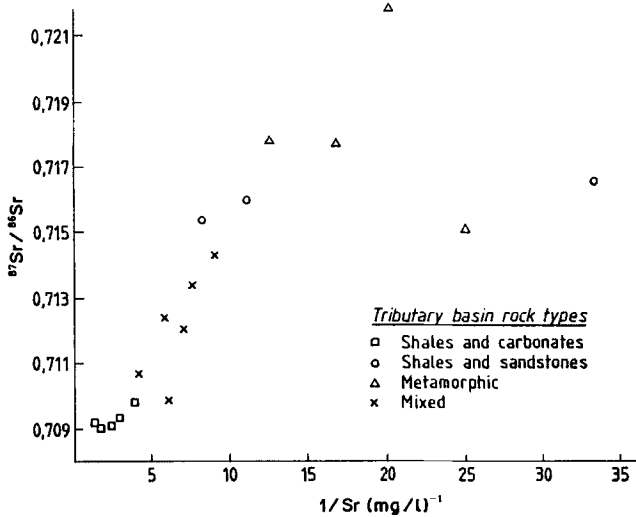


Figure 4: Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $1/\text{Sr}$ values of waters of tributary streams of the Susquehanna drainage basin, relative to the rock types (Fisher and Stueber, 1976)

that the range of Sr isotopic compositions of the waters could be described in terms of mixing in varying proportions of two isotopically distinct sources of dissolved Sr. But the variations in $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$ values for the waters of the Susquehanna River itself along the whole 150 km course could not be described in a linear trend. Fisher and Stueber suggested that the lack of linearity in the $^{87}\text{Sr}/^{86}\text{Sr}$ and the $1/\text{Sr}$ values of the waters reflects an incomplete mixing of tributary and main waters due to very small depth to width ratio of the main river channel.

Palmer and Edmond (1989) also examined the relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations of main river and respective tributary waters from Orinoco, Amazon, Ganges rivers and East African rift valleys (Fig. 5). The two variables are well correlated for the waters in the Ganges and, to some degree, for the waters in the Orinoco. The correlation becomes apparent for waters of the East African rift valleys only when the drainage is divided into northern and southern basins. Although the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr contents of the waters for the entire Amazon basin are not well-correlated, those of the sub-basins tend to show some good correlation. Palmer and Edmond remarked that the variation in

the relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$ values of waters within a drainage basin or among different drainage basins is related to lithologic, tectonic, and climatic controls in the drainage basins.

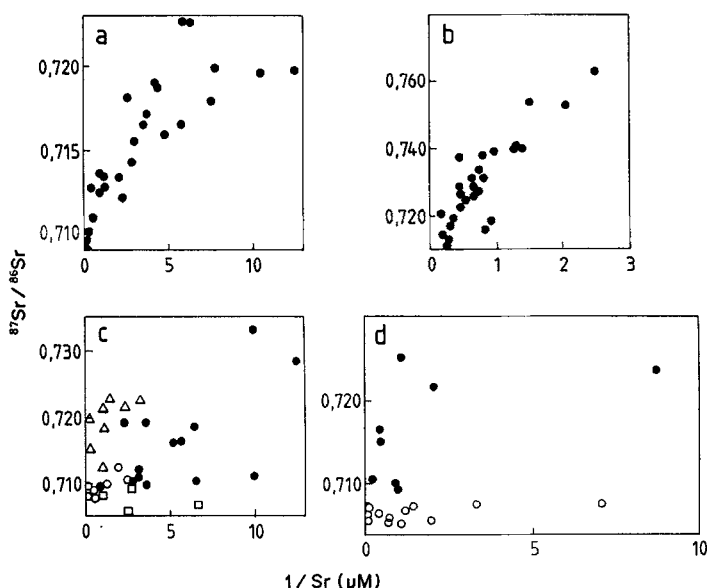


Figure 5: Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$ ratios of surface waters from drainage basins of: (a) Orinoco River, (b) Ganges River, (c) Amazon River, open symbols for mainstream at central (circle), northern (squares) and southern Andes (triangles) and closed circles for tributaries at the confluence with mainstream, (d) East African rift (Palmer and Edmond, 1989).

Strontium Isotopic Relations between Suspended and Dissolved Loads

The study of Hart and Tilton (1966) can be considered as the pioneer work on the determination of the relationship between the Sr isotopic compositions of dissolved and suspended loads in fresh water. They noted in Lake Superior in North America, that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the dissolved Sr was less than that of the Sr in the sediments. The recent study of Goldstein and Jacobsen (1987) is the most informative work to date about the range of isotopic relationships between dissolved and suspended loads in major rivers of the world (Fig. 6). They noted that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the dissolved load is lower than that of the suspended load for a vast majority of rivers in the world. Nevertheless, a small number of rivers were found with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of their dissolved loads

being higher than that of suspended loads, as illustrated by the data on rivers in West Greenland, the Columbia River in North America, and some rivers in Philippines and Japan. Whereas Sr isotopic disequilibrium between suspended and dissolved loads is common among a vast majority of rivers, isotopic equilibrium between the two loads has been observed for a small number of rivers such as the Colorado River in North America and the Tone River in Japan (Goldstein and Jacobsen, 1987). Closely identical Sr isotopic values between dissolved Sr and associated sediments were also reported by Jones and Faure (1967) in their study of Lake Vanda, Antarctica.

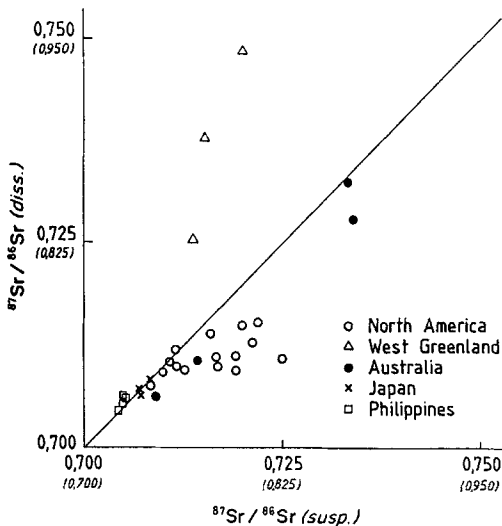


Figure 6: Sr isotopic relationship between suspended and dissolved loads in major rivers of the world. The solid line represents the 1:1 ratio between the two loads (Goldstein and Jacobsen, 1987).

Selective dissolution of minerals and preferential leaching of intracrystalline Sr from isotopically heterogeneous minerals in rocks are a prime cause for the difference in the Sr isotopic composition between dissolved and suspended loads in rivers. Among those rivers which have been found to have the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the dissolved load being lower than that of the suspended load, many drain primarily over both siliciclastic and marine chemical sedimentary rocks. In drainage basins with mixed lithology of siliciclastic and chemical sedimentary rocks, selective disso-

lutions of calcite, dolomite, gypsum, and celestite, which are typically low in $^{87}\text{Sr}/^{86}\text{Sr}$, dictate the low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the dissolved loads. Leaching of radiogenic Sr from ^{87}Sr -enriched silicate phases in rocks from drainage basins starved of marine chemical sedimentary rocks will account for the elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of dissolved loads. Aside from the effects of selective dissolution of minerals and leaching of radiogenic ^{87}Sr from minerals, the isotopic disequilibrium between the two loads in a river could also arise from mixing of the loads in varied amounts from two or more flow systems which are isotopically distinct but each with isotopic equilibrium between its own two loads.

The occurrence of Sr isotopic similarity between the two loads in a river requires specific lithological characteristics of the drainage basin. Isotopic similarity would occur where the drainage basin contains rocks made up of isotopically similar monomineralic phases, such as in limestone, or of isotopically similar polyminer-
al phases, such as in young volcanic igneous rocks.

Strontium Isotopic Characteristics of Continental Run-Offs

The average isotopic composition and the amount of Sr delivered annually to the oceans by rivers are essential components to the equation for the Sr isotopic mass-balance of the sea water. Knowledge of the global average isotopic composition of the flux of Sr delivered to the oceans by rivers has emerged from two lines of investigation, an indirect approach based on calculations from isotopic mass balance of Sr in sea water and a direct approach based on measurements of Sr contents and the isotopic composition of dissolved Sr in major rivers of the world. Many different suggestions have been made as to the estimate of Sr from ocean ridges in the marine cycle (Albarède et al., 1981; Clauer and Olafsson, 1981). From an estimate of the exchange of Sr between sea water and basalt of the East Pacific Rise, Albarède et al. suggested that the global average isotopic composition of riverine Sr should be between 0.7097 and 0.7113. Taking into account the potential effects of diagenetic reflux of Sr from marine carbonate rocks, in addition to considering the flux of Sr from the mid-

oceanic ridge activities, Elderfield and Greaves (1981) concluded that the global average isotopic composition of riverine Sr delivered to the oceans is about 0.7112.

Brass (1976) was the first to suggest a value of 0.7110 for the Sr isotopic composition of global riverine Sr flux based on measurement of the $^{87}\text{Sr}/^{86}\text{Sr}$ of water from the mouth of the Amazon River, which has the largest drainage basin with nearly 20% of the total river discharge to the ocean. Wadleigh et al. (1985) reported Sr isotopic data for major Canadian rivers which represent about 4% of the total discharge and about 6% of the Sr flux to the oceans. They concluded that the global average isotopic composition of the riverine Sr flux to the oceans is about 0.7111. Goldstein and Jacobsen (1987) published isotopic data of dissolved Sr in some major rivers of the world, which make up about 23% of the total river water being discharged to the oceans. They recommended an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7101 and the average Sr concentration of 0.062 mg/l for the global annual riverine flux to the oceans. More recently, Palmer and Edmond (1989) suggested, based on data from rivers which constitute about 47% of the total run-off, that the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and Sr content to be 0.7119 and 0.078 mg/l, respectively. The values recommended by Goldstein and Jacobsen are lower than those favored by others because the former included in their estimation a large number of run-offs on young volcanic rocks which have characteristically low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. While the disagreement is small among the estimates for average $^{87}\text{Sr}/^{86}\text{Sr}$ and the flux of continental Sr delivered annually to the oceans, we might recall that $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for rivers are known to be varied from one season to another or even from one year to another (Eastin and Faure, 1970; Palmer and Edmond, 1989). As recent recommendations concerning the isotopic composition of global riverine Sr flux to the oceans are essentially based on a data set developed from one time measurement for each river, the recommended values can be quite different from the real average value.

The different studies of Sr isotopic compositions of river waters clearly demonstrate that their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary widely and that in many rivers the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of dissolved Sr exceed

the values of Phanerozoic marine carbonate rocks, which range approximately between 0.7068 and 0.7091. The sources of radiogenic ^{87}Sr in those rivers with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios higher than that of marine carbonate rocks have not been clearly identified. Clay minerals have been considered by some as a contributor of radiogenic ^{87}Sr to surface waters or shallow subsurface ground-waters because these minerals, especially illite, are abundantly common in shales and soils. While these minerals could have some influence on the Sr isotopic composition of river waters, we do not consider that these minerals would be a major contributor of radiogenic ^{87}Sr to surface waters. The exchangeable Sr in clay minerals is mostly surface adsorbed and not specific to the structural sites and hence the isotopic composition of the exchangeable Sr is very nearly the same as that of Sr in the environment with which the clay minerals are associated (Thellier and Clauer, 1989; Clauer et al., 1990). We believe that weathering of Rb-bearing silicate minerals such as K feldspar and biotite, and even of some plagioclase minerals with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, is the major factor for the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of many river waters.

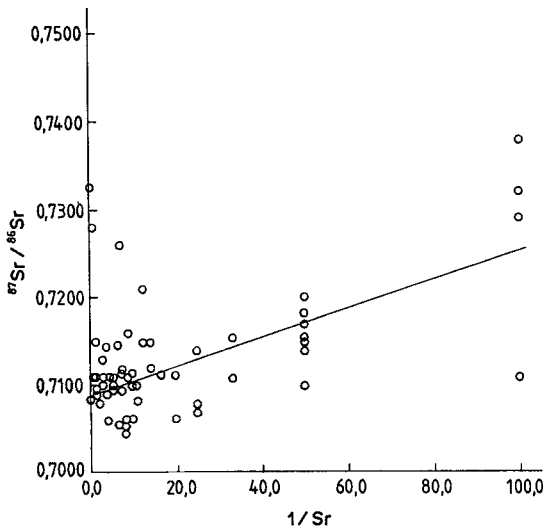


Figure 7a: Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $1/\text{Sr}$ values of major rivers in the world (Palmer and Edmond, 1989)

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and the Sr concentration of any major river may provide, in some instances, important clues as to the crustal

history of rocks in a drainage basin. Palmer and Edmond (1989) observed an approximately linear relationship between Sr isotopic compositions and $1/\text{Sr}$ values among a large number of major rivers in the world (Fig. 7a). This is basically a reflection of two general sources of Sr in the drainage basins. But the Sr isotopic compositions and Sr contents of some rivers, for example those of the Ganges and the Brahmaputra rivers in India and the rivers of Greenland (Fig. 7b), deviate considerably from the global trend. Palmer and Edmond attributed the anomaly found in the Indian rivers to the effect of high weathering rates of the Himalayas. We think that the anomaly is related to the high susceptibility to weathering of some Sr-enriched silicate minerals, possibly plagioclase minerals, having high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Plagioclase minerals in some leucogranites in the main Higher Himalayan Range have been found with high $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratios (0.750; Deniel et al., 1987).

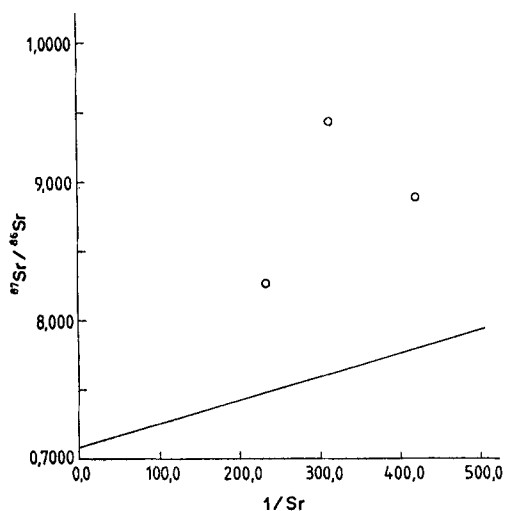


Figure 7b: Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $1/\text{Sr}$ values of three rivers in Greenland. The line is that of figure 7a (Palmer and Edmond, 1989)

Similar rocks in the Himalayas could have been a major source of the dissolved Sr in the Ganges and the Brahmaputra rivers. Hence, we believe that the isotopic compositions of dissolved Sr in the Ganges and the Brahmaputra rivers more likely reflect the tectonic

evolutionary history of rocks in the Himalayas, rather than the weathering rates as Palmer and Edmund (1989) suggested.

The three major sources for riverine Sr are old continental crystalline rocks, young igneous rocks, and marine carbonate and sulfate rocks. We have yet to determine the relative importance of these sources in the Sr budget for the global river. A simplified view has often sought to find out the relative importance between silicate and carbonate sources for riverine Sr. From a calculation based on Sr/Ca ratios of river waters, Brass (1976) suggested that nearly 80% of the flux of Sr in river waters is from limestone and that the average isotopic composition of the flux of limestone Sr is about 0.708, which would make the average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the flux of silicate Sr in river waters to be about 0.723. From data of river waters in Canada, Wadleigh et al. (1985) found that about 21% of the Sr could have come from a silicate source, a value in agreement with the estimate by Brass. Wadleigh et al., however, also suggested that Sr/Ca and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of river waters in Canada can also be generated by mixing of Sr derived from old and young silicate sources, in which case the relative importance of the silicate source may be even higher than the value of Brass (1976).

Goldstein and Jacobsen (1988) gave estimates of $0.7 \times 10^{12} \text{ gy}^{-1}$ and $2.52 \times 10^{12} \text{ gy}^{-1}$ for the fluxes of Rb and Sr, respectively, in dissolved load of the present-day global runoff, based on the calculation from total runoff of about $4.2 \times 10^{12} \text{ gy}^{-1}$. By comparison, the estimated fluxes of Rb and Sr in the suspended load of the global runoff are $1.47 \times 10^{12} \text{ gy}^{-1}$ and $2.98 \times 10^{12} \text{ gy}^{-1}$, respectively. While the fluxes of Sr between the two loads are comparable, more than 95% of the total flux of Rb in the global runoff is transported in the suspended fraction as a reflection of large differentiation between Rb and Sr behaviors during weathering, erosion and transportation. The high degree of differentiation between the two elements is further evident in the unrealistic calculated Rb-Sr isotopic model age for the dissolved load. Goldstein and Jacobsen reported a depleted mantle based Rb-Sr age of about 29 Ga for the dissolved load and about 0.7 Ga for the suspended load.

The discussions earlier emphasized that river waters may or may not be in Sr isotopic equilibrium with bedrocks or soils of the drainage basin, depending on the mineralogy of the bedrocks and the soils, as well as topography, climate, and time which control the degree of weathering in the drainage basin. To date, studies on Sr-isotope systematics in weathering environments are very few (Clauer, 1979), and we have yet to understand fully the various factors which govern the fractionation of ^{87}Sr between waters and bedrocks and soils. Such knowledge is essential to explain clearly the variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of run-offs and the significance of the global average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of riverine Sr as they relate to continental weathering and denudation.

NEODYMIUM ISOTOPIC COMPOSITIONS OF SURFACE WATERS

From analyses of several run-off samples, Martin et al. (1976) and Keasler and Loveland (1982) reported that Nd contents are less than 9×10^{-5} mg/l. Goldstein and Jacobsen (1987) measured Nd contents of waters from different rivers in Canada, the U.S.A., Australia, West Greenland, Japan, Philippines, and Venezuela and obtained Nd values ranging from 3×10^{-6} to about 3×10^{-3} mg/l. These low Nd contents are thought to be due to the extremely low solubility of the rare-earth elements (REE) in aqueous form.

The paucity of Nd isotopic data of surface waters is largely attributed to the difficulty of analyzing materials with extremely low concentrations. The study of Goldstein and Jacobsen (1987) is at present represents the major source of information (Table 2). It shows that the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the waters range from about 0.509596 to about 0.512192. Like the Sr isotopic compositions, the Nd isotopic compositions of surface waters also broadly reflect the composition of rocks in drainage basins. In general, the more negative are the ϵ_{Nd} values, the greater is the influence of very old continental rocks and less is the influence of young island arc and continental arc volcanic rocks.

Table 2: Nd isotope data of waters from major rivers and lakes

Sample	Sm(1)	Nd(1)	$^{143}\text{Nd}/^{144}\text{Nd}$
<u>North America</u>			
Mississippi 1	4.86	23.8	0.511412
Mississippi 2	9.59	45.9	0.510854
Missouri	4.98	23.0	0.511451
St Lawrence	2.25	10.7	0.511233
Columbia	4.41	20.1	0.511693
Colorado	1.18	6.0	0.511435
Ohio	1.62	8.2	0.511331
Ottawa	43.5	264	0.510833
Tennessee	2.02	8.5	0.511341
Hudson	20.9	105	0.511429
Michigan Lak	1.40	6.0	0.511196
Huron Lake	1.08	5.3	0.510989
Superior Lake	2.19	9.7	0.511004
<u>West Greenland</u>			
Isua-B	37.3	237	0.509656
Isua-F	40.7	274	0.509645
Nigrik	72.2	478	0.509596
<u>Australia</u>			
Murray	3.49	15.2	0.511539
<u>Japan</u>			
Mogami	--	--	0.511851
<u>Philippines</u>			
Abra	--	--	0.512186
Agno	--	--	0.512190
Cagayan	--	--	0.512192
Pampanga	2.49	8.6	0.512160

(1) amounts in $\mu\text{g/g} \times 10^{-6}$; $^{143}\text{Nd}/^{144}\text{Nd}$ normalized to $^{146}\text{Nd}/^{142}\text{Nd} = 0.636151$; the data are from Goldstein and Jacobsen (1987)

Neodymium Isotopic Compositions in Dissolved and Suspended Loads

Goldstein et al. (1984) noted the ϵ_{Nd} values to range from -3.3 to -16.1 for particulate matters of major rivers. But from a study of rivers draining a basin with a varied lithology, Goldstein and Jacobsen (1988) observed an even wider range of ϵ_{Nd} values from +7.1 to -44.9. Goldstein and Jacobsen (1987) found that in nearly half of the rivers the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of dissolved loads were different from that of the corresponding suspended loads. Dissolved loads of most of the rivers in North America had higher Nd isotopic values and those of the Nigrik River in West Greenland and the Murray River in Australia had lower Nd isotopic values than corresponding suspended loads (Fig. 8). However, the correlation obtained is much better than that for Sr, primarily because little or no fractionation occurs for the Sm-Nd isotope systems, unlike for the Rb-Sr systems, during continental weathering processes. The extent of ϵ_{Nd} differences between the two loads is no more than 4 units, which is significant. The differences can be related to such factors as selective dissolution of minerals with different Nd isoto-

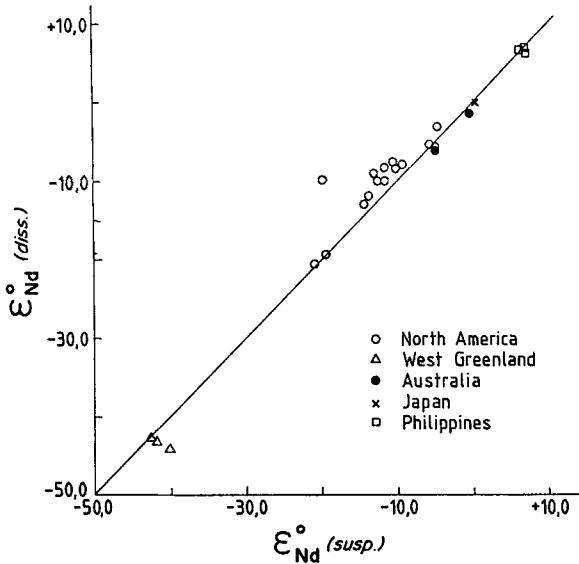


Figure 8: Nd isotopic relationship between dissolved and suspended loads in major rivers of the world (Goldstein et al., 1987)

pic compositions, preferential dissolution of domains in very old minerals having internal isotopic Nd heterogeneities, and varied inputs of loads to a main river by its tributary rivers draining over isotopically different bedrocks in their drainage basins. Mineralogic and isotopic analyses of stream sediments in conjunction with the isotopic analyses of dissolved loads are necessary for a full understanding of the process of rock weathering in drainage basins.

The Sm/Nd ratio of dissolved load is almost always higher than that of suspended load for most rivers (Fig. 9). The Sm/Nd of dissolved load can be as much as 70% higher than that of the suspended load, although on average the ratio is only about 14% higher. Goldstein and Jacobsen (1987, 1988) observed that the increase in the Sm/Nd of the dissolved load is to some extent pH-dependent, and they attributed the high Sm/Nd ratio of the dissolved loads to increased stability of carbonate and hydroxide complexes of the heavy REE. Another factor for the elevated Sm/Nd of dissolved loads could be the higher stability of heavy REE organic

complexes as compared to the light REE complexes.

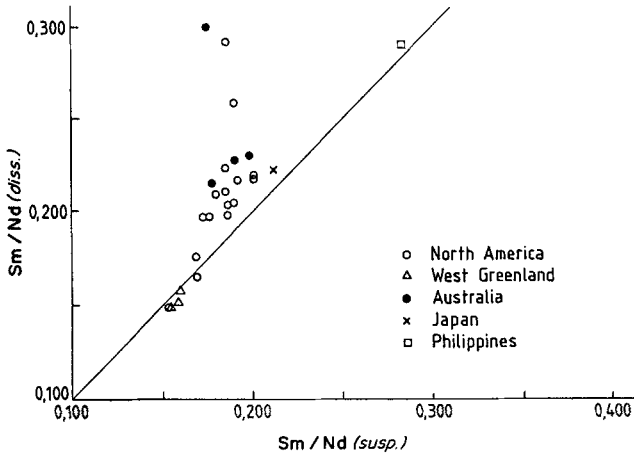


Figure 9: Sm/Nd ratios between dissolved and suspended loads in major rivers of the world (Goldstein and Jacobsen, 1987)

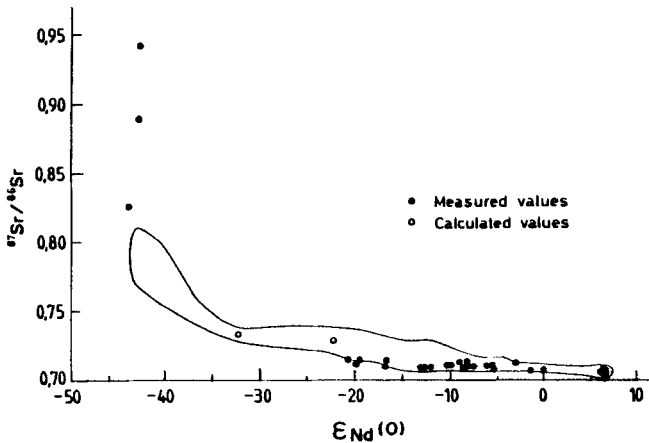


Fig. 10: Relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and ϵ_{Nd} values for dissolved loads of rivers. Calculated values are from estimates from data on suspended loads. The encircled area includes the trend between the two parameters (Goldstein and Jacobsen, 1987)

Goldstein and Jacobsen (1987) observed an approximately inverse relationship between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and ϵ_{Nd} values for dissolved loads of major rivers of the world (Fig. 10). They also observed a similar relationship for the suspended loads. The rela-

tionship relates to the isotopic compositions of the loads being influenced by the ages of the rocks in the drainage basins, older rocks having higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and lower ϵ_{Nd} values than younger rocks.

River waters widely vary in their Nd/Sr ratios from 10^{-1} for those with predominantly crystalline rocks in their drainage basins, to 10^{-5} for those with predominantly marine chemical sedimentary rocks. Mixing of waters from drainage basins with such contrasting lithologies would produce a hyperbolic relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and ϵ_{Nd} values. Goldstein and Jacobsen (1987) observed such a hyperbolic trend among the Lake Michigan, Lake Huron, Mississippi, St Lawrence, Ottawa, and St Louis waters.

Neodymium Isotopic Composition of Global Runoff

Goldstein and Jacobsen (1987) calculated a weighted average ϵ_{Nd} value of the present-day runoffs to the Atlantic, the Pacific, and the Indian oceans. The estimated value for the Atlantic Ocean is -12.6, the Pacific Ocean is -2.9, and the Indian Ocean is -8.7. As these values are close to the average ϵ_{Nd} value of sea water in each of the ocean basins, the authors suggested that the river runoff is a major influence on the ϵ_{Nd} value of sea water. Any definite conclusion about the specific role of the runoff still awaits determination of the importance of various potential roles of the suspended loads in transferring Nd to the oceans.

Goldstein and Jacobsen (1987) also estimated the average ϵ_{Nd} value of global runoff to the oceans to be -10.2 and the average Sm and Nd concentrations to be about 8×10^{-6} mg/l and 4×10^{-5} mg/l, respectively. However, assuming some removal of Nd by estuarine processes, the authors suggested an ϵ_{Nd} value of -8.4 for the effective flux of runoff Nd to the oceans. Goldstein and Jacobsen (1988) calculated a depleted mantle based Sm-Nd model age of 1.63 Ga for the global dissolved load, having the fluxes of Sm and Nd of approximately 2×10^8 gy^{-1} and 1×10^8 gy^{-1} , respectively. The Sm-Nd model age for the dissolved load is nearly the same as that for the suspended load. The average model ages reflect the weathering and

erosion of rocks on exposed surfaces of the crust. As rocks from young orogenic belts are weathered and eroded to a greater extent than those from old stable cratonic regions with low relief, the calculated Sm-Nd model age of the dissolved or the suspended load can be considered as the minimum average age of the exposed rocks.

CONCLUDING REMARKS

The foregoing discussions have shown that isotopic characteristics of dissolved Sr in waters in a drainage basin are influenced by lithologic composition, tectonic factor, and climatic control. Relations in Sr isotopic compositions between a main river and its tributaries in a drainage basin are often extremely varied. Poor correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $1/\text{Sr}$ values reflects varied inputs of isotopically very different Sr from the tributary rivers to the main river and also incomplete mixing between tributary and main river waters due to low depth to width ratio of the channels. Good correlation between the two parameters suggests a mixing of Sr derived essentially from two sources, which can often be described as being a silicate source with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and low Sr concentrations and a carbonate source with a marine Sr isotopic value and high Sr concentrations.

Seasonal Sr isotopic variations have been noted in some studies on dissolved Sr in river waters. Present estimates of average Sr isotopic composition of global run-offs are based on data from one-time measurements on rivers. As the isotopic compositions of rivers can be significantly varied seasonally and annually, caution should be taken in the use of any of the presently given estimates for the average Sr isotopic compositions of global run-offs.

The Sr isotopic relationships between suspended and dissolved loads of rivers are varied. Isotopic similarities are much less frequent than dissimilarities, but most often these similarities occur with $^{87}\text{Sr}/^{86}\text{Sr}$ values less than 0.710. This can be attributed to weathering of predominantly marine chemical sedimentary rocks

or young volcanic rocks in the drainage basin. Only in very limited cases Sr isotopic similarities were found between dissolved and suspended loads, when the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is far in excess of 0.710. But lack of mineralogic and chemical information about the suspended loads presently does not offer the real cause for that isotopic similarity between the loads. Preferential dissolution of phases with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios or domains with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in isotopically heterogenous mineral phases and mixing in varied amounts of isotopically different loads from tributary streams may account for the lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of dissolved load relative to corresponding suspended load in a river. Selective removal of radiogenic ^{87}Sr is a major cause for dissolved load to be higher in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than suspended load, which may explain why dissolved loads of three rivers in West Greenland were found to be extremely high in $^{87}\text{Sr}/^{86}\text{Sr}$, from about 0.826 to 0.943.

Like Sr isotopic compositions, the Nd isotopic compositions of dissolved loads can be different from that of suspended loads. The isotopic difference could arise from preferential weathering of minerals which are isotopically heterogenous or from varied mixing of loads with different isotopic compositions from tributary rivers to the main river. River waters are known to have seasonal variations in the flow and the chemical composition, which might induce changes in the inputs by the tributary streams. We, therefore, believe that the differences in the Nd isotopic composition between dissolved and suspended loads of a river is commonly an effect of mixing of loads from tributary streams with different isotopic compositions.

The Sm/Nd ratios range from 0.15 to 0.30 and the ϵ_{Nd} values between +7 and -44 for dissolved loads of major rivers in the world, the more negative ϵ_{Nd} values reflecting the influence of very old continental rocks. In nearly 50% of the rivers, the Nd isotopic composition of dissolved load was found to be different from that of the corresponding suspended load, but the difference in the ϵ_{Nd} values between the two loads is no more than 4 units. The difference can be ascribed to selective dissolutions of minerals with different Nd isotopic compositions or of domains of old minerals with internal chemical heterogeneity, or to varied inputs of loads

from isotopically different drainage sub-basins. The Sm/Nd ratios of dissolved loads relative to that of suspended loads tend to increase with increasing pH values, suggesting some degree of differentiation between the two elements as a result of their complexation by carbonate, hydroxide and organic radicals during weathering, erosion and transport.

Both dissolved and suspended loads have an approximately inverse relationship in their $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{144}\text{Nd}/^{143}\text{Nd}$ ratios, which apparently relates to the isotopic compositions of the loads being influenced by ages of the rocks in the drainage basins. Calculated weighted average ϵ_{Nd} value of the present-day runoffs to each major ocean basin shows that the Nd isotopic compositions of sea waters are strongly influenced by the runoff inputs. The global runoff ϵ_{Nd} value is about -8.4, and the average Sm-Nd of the dissolved load is about 1.63 Ga, which is about the same as that of the suspended load. This age can be considered as the minimum average age of rocks on the exposed surface of the crust.

Knowledge of the isotopic compositions of dissolved loads in rivers has increased understanding of the weathering of continental crust. Additional understanding would come by combining the chemical and isotopic data of dissolved, suspended, and bed loads with the mineralogic data of the two latter. A cautionary remark must be made here for isotopic studies of all surface waters. Careful filtration of such waters, however difficult it may be, is absolutely necessary to define appropriately the isotopic characteristics of the dissolved constituents. Using $<0.45\mu\text{m}$ filter is apparently not enough to trap all the fine suspended materials in waters. This is clearly evident from the data presented by Stordal and Wasserburg (1986). They observed an increase in the Sm/Nd ratio by about 5%, a decrease in the ϵ_{Nd} value by about 2 units, and a decrease in the ϵ_{Sr} value by 1 unit for $<0.1\mu\text{m}$ filtered water compared to $<0.4\mu\text{m}$ filtered water from the Mississippi River. They also reported an increase in the Sm/Nd ratio by about 20% for $<0.1\mu\text{m}$ filtered water compared to $<0.4\mu\text{m}$ filtered water from the Amazon River.

Recently some investigators, working especially on the effect of atmospheric input of acidity to the waters, have begun to use

Sr isotopes as a tracer to determine the predictability of geochemical models depicting the precise steps of dissolution of minerals in rocks within a drainage basin (Probst et al., 1992).

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