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The Strontium Geochemistry of Some Precambrian Carbonate rocks of Sri Lanka

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Abstract : The Highland Group of Sri Lanka is a narrow belt of granulite grade Precambrian rocks composed of metasediments and associated charnockites. Crystalline limestones intimately associated with quartzites are found predominantly in the north eastern part of the Highland Group with some bands extending for nearly 100km along strike.

The average Sr content of the Precambrian carbonates is 57 ppm whereas that of the Miocene sedimentary carbonates is 675 ppm. Some high calcite bearing samples from the carbonate sequence of the Highland Group contain Sr of about 400 ppm and these are presumed to be of primary origin as opposed to those formed by dedolomitization, and possibly reflect the Sr contents of the original environment of deposition. A comparison of the Precambrian marbles with limestones of Miocene age is made on the alkali-Sr variations.

1. Introduction

Sri Lanka is underlain in 9/10 ths of its area by metamorphic rocks of Precambrian age. These are broadly divided into 3 major groups termed the Highland Group, Vijayan Complex and the Southwestern Group (Fig. 1). In the northwest of Sri Lanka an extensive sedimentary formation of limestones of Miocene age is present. Both the Highland and Southwestern Groups together form a central belt of granulite-grade rocks. These are mainly metasediments originally laid down as clastic and chemical sediments. Associated intimately with these metasediments are charnockites[12,14] now considered to be metamorphosed volcanic rocks of basaltic origin.[25] Even though the tectonic history and the geologic evolution of Sri Lanka has recently been the subject of much debate[6,14,20,24] very little emphasis had been laid on the study of the carbonate rocks which form an integral part of the Highland Group.

Carbonate rocks are known in some of the oldest sedimentary sequences in the world as in the ~ 3760 Ma old sedimentary rocks of Isua, S. W. Greenland[1] and in the Archean schist belts of Rhodesia. Large and extensive carbonate rock sequences however first occur in the Precambrian stratigraphic record around 2000 Ma ago.[9,27,28] According to Garde,[18] it was current belief some years ago that calcium carbonate was virtually absent in the Archean and Lower Proterozoic carbonate rocks.[11] As such the Mg and Ca contents of the Precambrian seas as compared to modern oceans were thought to be very different. The existence of pure limestones in sedimentary sequences dating back to the Archean has now been proved as evidenced by the work of Bond *et al*[8] on the 2700 Ma old Bulawayan Huntsman limestone and Toens[31] on the 2100 Ma old Dolimite Series of Northern Cape Province.

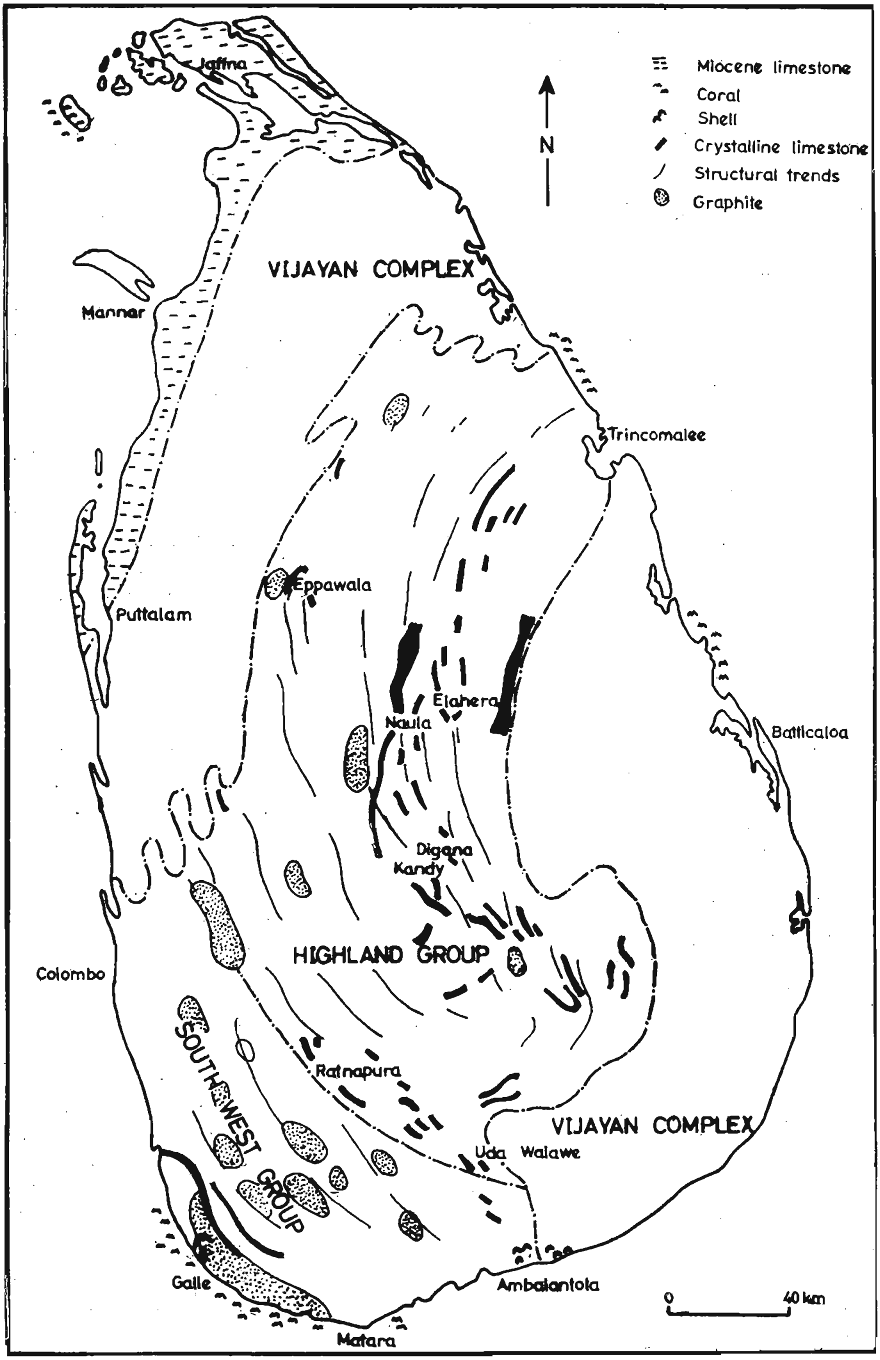

Figure 1. Map showing the main geological division of Sri Lanka and the occurrence of the carbonate rocks.

It is the aim of this paper to study the carbonates in the Precambrian metasedimentary sequence in the Highland Group of Sri Lanka in comparison to the sedimentary Miocene limestones in the northwest of Sri Lanka. The distribution of Sr in the sedimentary carbonates and the metamorphosed limestones is studied from the point of view of the geochemical status of Sr during the early recrystallization of the carbonates on Sri Lanka.

2. The Carbonate rocks of Sri Lanka

Figure 1 shows the distribution of the carbonate rocks of Sri Lanka which can be classified into 4 main types.

1. Limestones of Miocene age
2. Crystalline limestones (marbles) of Precambrian age.
3. Coral and Shell deposits

Whereas the limestones of Miocene age are well developed only in the NW sector of the island, the crystalline limestones (marbles) of Precambrian age are found in the central region of the island closely associated with quartzites and charnockites in well - defined bands extending for many kms (in some cases as much as 100 km) along strike. In chemical composition the marbles vary from pure $CaCO_3$, through magnesium limestone to dolomite.

3. Materials and Methods

The carbonate samples were collected from each location marked in Fig. 1. In the case of sedimentary limestones from the Miocene terrain, the samples were obtained from different strata.

In order to estimate the calcite and dolomite percentages, polished sections of the carbonate samples were washed and allowed to soak in 1 % W/V $FeCl_3$ solution and washed. These were then soaked in 1 % W/V $(NH_4)_2$ SO_4 solution and again washed. The calcite grains appear black at first due to FeS and later brown due to $FeSO_4$. The dolomite remains unstained.

In order to determine the insoluble residue, the samples were crushed to pass through a 250 mesh sieve. 2.5 g of the powder were treated with 25 ml of 25 % V/V acetic acid at room temperature for 12 hours. Under these conditions the acid rapidly reacts with calcite but gives only a faint reaction with dolomite.[4] In order to ensure the removal of dolomite from the residue the dolomitized samples were treated with acid at 60°C for the same period. The soluble and insoluble fractions were separated by filtration and washing with 5 % V/V acetic acid. Analyses for Na, K and Sr were carried out by atomic absorption spectrophotometry.

4. The Geochemistry of Strontium in Carbonate Rocks

The strontium geochemistry of carbonates has been the subject of extensive research particularly from the point of view of the history of sedimentation, diagenesis, dolomitization and dedolomitization.[2,7,10,18,29] Sr is a main trace element in limestones and dolomites and hence is presumed to be located in the lattices of carbonate minerals. It is known that the Sr content decreases with diagenetic evolution and its geochemical path during dolomitization and dedolomitization is one of further decreasing Sr content.[5,15,21,29] The Sr content of limestones depend on many factors such as age, salinity, clay mineral content and the depositional environment.[3] The Sr content of recent carbonates is known to range from 100 - 200 ppm whereas in the dolomites it varies from 30-200 ppm.[29]

Sr^{2+} with an ionic radius of 1.12°A is expected to be associated with Ca^{2+} (1.08°A). The enrichment of Sr in limestones is explained by supposing that Sr^{2+} substitutes for Ca^{2+} as against Mg^{2+} which is a major component in dolomites and which has a much smaller ionic radius of 0.66°A. The uptake of Sr by various minerals have been studied by Kinsman[21] and Jacobsen and Usdowski.[19] Among their conclusions are :

(*a*) The value of the distribution coefficient K_{Sr} calcite for inorganically precipitated calcite (defined as m Sr^{2+} /m Ca^{2+} in calcite to m Sr^{2+} /m Ca^{2+} in solution) varied between 0.14 at 25°C to 0.08 at 100°C.

(*b*) K_{Sr} calcite remains almost constant at least upto 350°C and is essentially independent of pressure. The value of the Sr - Ca distribution coefficient for K_{Sr} dolomite is about half that for calcite.

Consistent with these experimental results is the observation of Shearman and Shirmohammadi[29] that decreasing Sr content is a function of the number of diagenetic recrystallizations.

5. Results and discussion

Table 1 shows the analytical data for the carbonate samples. It is seen that the Sr contents of the sedimentary carbonates of Miocene age are much higher than those of the marbles of Precambrian age. The average Sr content of the sedimentary limestones is 675 ppm whereas that of the marbles is 57 ppm — a decrease by a factor of nearly 12. Figure 2 illustrates the Sr contents of the samples plotted against the calcite-dolomite proportions, and Figure 3 shows the variation of the Sr contents with the insoluble residues of the samples. The preferential substitution of Sr^{2+} for Ca^{2+} in calcite as against Mg^{2+} is clearly seen in Figure 2 where the sedimentary limestones with a higher calcite content show a higher Sr concentration. The lower Sr concentrations of the metamorphosed carbonates of Precambrian age are worthy of special note. It is known that the increasing number of diagenetic recrystallizations the Sr content decreases. The number of sites of Ca^{2+} in dolomite is less than in calcite and due to the difficulty of Sr^{2+} to proxy for the much smaller Mg^{2+} a lower abundance of Sr^{2+} in dolomitic marble can be expected. Even during dedolomitization of dolomitic marble the Sr content decreases possibly due to the removal of Sr by solutions bringing about the replacement of Mg by Ca[2,16] - i. e. $Ca^{2+}_{aq} + Mg_{solid} \longrightarrow Mg^{2+}_{aq} + Ca_{solid}$. Thus the decrease in Sr during dedolomitization is more readily accounted for by leaching than by reaction within a closed system. Thus the lower Sr contents of marbles in the Highland Group of the Precambrian of Sri Lanka indicate that the loss of Sr from the parent limestones during metamorphism and dolomitisation can be presumed to be due to the removal of Sr by circulating solutions.

TABLE 1. Table showing the analytical data of the carbonates of Sri Lanka.

Sample No.	Location	Metamorphic grade	Calcite %	dolomite %	Sr ppm	Na_2O/ ppm	K_2O/ ppm	Insoluble residue %
Digana	UG 1	Crystalline limestone (marbles)	29	71	60	117	14	22.8
	UG 2		0	100	40	128	30	36.9
	UG 3		3	97	60	25	8	43.5
	UG 9		2	98	10	35	6	26.2
	UG 10		10	90	n. d.	45	40	42.6
Kandy	UG 34		15	85	30	80	474	24.4
	UG 35		11	89	n. d.	n.d.	4	48.9
	UG 40		1	99	n. d.	36	181	32.0
	UG 41		6	94	20	31	520	33.1
	UG 42	-do-	3	97	20	39	38	26.0
	UG 44		5	95	10	51	38	15.8
	UG 45		3	97	n. d.	39	10	27.2
	UG 46		99	1	380	47	32	42.1
	UG 47		99	1	410	18	3	23.6
Naula	UG 50		2	98	n. d.	38	9	21.2
	UG 52		9	91	n. d.	28	15	37.2
	UG 55		0	100	30	91	120	28.8
	UG 57		1	99	50	89	214	35.6
	UG 59	-do-	3	87	80	63	14	36.9
	UG 60		4	86	n. d.	56	18	18.5
	UG 63		17	83	n. d.	25	24	21.2
	UG 64		27	73	n. d.	63	36	18.8
	UG 65		4	96	n. d.	46	38	39.3
Puttalam	UG 71	Sedimentary limestones	70	30	240	466	2560	10.7
	UG 74		50	50	210	333	83	47.9
	UG 75		100	00	560	61	14	1.1
Mannar	UG 101		90	10	710	113	114	11.3
	UG 102	-do-	100	0	680	67	12	2.4
	UG 103		95	5	340	63	29	4.8
KKS	UG 104	-do-	98	2	1370	91	338	4.2
	UG 105		95	5	340	101	1370	9.4
	UG 106		100	0	1620	198	1310	8.5

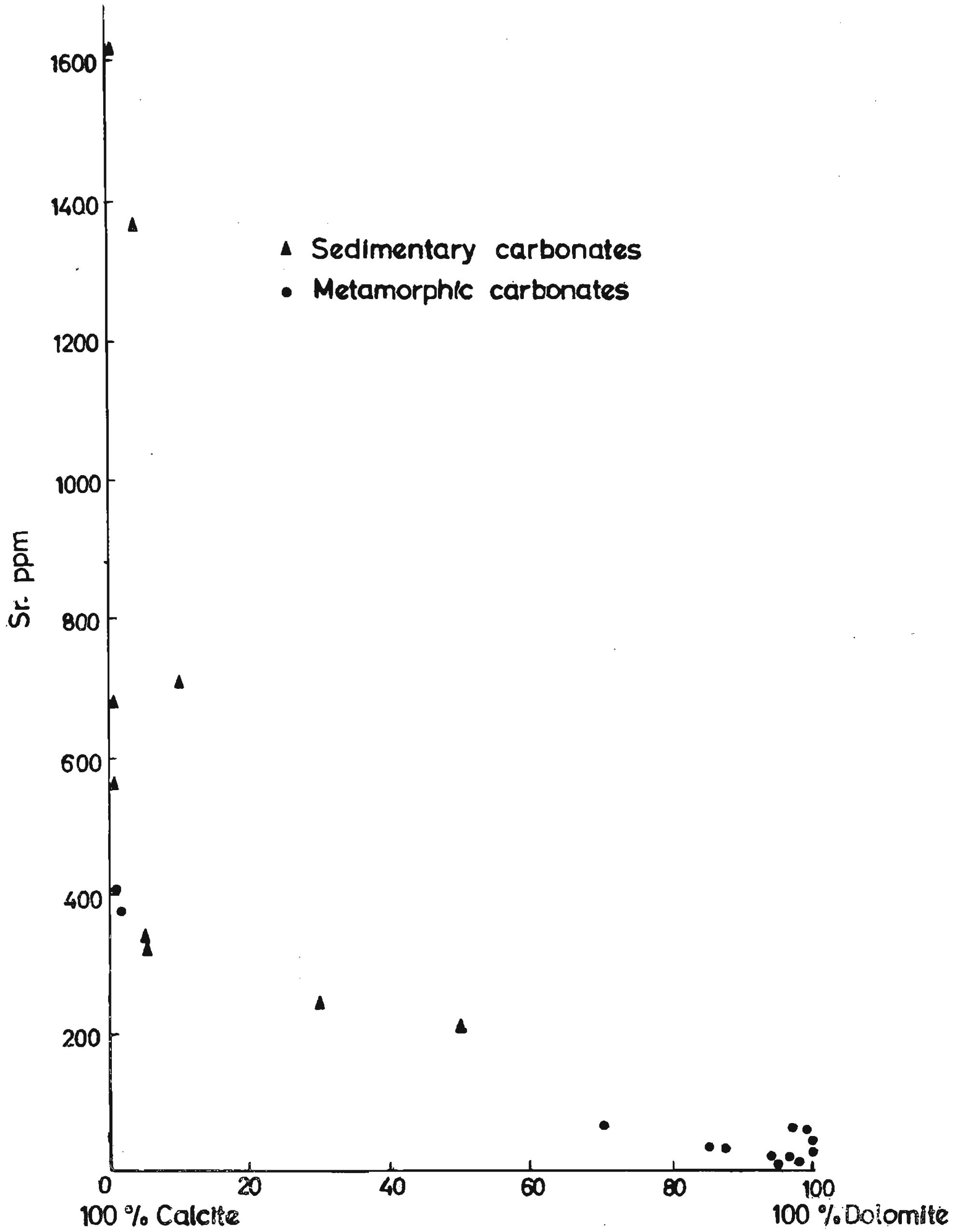

Figure 2. Variation of strontium with respect to the calcite and dolomite percentages.

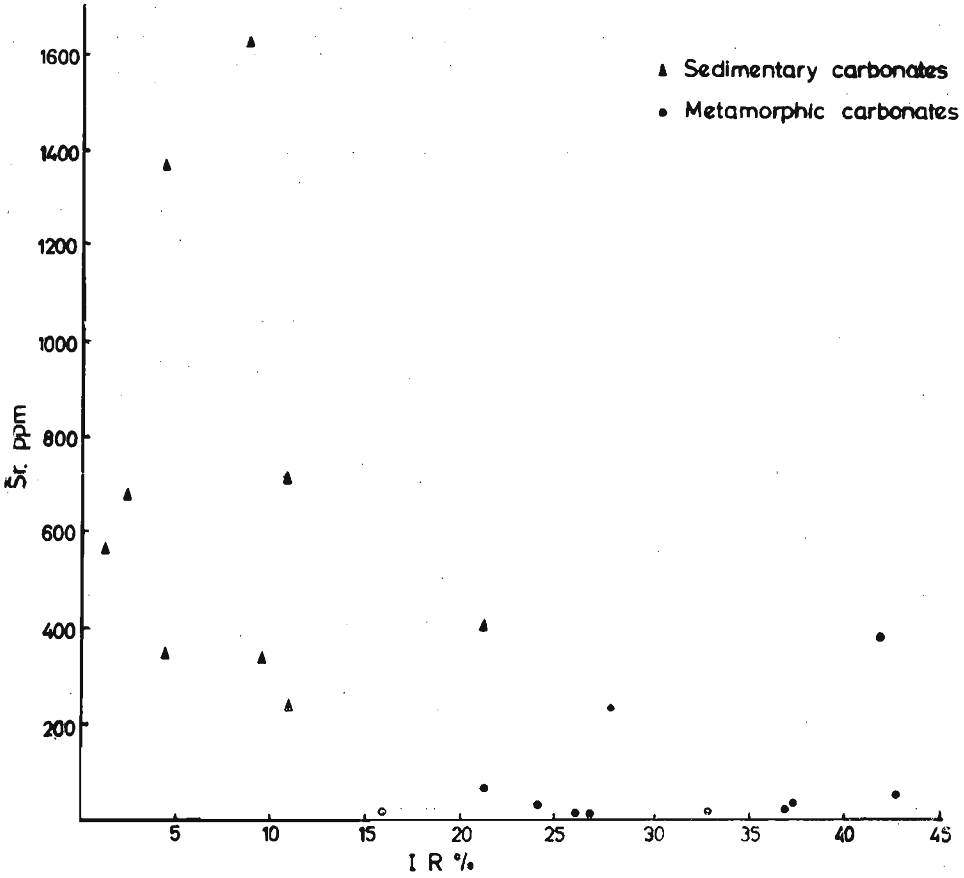

Figure 3. Variation of strontium with respect to the insoluble residue of the samples.

The presence of high concentrations of Sr in two calcite marble samples (UG 46 and UG 47) from Kandy (Fig. 1) points to the fact that these calcite marbles were of "primary" origin as opposed to calcite marbles formed by dedolomitization. Since it is known that dedolomitization lowers the Sr content of a rock, it appears very unlikely that the two calcite marbles from Kandy could have resulted by such a process, bearing in mind that their Sr content is higher by a factor of about 10 when compared to the dolomites in the same metamorphic terrain.

It was mentioned earlier that the lithological layering in the Highland Group of Sri Lanka of marbles occur in some cases for over 100 km along strike. These therefore predate the deformation and subsequent metamorphism experienced by the Highland Group. The Sr contents of the unmetamorphosed limestones of equivalent high calcite content of Miocene age (Fig. 2) bring about an interesting comparison. The Sr content of the two samples from Kandy of around 400 ppm Sr is lower than that of the Miocene sedimentary limestones of equivalent calcite content by about 200 ppm Sr. This difference could be accounted for by the differences in the Sr contents of the sea water, from which the original limestones were deposited and also by the post-depositional recrystallizations and metamorphic overprint.

The geochemical status of Sr during the formation of carbonates in the Precambrian of Sri Lanka can best be viewed in the light of the current views on the origin of the Highland Group. Even though our understanding of the origin of the Highland Group is not yet satisfactory the current trend of thought is as follows.

The Highland Group has been formed in between two closing blocks now represented as the Eastern and Western Vijayan Complex. The present configuration of the Highland Group resulted due to a collision of these two continental blocks during the Precambrian. Fig. 4 (after Munasinghe and Dissanayake,[26]) illustrates the model for the formation of the Highland Group. The pre-metamorphic Highland Group now termed the Highland Basin was presumed to have been a narrow elongated marine basin shallow in the northern part. The occurrences of 100-2000 ft thick limestone bands extending over 100 km and 50 km long quartzites suggest the existence of quiet seas in which calcareous sediments were laid down from time to time mixed with sand and clay.[13] The sedimentary basin subsequently sank during the permobile and transitional phases, and due to the high P-T conditions prevailing metamorphism coupled with igneous activity took place converting the sandstones, limestones, shales, etc., to quartzites, marbles and aluminous gneisses. Lateral pressures due to the collision of the two blocks folded the strata to form the present configuration of the Highland Group[23,26] which in effect had been a volcano-sedimentary basin.

Veizer and Garret[36] and Veizer[33] in detailed studies on the secular variations in the compositions of sedimentary carbonate rocks, noted that the positive correlation of MgO/CaO with geologic age is one of the best established secular trends, the trends being essentially due to the increasing dolomite/calcite ratio in many lithological types. Among the other secular variation studied by Veizer and Garret[36] was that of sodium. Due to its similar ionic size with that of Ca and Sr, Na is expected to be present in the lattices of Ca - Mg carbonates or form inclusions in these phases.[17,22] Due to the fact that hypersaline facies contain higher Sr concentrations than normal carbonates[32,35] Sr and Na are expected to correlate positively if their distributions are controlled by carbonate facies. Fig. 5 illustrates the plot of Na_2O vs Sr in the Precambrian and the Miocene carbonates of Sri Lanka, where a distinction between the two carbonate populations can be seen. The variation of the alkali metals with Sr is shown in Fig. 6 and the separation of the two types is again noted. The high calcite marbles of Kandy do not differ significantly from the high calcite sedimentary limestones of Miocene age (Fig. 6) in their alkali-Sr variations. If the calcitic marbles are indeed primary, it would retain most or all of its original Sr.[18] As such this would reflect the geochemical status of the Sr in sea water in which the carbonate minerals were deposited in the Precambrian.

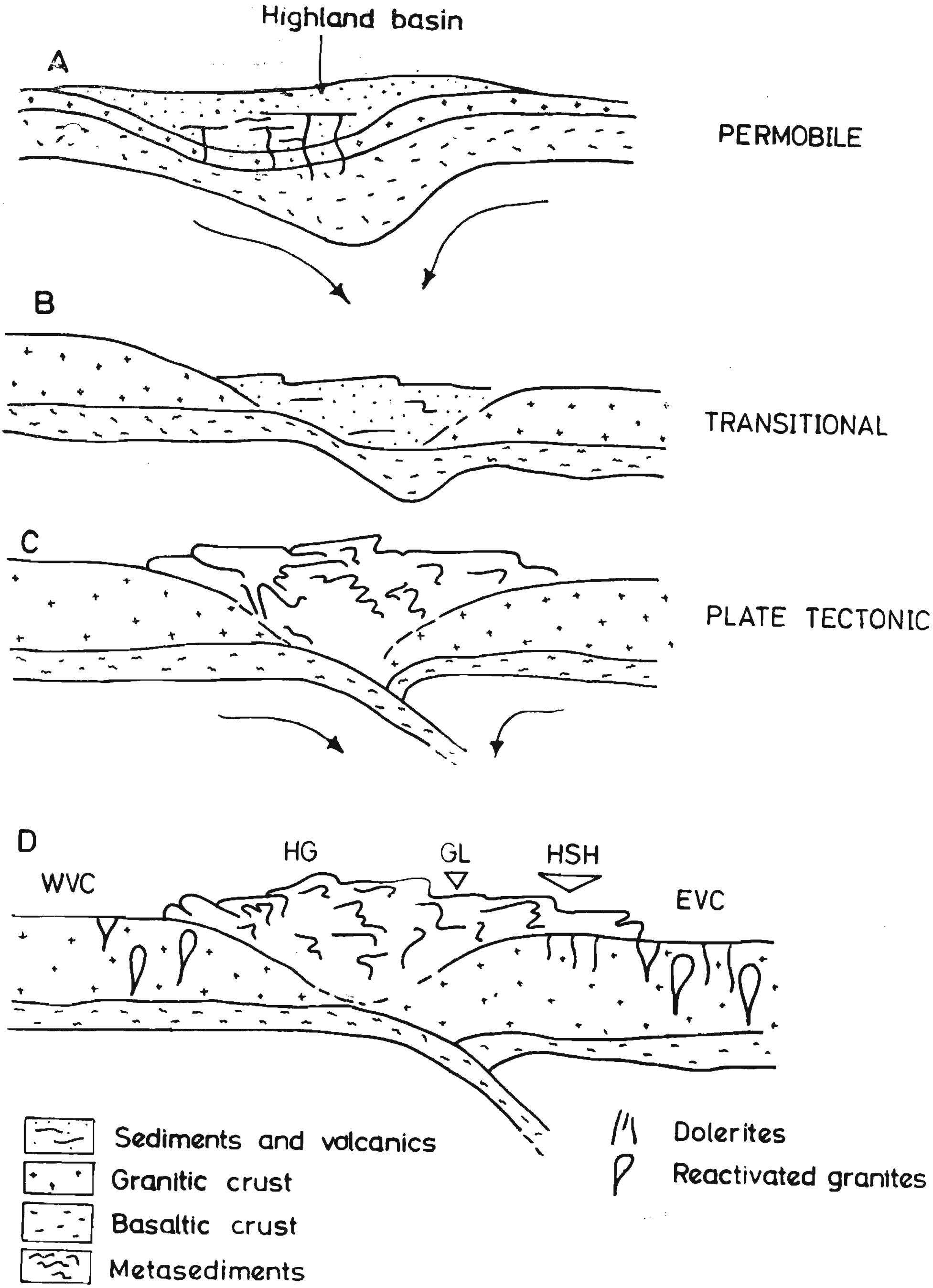

Figure 4. Model showing the evolution of the Highland Group of Sri Lanka.

WVC – Western Vijayan Complex
HG – Highland Group
HSH – Hotspring and high heat flow zone
EVC – Eastern Vijayan Complex

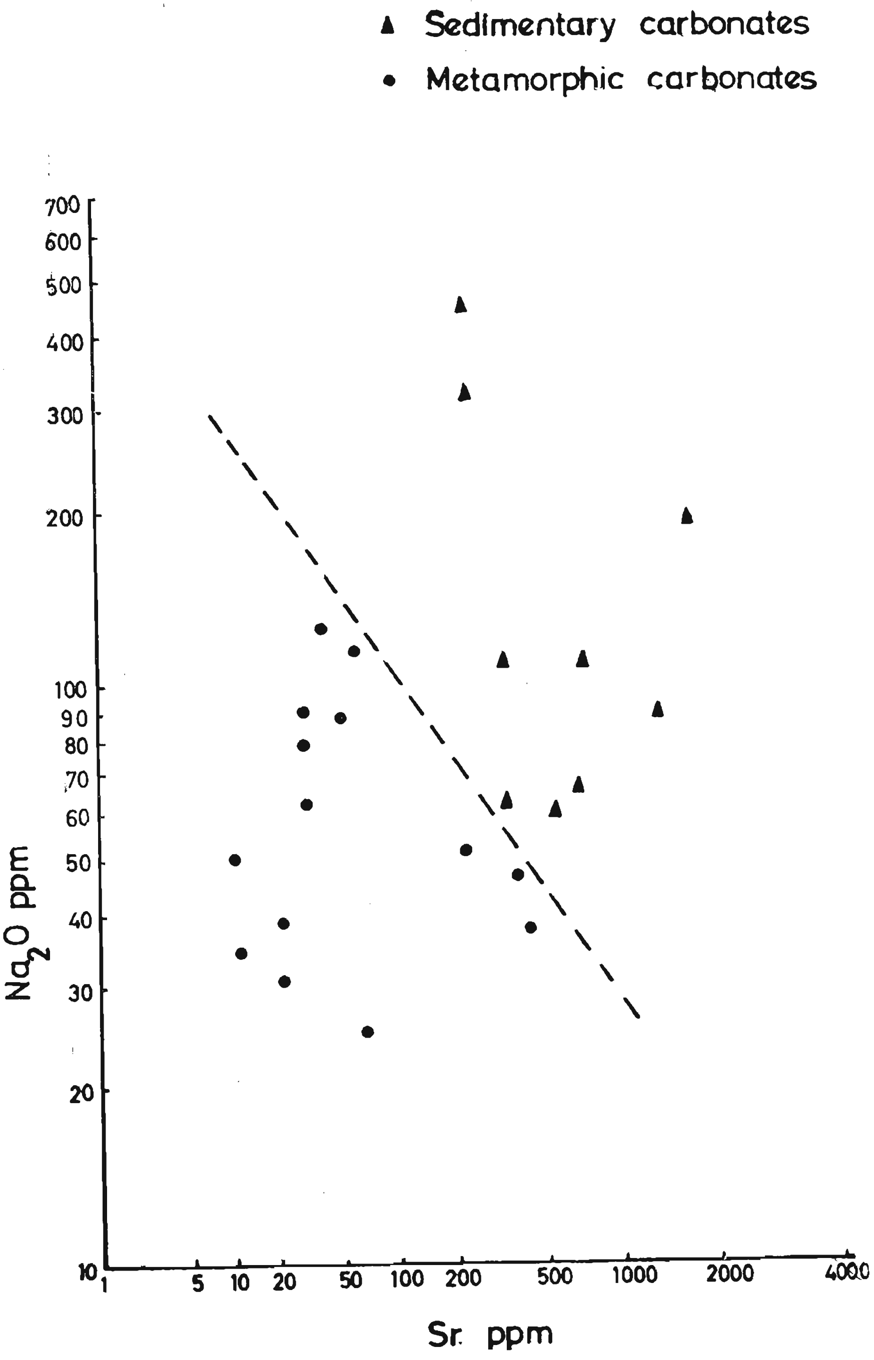

Figure 5. Variation of strontium with respect to Na_2O.

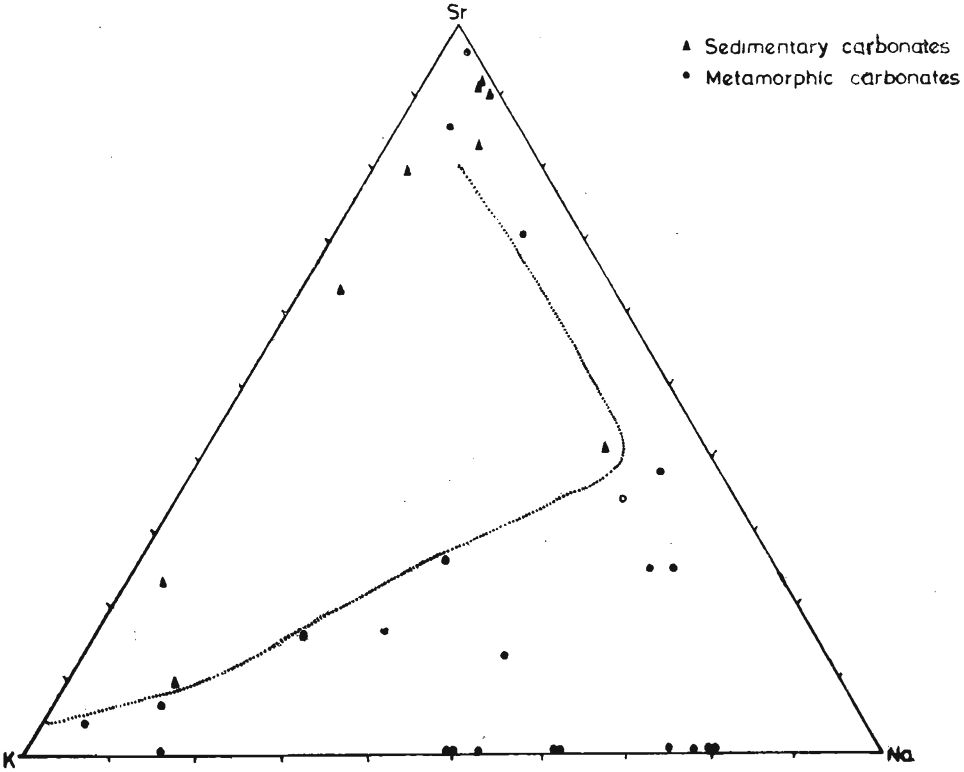

Figure 6. Ternary diagram showing the relative variation of strontium with respect to the alkali metals.

Veizer and Compston[34] studied the $^{87}Sr/^{86}Sr$ in Precambrian carbonates as an index of crustal evolution and concluded that all data known at present for the Archean resemble $^{87}Sr/^{86}Sr$ values of the contemporaneous upper mantle, and that the Sr isotopic trend for sea water parallel the average K_2O/Na_2O trend for igneous and sedimentary rocks. If these trends define the fractionation stage of the contemporary crust, Sr isotopic studies of the Precambrian Highland Group carbonates with high calcite contents should provide an insight into the geochemical status of the environment of deposition and also crust - sea water interaction during the formation of the Highland Basin. The recent application of the plate tectonic theory to sedimentation and diagenesis[30] helps in the better understanding of the geochemical variation that control diagenetic histories and the Precambrian carbonates of the Highland Group of Sri Lanka is ideally suited for such a detailed study.

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