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Strontium isotopic geochemistry of the Changjiang estuarine waters: Implications for water-sediment interaction

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Abstract The Sr concentrations and $^{87}Sr/^{86}Sr$ ratios have been measured for the Changjiang estuarine waters with a main purpose to understand physical and chemical processes at the estuary. The result shows that the Changjiang River water has higher Sr concentration (150 ng/g) and lower $^{87}Sr/^{86}Sr$ ratio (0.7105) when compared with the average values (0.7119 for $^{87}Sr/^{86}Sr$ and 78ppb for Sr, respectively) of large world rivers. In the mixing process, no simple mixing of two end-members has been found according to the variations of Sr concentration and isotope ratios. There is an abrupt rise of Sr isotope ratios at the salinity about 1mg/g during river-sea water mixing at the estuary. This abrupt rise of Sr isotope ratios is mostly ascribed to the strong water-sediment interaction, because there exists the same rise of suspended particulate materials due to energetic resuspension of bottom sediments.

Keywords: $^{87}Sr/^{86}Sr$, Changjiang estuary, mixing, water-sediment interaction.

1 Introduction

Unlike lighter isotopes (e.g., $\delta^{13}C$, $\delta^{18}O$), ^{87}Sr and ^{86}Sr are not fractionated by processes such as phase separation, chemical speciation, evaporation, or biological assimilation[1—5]. The only change to the $^{87}Sr/^{86}Sr$ ratio in surface aquatic environment will be due to the mixing of Sr from the different sources. Therefore, strontium isotopes are an excellent tracer in geochemical research[5—9]. For example, the variations of strontium isotopic composition in estuaries can give us useful information about the mixing of distinct water masses (river water, groundwater, pore water and seawater) and sources of suspended material. Furthermore, the strontium isotope systematics of rivers can also reflect factors such as basin lithology, climate, weathering rates, water-rock interaction, etc[9—11].

2 Sampling and analysis

Water samples were collected in surface waters of the Changjiang estuary during November 4 to 5, 1998. Sampling was made by using 10-L nitric acid-cleaned polyethylene bucket. Salinity, pH and temperature were measured on site. The samples used for the determination of the Sr isotope were filtered through 0.45 μm fibers (Milli pore) immediately after collection and were acidified to pH≈1.6 using Q-HCl and stored in 100ml high-density polyethylene bottles. Additional water samples were also obtained at each station to measure major anions and cations. The concentrations of strontium were determined by AAS. Strontium separation for isotopic analysis was carried out by conventional ion-exchange techniques by using a Dowex 50 W-8X 200-400 mesh resin. The Sr isotopic ratios were measured on a VG 354 mass spectrometer. The details of their precision and accuracy are summarized in Table 1.

Table 1 The $^{87}Sr/^{86}Sr$ ratios, salinity and concentrations of SPM and Sr in the Changjiang estuarine waters

Sample No.	$^{87}Sr/^{86}Sr$	2σ	Salinity/mg • g^{-1}	SPM/mg • L^{-1}	Sr/ng • g^{-1}
33	0.710514	10	0.15	238.53	130.03
32	0.71043	15	0.3	206.03	160.04
31	0.710408	12	0.34	137.14	150.03
31*	0.710443	16	0.34	137.14	150.03
29	0.710424	11	0.38	120.42	170.04
27	0.710415	11	0.4	74.09	170.04
25	0.709971	10	1.05	74.14	270.06
23	0.709877	13	1.2	88.84	340.08
21	0.71036	16	0.8	129.10	280.06
20	0.710081	11	0.9	93.41	280.06
19	0.709517	8	3.4	43.65	665.91
18	0.709501	9	4.4	27.92	823.63
16	0.709418	14	6	38.43	1090.25
14	0.709354	12	8.2	28.26	1440.33
14*	0.709416	9	8.2	28.26	1440.33
9	0.70931	10	11.5	30.34	2010.46
5	0.709272	18	19	19.51	3130.71
5*	0.70923	13	19	19.51	3130.71
NBS987	0.710264	11			
NBS987*	0.710285	9			
NBS987*	0.710266	10			
NBS987*	0.710263	12			
NBS987*	0.710261	15			

3 Results and discussion

The measured values of $^{87}Sr/^{86}Sr$, together with the concentrations of strontium, salinity and the concentrations of suspended particulate matter (SPM) are given in Table 1.

3.1 Sr isotope composition in freshwater end-member of the Changjiang

The Sr concentrations and isotope ratios are listed in Table 1. Comparison with Amazon, Zaire (Congo), Orinoco and other large rivers of the world (the average river values 0.7119 for $^{87}Sr/^{86}Sr$ and 78ppb for Sr, respectively), the Changjiang River has higher Sr concentrations (150 ng/g) and lower $^{87}Sr/^{86}Sr$ (0.7105) ratios, reflecting the lithological and weathering features of the Changjiang drainage basins[12]. The Sr isotopic compositions of the Changjiang water that obtained in this study also approaches the only one $^{87}Sr/^{86}Sr$ ratio (0.7109) that had given by Palmer and Edmond in 1989[12]. It is worth pointing out here that the $^{87}Sr/^{86}Sr$ ratios of the Changjiang waters are not affected obviously by that of Himalayan source waters which has highest $^{87}Sr/^{86}Sr$ ratio (0.73—0.93) in the world though the Changjiang River originates from the Tibet plateau[7,11,13,14].

Furthermore, there is a small difference among the Sr concentrations and isotopic compositions of the three large Chinese rivers, Changjiang (0.7105 for $^{87}Sr/^{86}Sr$, 150ppb for Sr), Yellow River (0.7111 for $^{87}Sr/^{86}Sr$, 650ppb for Sr) and Pearl River (0.7119 for $^{87}Sr/^{86}Sr$, 67ppb for Sr)[12]. These differences indicate that erosion and lithological features, possibly as well as human activities are different in the drainage areas of these three rivers.

3.2 Variation of $^{87}Sr/^{86}Sr$ ratios during estuarine water mixing

If no other strontium sources joins during estuarine water mixing, the mixing line in the $^{87}Sr/^{86}Sr$ versus 1/Sr plot between river water and seawater should be a perfect linear line according to the explanation about Sr isotope geochemistry of two-component mixtures by Faure[15]. In previous studies, the strontium and its isotope are very conservative in estuarine process [9]. However, $^{87}Sr/^{86}Sr$ versus 1/Sr plot of the Changjiang estuarine waters does not show a perfect linear relation: the data distributions consists most likely of two mixing lines (Fig. 1(a)). The $^{87}Sr/^{86}Sr$ ratio and SPM variations show a general decrease with distance from the mouth of the Changjiang River toward the East China Sea, but there is a peak or abrupt elevation at about 32 to 42km zone (Fig. 1(a) and (b)). Obviously, there must be additional substance input into this region, since the $^{87}Sr/^{86}Sr$ ratio is not significantly altered in chemical reactions. There are two possible explanations for this elevation of $^{87}Sr/^{86}Sr$ ratios. One is the input of other water endmember that is enriched radiogenic strontium other than the freshwater of the Changjiang and seawater. The other possible explanation is that strong water-sediment interaction at this salinity region releases radiogenic Sr from silicate suspended matter or sediments. We favor the second interpretation. Because there is an abrupt elevation of the concentration of suspended

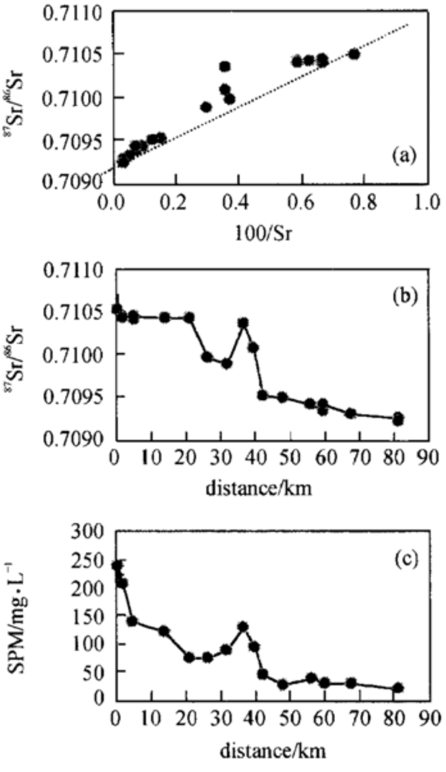

Fig. 1. (a) The $^{87}Sr/^{86}Sr$ versus 1/Sr Plot of the Changjiang estuarine water (the dashed line is the conservative mixing line) and the $^{87}Sr/^{86}Sr$ (b) and SPM (c) distributions at the Changjiang Estuary. Note that the elevation peaks of $^{87}Sr/^{86}Sr$ and SPM at 32 to 42km zone from the river mouth.

material which is very nearly the same as the rise of $^{87}Sr/^{86}Sr$ ratios at the same salinity region? (Fig. 1(c)). On the contrary, there is not any clue that can prove the existence of other water end-member with high $^{87}Sr/^{86}Sr$ ratios.

In aquatic geochemical studies, the water sample is commonly separated and defined "dissolved" phase and "suspended" material by filter pore size 0.45 or 0.22 μm arbitrarily. "*" Refers to replicate analyses. In fact, the "dissolved" phase is not the really soluble constituent. It is composed of colloids, organic complexes, inorganic complexes and free ions. The four fractions have different grain-size, structure, chemical component and surface properties. If the relative proportions of these fractions are changed, the concentrations or isotopic compositions of elements in the "dissolved" pool may be altered. Douglas et al[5] had separated the river water samples in four fractions (1—0.2 μm, 0.2—0.006 μm, 0.006—0.003 μm and <0.003 μm) and measured their strontium isotopic compositions respectively. The result shows that strontium isotopic composition is a function of particle size: with the particle size decreasing, the $^{87}Sr/^{86}Sr$ ratio decreases and Sr concentration increases[5].

The Changjiang estuary is a high-energy system where a strong physical connection exists between beithic processes and surface water chemistry. Because the upper estuary of the Changjiang (salinities ranging from 0 to 20 mg/g) is very shallow (5—6 m), river input mainly runs through four submerged long channels to the East China Sea[16]. Water mixing is forceful in these long channels and water-sediment interaction is very strong, which leads to energetic resuspension of bottom sediments[16]. The surface sediment reservoir therefore oscillates between suspension (mainly in winter) and deposition (mainly in summer). This process can alter the trace element composition of surface waters. Strong water-sediment exchange can also change the size distribution of suspended materials in the estuarine surface waters, and hence change the composition of Sr isotope. Accordingly, trace element and Sr isotopic compositions of the Changjiang Estuary water are more intensely affected by hydrodynamic and sedimentologic factors than most of other rivers of the world.

3.3 Influence on ocean Sr isotope composition

Rivers provide the major flux of strontium to the oceans and play a major role in defining the marine $^{87}Sr/^{86}Sr$[3,7,11,12,17]. The Changjiang River is large in scale, thus, study on Sr isotope of the Changjiang and the Changjiang estuary is of great significance in interpreting the Sr isotopic geochemistry in the East China Sea and the West Pacific. Due to intense weathering, or the geology of the drainage basins and human activities, as mentioned above, the Changjiang River is an important source of strontium to the West Pacific and world oceans. By taking the concentration of Sr=150ppb and the annual river discharge of 9.282×10^{14}kg/yr, we obtain the dissolved Sr annual flux from the Changjiang River to the East China Sea is about 1.4×10^{8} kg/yr with more nonradiogenic strontium ($^{87}Sr/^{86}Sr=0.7105$) than most of other rivers of the world.

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References

1. Eisenhauer, A., Meyer, H., Rachold, V., et al., Grain size separation and sediment mixing in Arctic Ocean sediments: evidence from the strontium isotopes systematic, Chemi. Geology, 1999, 158: 173.
2. Asahara, Y., Tanaka, T., Kamioka, H., et al., Provenance of the north Pacific sediments and process of source material transport as derived from Rb-Sr isotopic systematics, Chemi. Geology, 1999, 158: 271.
3. Goldstein, S. J., Jacobsen, S. B., The Nd and Sr isotopic systematics of river-water dissolved material: implications for the sources of Nd and Sr in seawater, Chemi. Geol., 1987, 66: 245.
4. Palmer, M. R., Edmond, J. M., Controls over the strontium isotope composition of river water. Geochimca, Cosmochimica. Acta, 1992, 56: 2099.
5. Douglas, G. B., Gray, C. M., Hart, B. T., et al., A Strontium isotopic investigation of the origin of suspended particulate matter (SPM) in the Murray-Darling River system, Australia, Ceochim. Cosmochim. Acta, 1995, 59: 3799.
6. Neumann, K., Dreiss, S., Strontium 87/Strontium 86 ratios as tracers in groundwater and surface waters in Mono basin, California, Water Resources Res., 1995, 31: 3183.
7. Derry, L. A., France-Lanord, C., Neogene Himalayan weathering history and river ^{87}Sr/^{86}Sr: impact on the marine Sr record, Earth Planet Sci. Lett., 1996, 142: 59.
8. Semhi, K., Clauer, N., Probst, J. L., Strontium isotope compositions of river waters as records of lithology-dependent mass transfers: the Garonne river and its tributaries (SW France), Chemi. Geology, 2000, 168: 173.
9. Ingram, B. L., Sloan, D., Strontium isotopic composition of estuarine sediments as paleosalinity-paleoclimate indicator. Science, 1992, 255: 68.
10. Åberg, G., Jacks, G., Joseph Hamilton, P., Weathering rates and ^{87}Sr/^{86}Sr ratios: an isotopic approach, J. Hydrology, 1989, 109: 65.
11. Chesley, J. T., Quade, J., Ruiz, J., The Os and Sr isotopic record of Himalayan paleorivers: Himalayan tectonics and influence on ocean chemistry, Earth Planet Sci. Let., 2000, 179: 115.
12. Palmer, M. R., Edmond, J. M., The strontium isotope budget of the modern ocean, Earth Planet. Sci. Lett., 1989, 92: 11.
13. Krishnaswami, S., Trivedi, J. R., Sarin, M. M., et al., Strontium isotopes and rubidium in the Ganga-Brahmaputra river system: Weathering in the Himalaya, fluxes to the Bay of Bengal and contributions to the evolution of oceanic ^{87}Sr/^{86}Sr, Earth Planet. Sci. Lett., 1992, 109: 243.
14. Galy, A., France-Lanord, C., Derry, L. A., The strontium isotopic budget of Himalayan Rivers in Nepal and Bangladesh. Geochimca, Cosmochimica. Acta., 1999, 63: 1905.
15. Faure, G., Principles of isotope geology, John Wiley & Sons: New York, 1986, 141.
16. Pan, D. A., Sun, J. M., The sediment dynamics in the Changjiang River Estuary Mouth bar area, Oceanol. Limnnol. Sinica. (in Chinese), 1996, 27: 279.
17. Wadleigh, M. A., Veizer, J., Strontium and its isotopes in Canadian rivers: Fluxes and global implications, Geochimca. Cosmochimica. Acta, 1985, 49:1727.