Chemical and strontium isotopic composition of Kaveri, Palar and Ponnaiyar rivers: Significance to weathering of granulites and granitic gneisses of southern Peninsular India

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Strontium (Sr) isotope ratios and major ion abundance were determined on water samples of Kaveri, Palar and Ponnaiyar rivers, collected during the NE monsoon of 2005, when there was unusually heavy rainfall. Sr isotope ratios combined with major ion concentrations were used to determine relative contribution of Sr and major ions by weathering of various rock types exposed in the drainage basin. $^{87}Sr/^{86}Sr$ ratios were well correlated to Ca/Sr and Mg/Sr ratios in water samples indicating mixing of water with solute load essentially derived by weathering of granitoid gneisses, mafic volcanics and carbonates of the Archean schist belts in the upper reaches with the water draining felsic granulites in the lower reaches.

Keywords: Chemical weathering, Kaveri, Palar, strontium isotope, water chemistry.

THE strontium isotope ($^{87}Sr/^{86}Sr$) ratio of river water on a global scale varies mostly between 0.7036 and 0.7384, with an average ratio[1] of 0.7119; this is different from the rainwater ratio of 0.7098. Release of Sr by weathering of rocks influences the Sr isotopic composition of the river water. Each major river has a certain characteristic $^{87}Sr/^{86}Sr$ ratio that depends on the rocks exposed and their weathering pattern in the drainage basin. Rb/Sr ratios in different rock-forming minerals range from 0.01 to 100. Rocks consist of several minerals and their rates of weathering differ widely. Preferential weathering of minerals having high Rb/Sr ratio and older age will result in the release of Sr with higher $^{87}Sr/^{86}Sr$ ratio into the river water.

Dissolution of CO_2 in rainwater and pore-water of soil results in the lowering of pH and enhances weathering of minerals. Silicate weathering is responsible for CO_2 consumption and therefore is an important parameter while modelling climate change[2]. Sr isotope composition combined with major ion concentration of river water enables us to determine relative contribution of Sr by different minerals found in various rock types and to better understand complex processes of silicate weathering.

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Extensive geochemical and Sr isotopic studies have been carried out on Ganga–Brahmaputra and Indus river systems draining the Himalayas, to understand the chemical weathering and Sr flux to the Bay of Bengal[2–7]. Compared to the Himalayan rivers, fewer studies have been attempted on peninsular rivers[5,8,9]. Except for Krishna and Godavari, all other peninsular rivers are non-perennial and are fed mainly during monsoon rains. During non-monsoon period the flow is lean or non-existent. However, these rivers drain diverse Precambrian terrains and studying the abundance of various ions in them will help better understand weathering of various types of silicate rocks in the catchment area.

During the NE monsoon of 2005, eastward-flowing Kaveri, Palar and Ponnaiyar river basins received much higher rainfall (more than 1200 mm) compared to the previous 50 years. Palar river, which is usually ephemeral (flows only for about 15 days in a year) was flooded during November–December 2005. This has provided a unique opportunity to sample these rivers to study solute and Sr isotopic composition when there was natural flow. Due to the damming of these rivers, there is little natural flow during most part of the year.

Kaveri, Ponnaiyar and Palar river systems drain through Precambrian rocks of the Dharwar craton, which includes Archean granitoid gneisses and intrusives, metavolcanics, meta-sediments, granulites, Cretaceous sedimentary formations and Recent alluvium. Gunnell and Louchet[10] have suggested that the rate of weathering of granulites is lower compared to the Peninsular gneisses, and hence granulites occur as topographic highs. Valdiya[11] concluded that neotectonics was responsible for certain topographic features observed along the west coast and Mysore plateaus. This study aims to estimate relative contribution of different rock types to the solute load of the river water using Sr isotope composition and elemental abundance.

The geology of the river basin

Kaveri, Ponnaiyar and Palar are east-flowing, inter-State rivers in southern India, flowing through the States of

Karnataka, Kerala, Andhra Pradesh and Tamil Nadu. The river Kaveri rises at Talakaveri on the Brahmagiri range in the Western Ghats, Coorg District, Karnataka at an elevation of about 1341 m asl and flows for about 800 km before its outfall into the Bay of Bengal[12], draining an area of 87,900 sq. km. The important tributaries joining the Kaveri are the Harangi, Hemavati, Kabini, Suvarnavathi, Shimsha, Arkavati, Bhavani, Noyil and Amaravati and it starts forming a delta from Tiruchirapalli (Figure 1)[13]. Palar river starts from Talagavara village in Kolar at an elevation of about 900 m and flows for 348 km in Karnataka, Andhra Pradesh and Tamil Nadu, before it meets the Bay of Bengal, south of Kalpakkam, Tamil Nadu. Cheyyar, Poonai and Malatar are the main tributaries of Palar river. Ponnaiyar river rises near Nandi Hills of Kolar, Karnataka and falls into the Bay of Bengal at Cuddalore (Figure 1).

The catchment areas of these rivers are known to be a mosaic of different Precambrian terrains bounded by several N–S and E–W trending major shear zones. These shear zones are supposed to have been reactivated during later periods, resulting in the formation of block mountains, dominantly made up of granulites[11].

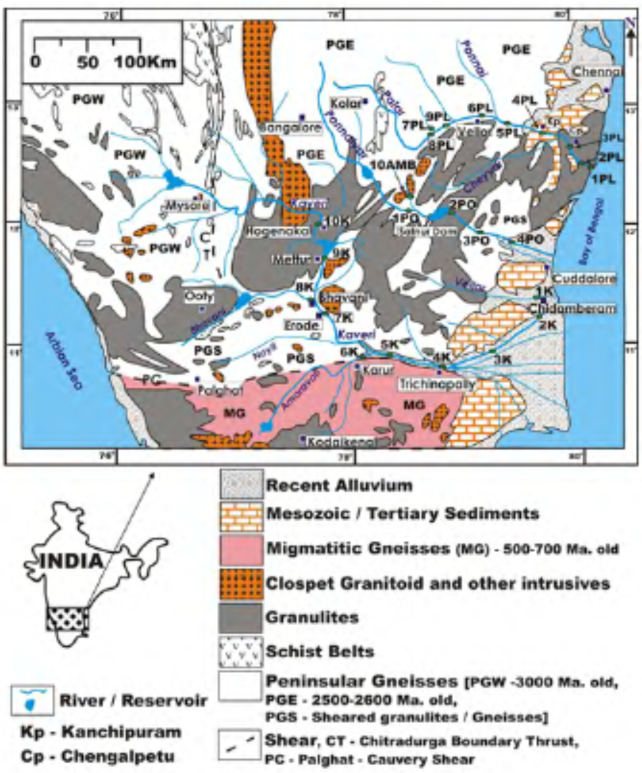

Figure 1. Map showing the geology of drainage basins of Kaveri, Ponnaiyar and Palar rivers (Geological Survey of India[13]), their major tributaries and sample locations numbered along the river course. Upper reaches of Kaveri river drain through the Archean granitoid gneisses of western Dharwar craton and Clospet granite. Middle and lower reaches pass through the granulitic terrain, sheared and migmatitic gneisses and recent alluvium. Both Palar and Ponnaiyar rivers originate from eastern Dharwar craton consisting of Late Archean granitoid gneisses and intrusives. Palar drains mainly through these granitoid gneisses and after Arcot, it enters into the Recent alluvium and Gondwana formations. Cheyyar (tributary of Palar) and lower reaches of Palar drain through the granulites. Ponnaiyar traverses granitic gneisses, granulites and Recent alluvium formation before entering the Bay of Bengal.

The Kaveri drainage system in the upper reaches flows through the Archean granitoid gneisses (amphibolite-facies) and intrusives, Closepet granite, Precambrian granulites (ranging in composition from granite to gabbro) and supracrustal belts. The supracrustal belts belonging to the Sargur group occur in southern Dharwar craton, in which marble bands of a few hundred metres long and few metres wide have been reported. The Dharwar group of supracrustal rocks consists of predominantly theoliitic metavolcanics, felsic volcanics, clastic and chemical sediments. The Bhavani, a major tributary of the Kaveri passes through granulites of the Nilgiri range, which include garnetiferous enderbites and basic granulites (gabbroic-to-anorthositic in composition). Two pyroxene granulites and pyroxinites occur as extended bodies, lenses and pods with increasing abundance towards north in the Nilgiri range[14].

Rocks in the middle reaches of the Kaveri river are predominantly granulitic gneisses, which have been subjected to high grade polyphase deformation and show banded migmatitic structure and fold patterns. They are composed of granulite facies assemblage of plagioclase, quartz, orthopyroxene, garnet and biotite[15]. A minor unit consisting of marbles, calc-silicates, garnet–sillimanite–schists occurs around Madukarai, NNE of Palghat[16]. Dykes and plugs of carbonatites having ~0.036 sq. km aerial extent have been reported from Hogenakal area[17]. Pedogenic calcretes are found in the banks of Amaravati, Noyil and Bhavani tributaries[18]. Cretaceous sediments are exposed north of Tiruchirapalli, where the Kaveri starts forming a delta (Figure 1). These sediments consist of conglomeratic sandstone, fossiliferous limestone and shale. The delta and mouth of the river consist of Recent alluvium deposits.

The Palar and Ponnaiyar originate from the eastern Dharwar craton, and flow through granitoid gneisses (hornblende gneiss, hornblende–biotite gneiss, migmatitic gneiss) and granitoid intrusives and supracrustal rocks of theoliitic and komatiitic affinity in the upper reaches[19]. Granulites are present at the middle reaches of Palar river, after the Arcot river passes through Recent alluvium and lower Gondwana Formation (conglomerate, limestone, sandstone and shale), followed by granulites and coastal alluvium. Palar joins the Bay of Bengal without forming any delta (Figure 1). Ponnaiyar river also passes through Archean rocks of eastern Dharwar craton, granulites and Recent alluvium near the east coast.

Most of the rock types that are subjected to extensive physical and chemical weathering in these drainage basins are Precambrian in age, which may have been uplifted during late Mesozoic period. Gunnell[20] suggested that due to the break-up of Madagascar, the western part of Peninsular India experienced passive margin uplift resulting in the formation of the Sahyadri range (Western Ghats) all along the west coast of Peninsular India. Subsequently high rainfall occurred along the west coast as well as the Sahyadri range with the onset of monsoonal climatic regime[21]. Thus eastward-flowing river systems, including the three rivers being studied, were developed due to the uplift of the Sahyadri range and easterly tilt of Peninsular India[22].

Analytical methods

Water samples were collected from Kaveri, Palar and Ponnaiyar rivers for chemical and Sr isotope analyses in 5 l clean polyethylene bottles from different locations. Electrical conductivity (EC) and pH values were measured immediately after sampling. Water samples were filtered through 0.45 μm Millipore® cellulose nitrate membrane filters of 47 mm diameter, to separate suspended sediments. In the laboratory, HCO_3^-, Cl^-, SO_4^{2-}, PO_4^{3-} and H_4SiO_4 were measured by potentiometric titration method, mercury-II thiocyanite method, turbimetric method, ascorbic acid method and molybdosilicate method[23] respectively, with analytical uncertainties better than 10%. Ca, Mg, Na and K were determined using ICP–AES with a precision better than 5%. Sr and Rb were analysed individually after calibrating ICP–AES using appropriate standards. In ICP–AES, the lower detection limit for Rb, Sr and Ba were 0.015, 0.001 and 0.002 ppm respectively[24], which is higher than the minimum concentration observed in the water samples.

Sr was concentrated from 100 ml aliquots of water by cation-exchange resin chromatography. Pre-concentrated Sr was loaded on purified and degassed Re filaments as $SrNO_3$ sandwiched between Ta activator. Sr isotope ratios were measured using a multi collector Thermal Ionization Mass Spectrometer (TRITON, Thermo-Finnigan). The $^{87}Sr/^{86}Sr$ ratios were corrected for fractionation by normalizing to $^{86}Sr/^{88}Sr$ ratio of 0.1194. Sr isotope analysis of international standard SRM 987 was carried out repeatedly during the course of analysis of river water, which gave a mean value and external precision of 0.710235 ± 7 (n = 10). The river samples were also replicated, the results of which agree within the analytical uncertainties (Table 1). Procedural blank for Sr was 0.7 ng, which is insignificant compared to ≥10 μg of Sr typically analysed.

Results

Major ion chemistry

The results of chemical analysis of Palar, Ponnaiyar and Kaveri water along with pH, EC and Total Suspended Load (TSL) are given in Table 1. Total cation and anions are related by the equation $TZ^+ = 0.9196TZ^- + 0.4466$ ($r^2 = 0.977$), with a correlation coefficient of 0.99 for 24 samples. The ratio of Total Dissolved Solids (TDS)/EC (0.84 for Palar, 0.77 for Ponnaiyar and 0.81 for Kaveri) is within acceptable limits, confirming the reliability of the analytical results.

Spatial variation of pH during the NE monsoon sampling suggests the alkaline nature of water. Palar river is neutral to mildly alkaline (pH 6.95–7.99), Ponnaiyar is mildly alkaline (pH 7.19–7.69) and Kaveri is mildly to moderately alkaline (pH 7.62–8.76). EC varies between 0.17 and 1.1 mS cm^{-1} in the Palar river, 0.43 to 0.66 mS cm^{-1} in Ponnaiyar and 0.31 to 0.59 mS cm^{-1} in Kaveri. Here all the EC values fall between 0.17 and 0.71 mS cm^{-1}, except for one sample (1.1 mS cm^{-1}) which was collected close to the sea at the Palar river mouth. This sample with seawater-like characteristics has not been considered for further discussions.

Bicarbonate is the most dominant ion in all the river samples followed by Ca^{2+}, Na^+, Cl^-, Mg^{2+}, SO_4^{2-} and K^+ in Palar and Ponnaiyar rivers, whereas in the Kaveri the sequence is $Ca^{2+} > Mg^{2+} > Na^+ > Cl^- > SO_4^{2-} > K^+$ (ions in meq/l unit). Ca constitutes 40–45% of cations; Mg and Na constitute 20–28 and 25–35% respectively, of the total cations (in meq/l unit) in all the three river waters. Other cations such as K, Sr, Rb and Ba have minor contribution to the total cations. Dissolved silica in river water comes entirely from weathering of silicate rocks, which varies between 511 and 973 μmol/l (8–13% of total ions in μmol/l) in all the river waters studied. It is relatively higher than the global average value of 427 μmol/l. Among these three rivers, concentration of dissolved silica is higher in the Palar river water than in Kaveri and Ponnaiyar.

Major ion compositions of river water have been corrected for atmospheric input based on the available regional rainwater data, following the method outlined by Das *et al.*[9]. Rainwater data from Tirupati[25] and Bangalore[26] were used to correct the atmospheric contribution in all the three river water samples, except for Bhavani and Amaravati, tributaries of the Kaveri, for which Nilgiri[27] rainwater data have been used (Table 2). The dissolved Na was corrected for contributions from sources other than chemical weathering, by subtracting an amount equal to dissolved Cl^- of the river water ($Na^* = Na_{riv} - Cl_{riv}$). Other cations such as Ca, Mg and K were corrected using the equation of Das *et al.*[9]: $[X^* = X_{riv} - \{(X/Cl_{rain}) \times (Cl_{rain}/f_{evp\text{-}trans})\}]$. Due to scarcity of run-off data in the drainage basin, the actual factor for evapo-transpiration loss could not be reliably estimated. However, samples were collected during heavy rainfall season having high run-off, and therefore the evapo-transpiration factor ($f_{evp\text{-}trans}$) could be close to unity. Further as elemental ratios instead of their abundance were used for data interpretations, slight deviation in this factor, if any, would not change the inferences drawn.

Water samples were collected during the northeast monsoon of 2005, when these rivers were flowing bank to

Table 1. Major ion abundance and $^{87}Sr/^{86}Sr$ ratios determined on water samples of Kaveri, Palar and Ponnaiyar rivers. The major ions determined corrected for atmospheric input (M*) are also given

Sample ID	pH	EC	TSL	Ca	Ca*	Mg	Mg*	Na	Na*	K	K*	Sr	Rb	Ba	H_4SiO_4	HCO_3	Cl	SO_4	PO_4	TDS	$^{87}Sr/^{86}Sr$
Palar																					
1PL	7.2	1.11	93.4	632		1297		11351		493		3.67	0.55	0.42	576	1363	13885	883	0.77	30485	0.710151 ± 5
2PL	7.0	0.18	103.2	369	323	204	187	548	202	47	29	1.71	0.12	0.25	661	1243	345	110	1.49	4071	0.711634 ± 3
																					0.711637 ± 5^r
3PL	7.0	0.17	45.0	361	315	180	164	490	112	28	10	1.36	0.27	0.20	868	1258	379	209	0.22	3552	0.712927 ± 7
4PL	7.5	0.52	15.1	1019	974	433	416	2515	823	103	85	5.15	0.38	0.81	672	3314	1693	314	1.21	11998	0.713096 ± 4
																					0.713086 ± 3^r
5PL	7.6	0.33	429.4	806	761	326	310	1013	371	61	44	2.86	0.21	0.44	655	2263	642	322	2.00	6901	0.716779 ± 5
																					0.716788 ± 5^r
6PL	7.5	0.31	320.9	771	726	318	301	916	380	48	30	2.70	0.18	0.31	617	2203	535	261	3.31	6692	0.717611 ± 3
7PL	8.0	0.40	79.7	1095	1050	552	536	1152	679	38	21	3.97	0.22	0.35	883	3224	473	361	1.49	9210	0.718850 ± 3
8PL	7.5	0.33	268.6	764	718	317	300	1136	375	51	33	2.45	0.34	0.27	676	2083	761	289	2.56	7100	0.718754 ± 7
9PL	7.6	0.35	302.4	801	755	344	327	1191	421	53	35	2.66	0.19	0.33	663	2323	770	348	2.51	7625	0.718226 ± 7
Ponnaiyar																					
10AMB	7.7	0.66	29.7	1244	1199	830	814	2861	859	119	101	6.84	0.20	0.71	973	4545	2002	398	3.05	15664	0.715666 ± 9
1PO	7.3	0.44	63.6	1074	1029	453	437	1446	409	105	87	3.66	0.37	0.63	686	2894	1037	186	6.34	9648	0.718446 ± 4
2PO	7.2	0.44	52.8	903	857	498	482	1588	410	100	82	3.61	0.09	0.63	625	2834	1178	284	5.56	9583	0.716793 ± 5
3PO	7.7	0.46	54.6	956	910	529	513	1608	323	101	83	3.64	0.29	0.60	651	1933	1285	264	2.91	9013	0.716659 ± 6
4PO	7.6	0.47	85.0	986	940	562	545	1624	291	101	83	3.83	0.23	0.71	697	3059	1333	283	4.84	10435	0.716045 ± 5
Vellar																					
1K	7.9	0.33	41.1	740	695	423	406	996	208	41	23	2.90	0.48	0.47	778	2984	789	200	1.43	7930	0.711703 ± 5
Kaveri																					
2K	7.6	0.32	194.4	810	765	468	451	828	268	45	27	2.69	0.30	0.65	597	2414	560	193	0.52	6990	0.714978 ± 9
3K	7.6	0.38	74.0	882	837	534	517	1057	150	55	37	2.94	0.02	0.71	588	2594	908	270	1.10	8126	0.715520 ± 5
																					0.715518 ± 4^r
4K	7.8	0.45	41.9	1004	959	635	618	1471	78	69	51	3.69	0.09	0.80	553	2954	1393	344	1.10	10135	0.714967 ± 6
5K	7.8	0.36	47.6	881	836	532	515	1009	248	51	33	2.97	0.37	0.62	731	2624	761	238	0.88	8466	0.715763 ± 8
																					0.715747 ± 5^r
6K	8.5	0.42	34.0	956	934	639	632	1292	358	51	47	5.14	0.02	1.06	574	2323	934	276	0.44	9023	0.712770 ± 7
7K	7.9	0.29	18.4	756	711	460	443	681	295	34	16	2.43	0.26	0.55	563	1573	387	186	0.27	6109	0.716171 ± 6
8K	8.1	0.60	22.2	1554	1533	1002	995	1604	438	119	115	5.79	0.37	1.16	965	4154	1166	682	2.91	14339	0.710002 ± 9
9K	8.8	0.26	17.1	722	677	430	413	636	308	30	12	2.11	0.08	0.42	511	2293	328	174	0.16	6538	0.717165 ± 7
																					0.717176 ± 5^r
10K	8.0	0.31	51.0	798	753	502	485	759	393	30	12	2.34	0.11	0.34	643	1918	366	177	0.27	6841	0.717931 ± 4

EC in mS cm^{-1}; TSL in mg/l; Major ions and TDS in µmol/l; *Corrected for atmospheric input; *r*, Replicates. Errors given for $^{87}Sr/^{86}Sr$ ratio are 1σ.

Table 2. Abundance of major ions in rainwater (μmol/l) from three different locations of southern India

Rainwater	Ca	Mg	Na	K	SO_4	Cl	Reference
Tirupati	67.45	25.31	32.38	32.72	62.02	32.80	25
Bangalore	23.45	8.23	17.83	3.07	16.24	20.59	26
Nilgiri	21.46	7.03	46.00	4.00	12.00	43.00	27

bank due to unusually heavy rainfall. Anthropogenic contribution to major ion abundance and Sr isotope composition was considered negligible.

Strontium isotope study

In the river Kaveri Sr concentration varied between 2.1 and 3.7 μmol/l in the main course and the tributaries had higher concentration (Bhavani – 5.8 μmol/l and Amaravati – 5.1 μmol/l). In the case of Ponnaiyar river, Sr concentration was almost uniform (3.6–3.8 μmol/l) and its tributary showed higher concentration of Sr (6.8 μmol/l). Lowest concentration of Sr was measured in the Palar river at Chengalpettu (1.3 μmol/l) and highest from Kanchipuram (5.14 μmol/l).

$^{87}Sr/^{86}Sr$ ratios in Kaveri water range from 0.714967 to 0.717931 in the main course, whereas the tributaries Bhavani and Amaravati had lower $^{87}Sr/^{86}Sr$ ratios of 0.710002 and 0.712770 respectively. In the Palar river, $^{87}Sr/^{86}Sr$ ratio varied from 0.710151 to 0.718754 in the main course, with the lowest ratio measured for the sample collected close to the Bay of Bengal. Sample 7PL collected from the Malatar river, a tributary of Palar, showed the highest $^{87}Sr/^{86}Sr$ ratio of 0.718850. In the Ponnaiyar river, $^{87}Sr/^{86}Sr$ ratio ranged narrowly from 0.716045 to 0.718446 in the main stream and its tributary showed a lower ratio of 0.715666. $^{87}Sr/^{86}Sr$ ratio gradually decreases towards the mouth in the main course of the Kaveri (Figure 2 *a*). In the case of Palar and Ponnaiyar, there is a sudden drop in the $^{87}Sr/^{86}Sr$ ratio between Arcot (5PL) and Kanchipuram (4PL), and Hanumantirtham (1PO) and Satnur dam (2PO) respectively (Figure 2 *b* and *c*).

Discussion

After correcting for atmospheric contribution, the river water samples were plotted in Ca, Mg and (Na + K) ternary diagram (Figure 3). The Kaveri samples had higher Ca and Mg abundances than the Palar samples. Dominance of Ca and Mg ions in the river sample could be due to weathering of dolomite and/or silicate minerals like clino-pyroxene, amphibole and plagioclase. Na and K ions were contributed mainly by weathering of alkali feldspar and feldspathoid.

The correlations observed between $^{87}Sr/^{86}Sr$ and 1/Sr of river water samples could be as a result of mixing between two end-members (Figure 4 *a* and *b*). In the case of Kaveri, the highest $^{87}Sr/^{86}Sr$ ratio (0.717931) was measured for the sample 10 K from the Hogenakal (Figure 1). This sample represents water-draining granitoid intrusives and gneisses, mafic rocks and minor carbonates exposed in the southwestern part of the Dharwar craton. Lowest $^{87}Sr/^{86}Sr$ ratio (0.710002) was measured on Bhavani, a major tributary of the Kaveri, draining mainly granulitic terrain, which had felsic and mafic granulites, calc-gneisses and minor amount of marble. Amaravati, another tributary of the Kaveri, also drains a terrain consisting of granulites, migmatitic gneisses and granites of Pan African (500 Ma) age having a low $^{87}Sr/^{86}Sr$ ratio (0.712770), but slightly higher than Bhavani (Figure 4 *a*). The $^{87}Sr/^{86}Sr$ ratios having intermediate values observed for the main course of the Kaveri could be explained by mixing involving two end-members, one having low $^{87}Sr/^{86}Sr$ ratio with higher Sr abundance and the other having high $^{87}Sr/^{86}Sr$ ratio with low Sr abundance.

In the case of Palar and Ponnaiyar rivers, the highest $^{87}Sr/^{86}Sr$ ratios were measured from Ambur (8PL) and Hanumantirtham (1PO) respectively (Figure 1), which represent water-draining granitoid gneisses and metavolcanics of the eastern Dharwar craton in the upper reaches. After Arcot (5PL) (Figure 1), the Palar enters into the Recent alluvium and Gondwana formations and $^{87}Sr/^{86}Sr$ ratio reduces from 0.716779 (5PL) to 0.713096 (4PL) (Figure 4 *b*) along with increasing Sr abundance. This could be due to contribution of Sr with low $^{87}Sr/^{86}Sr$ ratios from carbonates (limestones) associated with the Gondwana Formation and Recent alluvium exposed around these two locations (Figure 1). The $^{87}Sr/^{86}Sr$ and 1/Sr plot for Palar (Figure 4 *b*) shows that there is abrupt decrease in Sr concentration between Kanchipuram (4PL) and Chengalpettu (3PL), probably because of heavy contribution of floodwater from the Cheyyar that meets Palar between these two locations.

The $^{87}Sr/^{86}Sr$ ratio at Hanumantirtham (1PO) was 0.718446 and after Satnur dam (2PO) it was 0.716793. This reduction may be due to input from three tributaries, which meet the Ponnaiyar river between these two locations. Among the three tributaries, Pamber flowing from the north has low $^{87}Sr/^{86}Sr$ ratio of 0.715666 and high Sr concentration as it passes through syenite, carbonatite and ultramafic complexes occurring within the epidote–hornblende gneiss. Two other tributaries from the south also drain the granulites, thus lowering the $^{87}Sr/^{86}Sr$ ratio of the Ponnaiyar river. After Satnur dam (Figure 1), Sr isotope ratio decreases slowly towards the river mouth.

Major and minor cations are released to the river water in different proportions than found in the parent rock, because of differences in the mobility of elements and the nature of weathering. However, cations like Ca, Sr and Mg are not significantly fractionated with respect to each other during weathering and hence their ratios in the rocks and water are expected to be similar[28,29]. Hence

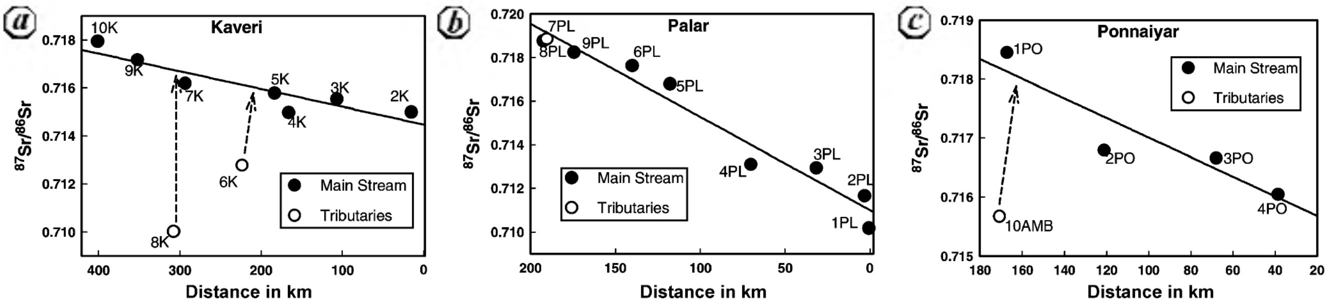

Figure 2. $^{87}Sr/^{86}Sr$ ratio vs distance from the upper reaches to the river mouth. ***a***, Kaveri, ***b***, Palar and ***c***, Ponnaiyar rivers. Note that the $^{87}Sr/^{86}Sr$ ratio for all the three rivers decreases towards downstream. Arrows indicate confluence points of the tributaries with the main stream.

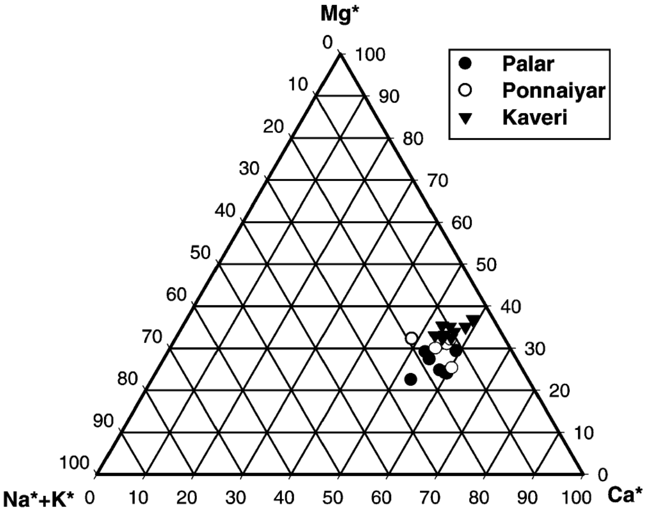

Figure 3. Major ion data for water samples from Palar, Ponnaiyar and Kaveri rivers plotted in ternary diagrams of Ca*, Mg* and (Na* + K*). Kaveri samples plot close to Ca*–Mg* line, and Palar samples had distinctly higher Na* + K* value than the Kaveri samples.

Ca/Sr and Mg/Sr along with $^{87}Sr/^{86}Sr$ ratios of the water samples can be used to understand the relative contribution of the major ions from different rock types. The Ca/Sr vs $^{87}Sr/^{86}Sr$, and Mg/Sr vs $^{87}Sr/^{86}Sr$ plots (Figures 5 and 6) of the river water samples also show a linear trend that could be considered as due to mixing between two end-members.

Based on the geological map of the Kaveri, Palar and Ponnaiyar drainage basins (Figure 1), the rocks exposed have been identified and grouped into four categories: (a) granitoid gneisses, (b) felsic granulites, (c) mafic volcanics and granulites, and (d) carbonates, including limestone, dolomites, marbles and carbonatites. The carbonates are exposed relatively to a much lower extent in the upper and middle reaches and hence were not marked as separate units in Figure 1.

The $^{87}Sr/^{86}Sr$, Ca/Sr and Mg/Sr ratios varied widely among the silicate rocks exposed in the drainage basin. The range of values for $^{87}Sr/^{86}Sr$, Ca/Sr and Mg/Sr ratios in the granitoid gneisses[30,31] were 0.71929–1.05281, 15–151 and 1–31 respectively. In felsic granulites[32] these ratios varied from 0.70366 to 0.70534, 37 to 108, and 1.3 to 31 respectively. Mafic granulites have similar composition as mafic volcanics[29], where the above ratios vary from 0.70766 to 0.71189, 170 to 559 and 67 to 373 respectively. There are no data available on $^{87}Sr/^{86}Sr$ ratios of carbonates present in the upper and middle reaches of the drainage basin, except for pedogenic calcretes[17] found around Coimbatore, where it varied between 0.709218 and 0.710493. In general, the carbonates are expected to have high Ca/Sr and Mg/Sr ratios and low $^{87}Sr/^{86}Sr$ ratios. Thus these four major rock types can be grouped into three end-members with distinct Ca/Sr, Mg/Sr and $^{87}Sr/^{86}Sr$ ratios, to evaluate their relative contribution to the river water. These three end-members are: (i) Granitoid gneisses (GG) having high $^{87}Sr/^{86}Sr$ ratio but low Ca/Sr and Mg/Sr ratios; (ii) Felsic granulites (FG) with low Ca/Sr, Mg/Sr and $^{87}Sr/^{86}Sr$ ratios, and (iii) Mafic volcanics/granulites and carbonates (MVG) which have high Ca/Sr and Mg/Sr ratios, but low $^{87}Sr/^{86}Sr$ ratio.

The range and mean values of $^{87}Sr/^{86}Sr$, Ca/Sr and Mg/Sr ratios for the above three end-members are given in Table 3. The equations used to calculate the $^{87}Sr/^{86}Sr$ ratio in the water formed by mixing different proportions of two end-members[33] are given below:

$$R_{\text{mix}} = [\{(f \times {}^{87}\text{Sr}_{\text{ab}}A \times \text{Sr}_{\text{conc.}}A)/\text{Sr}_{\text{at.wt.}}A\} + \{((1-f) \times {}^{87}\text{Sr}_{\text{ab}}B \times \text{Sr}_{\text{conc.}}B)/\text{Sr}_{\text{at.wt.}}B\}] / [\{(f \times {}^{86}\text{Sr}_{\text{ab}}A \times \text{Sr}_{\text{conc.}}A)/\text{Sr}_{\text{at.wt.}}A\} + \{((1-f) \times {}^{86}\text{Sr}_{\text{ab}}B \times \text{Sr}_{\text{conc.}}B)/\text{Sr}_{\text{at.wt.}}B\}],$$

$$\text{Sr}_{\text{at.wt.}}X = ({}^{87}\text{Sr}_{\text{ab}}X \times 87) + ({}^{86}\text{Sr}_{\text{ab}}X \times 86) + [({}^{88}\text{Sr}_{\text{ab}}/{}^{86}\text{Sr}_{\text{ab}})/\{({}^{84}\text{Sr}_{\text{ab}}/{}^{86}\text{Sr}_{\text{ab}}) + 1 + ({}^{88}\text{Sr}_{\text{ab}}/{}^{86}\text{Sr}_{\text{ab}}) + ({}^{87}\text{Sr}/{}^{86}\text{Sr in }X)\} \times 88] + [({}^{84}\text{Sr}_{\text{ab}}/{}^{86}\text{Sr}_{\text{ab}})/\{({}^{84}\text{Sr}_{\text{ab}}/{}^{86}\text{Sr}_{\text{ab}}) + 1 + ({}^{88}\text{Sr}_{\text{ab}}/{}^{86}\text{Sr}_{\text{ab}}) + ({}^{87}\text{Sr}/{}^{86}\text{Sr in }X)\} \times 84],$$

$${}^{87}\text{Sr}_{\text{ab}}X = [({}^{87}\text{Sr}/{}^{86}\text{Sr in }X)/\{({}^{84}\text{Sr}_{\text{ab}}/{}^{86}\text{Sr}_{\text{ab}}) + 1 + ({}^{88}\text{Sr}_{\text{ab}}/{}^{86}\text{Sr}_{\text{ab}}) + ({}^{87}\text{Sr}/{}^{86}\text{Sr in }X)\}],$$

$${}^{86}\text{Sr}_{\text{ab}}X = [1/\{({}^{84}\text{Sr}_{\text{ab}}/{}^{86}\text{Sr}_{\text{ab}}) + 1 + ({}^{88}\text{Sr}_{\text{ab}}/{}^{86}\text{Sr}_{\text{ab}}) + ({}^{87}\text{Sr}/{}^{86}\text{Sr in }X)\}],$$

$$Z/\text{Sr} = [\{(f \times Z_{\text{conc.}}A) + \{(1-f) \times Z_{\text{conc.}}B\}\}/\{(f \times \text{Sr}_{\text{conc.}}A) + \{(1-f) \times \text{Sr}_{\text{conc.}}B\}\}].$$

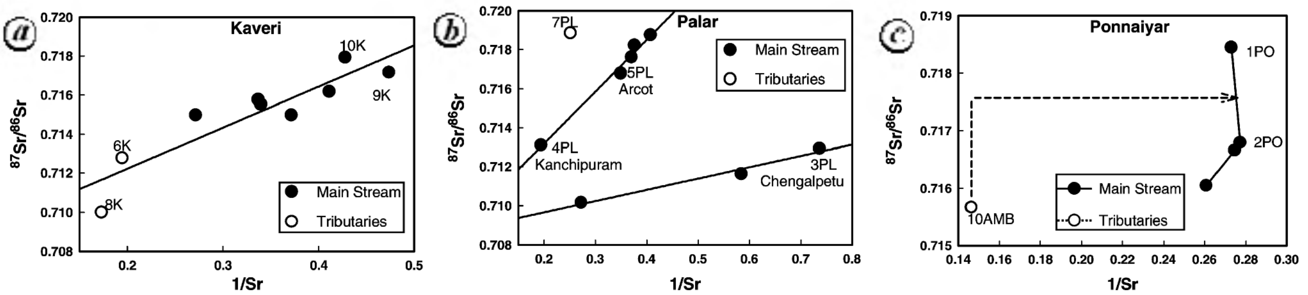

Figure 4. $^{87}Sr/^{86}Sr$ ratio plotted against 1/Sr (Sr in units of µmol/l) for (*a*) Kaveri, (*b*) Palar and (*c*) Ponnaiyar rivers. Arrow indicates confluence of tributary with the main stream. In case of Palar, there is an abrupt decrease in Sr concentration between Kanchipuram and Chengalpettu, where the Cheyyar joins the main stream.

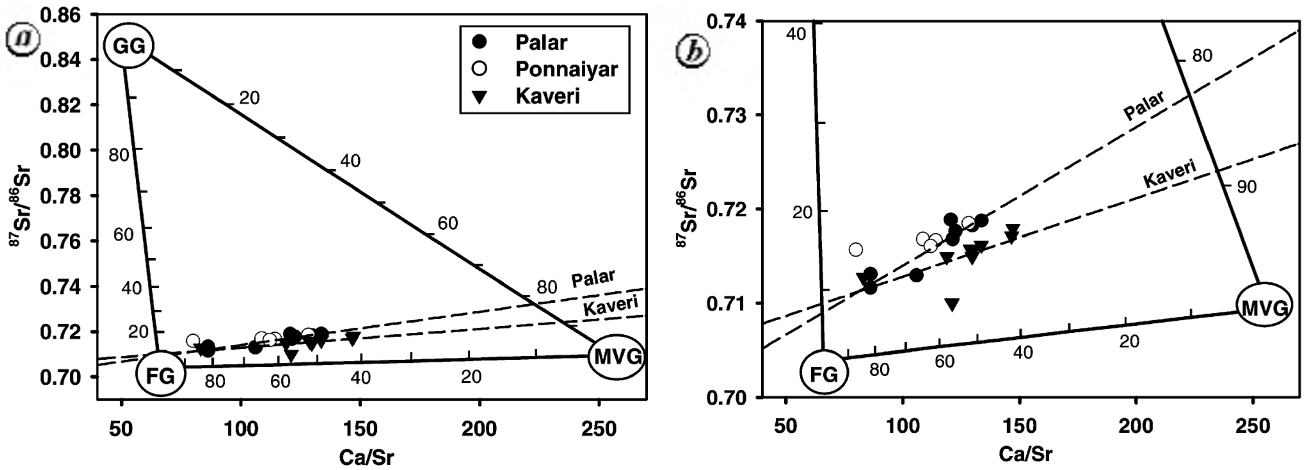

Figure 5. *a*, Ca/Sr vs $^{87}Sr/^{86}Sr$ ratio plotted for the three end-members, granitoid gneisses of Dharwar craton (GG), mafic volcanics/granulites with carbonates (MVG) and felsic granulites of Southern Granulitic Terrain (FG). Mixing between any two of these end-members has been calculated and plotted as a thick line with different proportions of mixing indicated. The Kaveri, Palar and Ponnaiyar river samples define two distinct collinear arrays. *b*, Expanded version of (*a*) showing distinction between trends defined by samples of Kaveri, Palar and Ponnaiyar rivers. Note that the regression lines for Palar and Ponnaiyar, and Kaveri intersect the mixing line between GG and MVG at about 80% and 90% respectively, of the contribution from MVG.

Here A and B are two end-members, f the factor for mixing, R_{mix} the $^{87}Sr/^{86}Sr$ ratio of the mixture, X any one end-member, subscript ab is abundance, conc. is concentration and at. wt. is atomic weight, and Z is Ca or Mg.

The $^{87}Sr/^{86}Sr$, Ca/Sr and Mg/Sr ratios in the river formed by mixing of water derived for GG and FG, FG and MVG, MVG and GG have been modelled. The results are shown in Figures 5 and 6 along with data for Kaveri, Palar and Ponnaiyar rivers. Simple two-component mixing between either felsic granulites–granitoid gneisses or felsic granulites–mafic volcanics (including mafic granulites and carbonates) does not explain the trend defined by the river water samples. The regression line for the Kaveri river samples passes close to the felsic granulites end-member on the lower side and intersects the mixing line between granitoid gneisses–mafic volcanics (including mafic granulites and carbonates) on the upper side (Figures 5 and 6). Based on this it could be inferred that major ion contribution to one of the end-members, possibly represented by water of the upper reaches of the Kaveri river was ~85% from metavolcanics and minor carbonates occurring in various schist belts and ~15% from granitoid gneisses (Figures 5 and 6). Preferential weathering of mafic minerals, such as calcic amphibole and plagioclase feldspar present in tonalite and granodiorite gneisses will also result in water having low $^{87}Sr/^{86}Sr$ and high Ca/Sr and Mg/Sr ratios, as observed for the MVG end-member.

The Kaveri river was sampled from the lower and middle reaches where it drains mainly felsic granulites and gneisses of the Southern Granulitic Terrain. Kaveri water samples also plot close to the felsic granulites end-member and contribution from this rock type is considerably higher (50–80%) compared to other end-members. The sample from Hogenakal (10 K) showed high Ca/Sr, Mg/Sr and $^{87}Sr/^{86}Sr$ ratios, due to higher contribution from weathering of granitoid gneisses and schists of western Dharwar craton found in the upper reaches. Samples from Bhavani and Amaravati (tributaries of the Kaveri) had lower $^{87}Sr/^{86}Sr$ ratio as well as Ca/Sr and

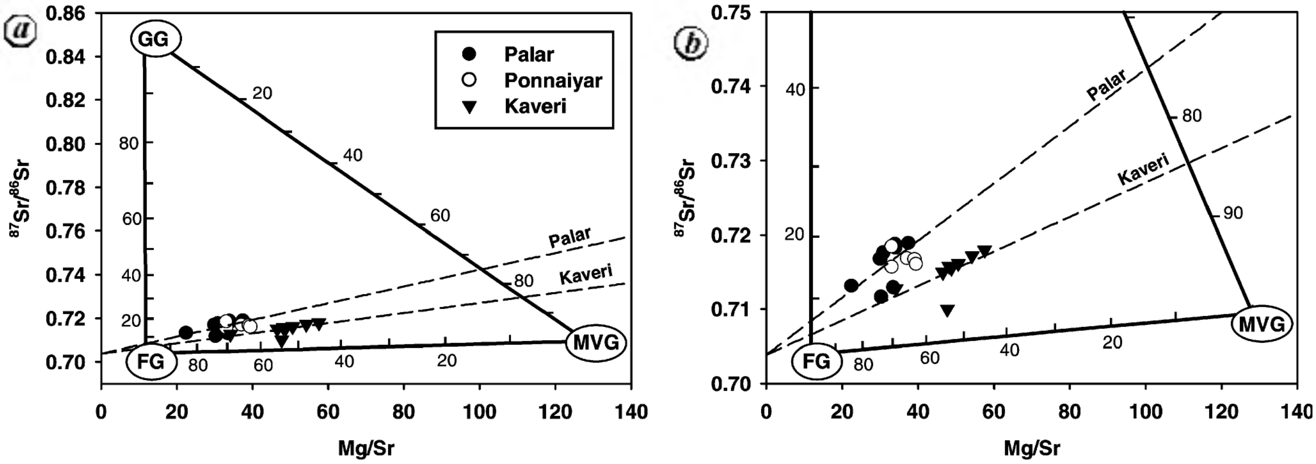

Figure 6. *a*, Mg/Sr vs $^{87}Sr/^{86}Sr$ ratio plotted for the three end-members, GG, MVG and FG. Mixing between any two of these end-members has been calculated and plotted as a thick line with different proportions of mixing indicated. The Kaveri, Palar and Ponnaiyar river samples define two distinct collinear arrays. *b*, Expanded version of (*a*) showing distinction between trends defined by samples of Kaveri, Palar and Ponnaiyar rivers. Note that the regression lines for Palar and Ponnaiyar, and Kaveri intersect the mixing line between GG and MVG at about 75% and 85% respectively, of the contribution from MVG.

Table 3. Range and average Ca/Sr, Mg/Sr and $^{87}Sr/^{86}Sr$ ratios reported for major rock types from the drainage basin of Kaveri, Palar and Ponnaiyar rivers

Rock types (*n*)	Ca/Sr average (range)	Mg/Sr average (range)	$^{87}Sr/^{86}Sr$ average (range)	Reference
Granitoid gneisses (10)	49.7 (15–151)	11.39 (1–31)	0.850425 (0.71929–1.05281)	30, 31
Felsic granulites (4)	66.08 (37–108)	11.73 (1.3–31)	0.70392 (0.70366–0.70534)	32
Mafic volcanics and granulites (3) and carbonates (3)	256.8 (170–559)	128.2 (67–373)	0.709423 (0.70766–0.71189)	30, 18

Mg/Sr ratios and could represent contribution predominantly from sheared enderbites and calc-gneisses of the Southern Granulitic Terrain.

Palar and Ponnaiyar river samples define a collinear array in Ca/Sr vs $^{87}Sr/^{86}Sr$ and Mg/Sr vs $^{87}Sr/^{86}Sr$ diagrams (Figures 5 and 6). These river samples also plot close to the felsic granulites end-member and their regression line intersects the mixing line between granitoid gneisses–mafic volcanics (including mafic granulites and carbonates; Figures 5 and 6). It is inferred that in the upper reaches of the Palar and Ponnaiyar rivers weathering of granitoid gneisses contributes to a higher extent (20–25%) than in the upper reaches of the Kaveri (Figures 5 and 6). Palar samples 3PL and 2PL plot below the regression line because $^{87}Sr/^{86}Sr$ values at these locations were considerably lowered by input from the Cheyyar (drains felsic granulites), and sediments of the Gondwana Formation (Figure 1).

All the three river samples collected in the lower reaches fall close to the felsic granulites end-member in the Ca/Sr vs $^{87}Sr/^{86}Sr$ and Mg/Sr vs $^{87}Sr/^{86}Sr$ diagrams (Figures 5 and 6), because they drain essentially felsic granulitic terrain. Mixing with water derived from the upper reaches resulted in higher $^{87}Sr/^{86}Sr$, Ca/Sr and Mg/Sr ratios in water sampled along the middle reaches of these rivers.

Conclusion

The lower and middle reaches of the Kaveri, Palar and Ponnaiyar rivers have low $^{87}Sr/^{86}Sr$ (0.710002–0.71885), Ca/Sr (80.2–147.2) and Mg/Sr (22.4–57.5) ratios. These river samples show two distinct collinear arrays when the $^{87}Sr/^{86}Sr$ ratio was plotted against the Ca/Sr and Mg/Sr ratios, which could be the result of two-component mixing. Comparing these ratios with those reported on various rocks exposed in these river basins, suggested that the felsic granulites predominantly contribute to the solute load. Weathering of granitoid gneisses and mafic volcanics (including carbonates present in the Archean schist belts) has possibly contributed to the solute load of the upper reaches of these rivers. Mixing between water from the upper and middle reaches has contributed to variations observed in the elemental and isotopic compositions of these rivers.

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