THE NIOBIUM AND YTTRIUM ABUNDANCES IN THE SEDIMENTARY GEM DEPOSITS OF SRI LANKA

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Abstract : A study of the abundances of Nb and Y in some gem-bearing sediments of Sri Lanka shows that Nb and Y are found at maximum concentrations of 229 ppm and 318 ppm respectively. The source rocks of Nb and Y are presumably rocks of the charnockite - granite association and related pegmatites found in the Highland Group of Sri Lanka. During weathering and sedimentation, Nb and Y enter the hydrolysates and are found to be concentrated in the sediments. Apart from the gem minerals themselves, the sediments found in the gem fields of Ratnapura and Elahara contain abundant rare elements of which Nb and Y are important.

1. Introduction

The sedimentary gem deposits of Sri Lanka which contain a variety of gemstones, dominated by various types of corundum, spinel, chrysoberyl, beryl, tourmaline, garnet, topaz and zircon, often harbour abundant rare elements. Rupasinghe and Dissanayake¹⁴ reported the rare-earth element contents of the gem-bearing sediments of Sri Lanka and found that the gem-bearing placer deposits contain rare-earth elements (REE). Table 1 shows the REE data for some samples from Ratnapura and Elahera. Overstreet¹⁰ commented on the abundance of monazite in placer deposits of Sri Lanka and emphasized their high thorium and rare-earth concentrations. Rupasinghe *et al.*¹³ studied monazites from stream sediments of Sri Lanka by neutron activation analysis and found maximum ThO₂ concentrations of 10%. This study forms a further contribution to the rare element geochemistry of the gem-bearing sediments of Sri Lanka and discusses the abundances and geochemistry of the two elements Nb and Y. At present, there is a dearth of information regarding the geochemistry of Nb and Y in the low-temperature environment, particularly in the sediments. This is especially so for tropical countries in the Asian region, as exemplified by Sri Lanka.

Table 1. Rare-earth element abundances in Ratnapura and Elahera gem-bearing sediments.

Sample No.	7	15	16	19	21	29	30	31	35	37	38
					(ppm)						
La	79.00	136.82	105.69	145.70	99.85	79.24	53.01	55.10	66.86	52.02	49.53
Ce	215.00	246.18	198.74	392.00	178.11	158.00	251.95	127.00	164.60	124.00	113.00
Pr	19.40	28.05	21.95	39.00	18.42	—	14.33	14.00	—	13.06	12.35
Nd	67.80	107.68	93.05	119.00	61.20	66.45	42.91	48.40	59.21	44.71	41.00
Sm	13.00	17.29	16.71	21.76	9.57	11.80	7.83	9.00	9.43	8.59	6.55
Eu	2.21	2.55	3.23	2.76	0.96	2.29	1.34	1.70	1.39	1.24	1.47
Gd	13.00	18.45	21.40	21.00	7.52	—	—	9.00	7.40	—	—
Tb	1.60	2.00	2.54	2.61	1.07	1.33	1.00	1.30	1.11	1.18	1.04
Dy	8.94	11.55	13.80	15.50	5.66	7.94	—	7.50	5.13	5.43	6.60
Ho	2.11	2.40	3.55	3.00	1.09	—	1.00	1.50	1.08	1.24	1.34
Er	—	—	8.66	10.40	2.71	—	—	4.20	—	3.35	3.97
Tm	—	—	—	—	—	—	—	—	—	—	—
Yb	5.80	6.70	7.75	8.22	2.55	4.33	2.30	4.40	2.70	3.48	3.78
Lu	0.87	1.03	1.15	1.25	0.40	0.66	0.38	0.64	0.42	0.58	0.48

Figure 1. Geochemical separation of some elements on the basis of their ionic potential (after Mason, 1966).

Heinrich⁵ discussed the types of Nb — Ta deposits in the western hemisphere and observed six types, namely :

1. In ordinary igneous rocks
2. In pegmatites
3. Nb — bearing carbonatites
4. Vein deposits of Nb minerals
5. Placer deposits
6. Bauxite deposits

In the case of the placer deposits, columbite-bearing pegmatites appeared to be the source. Further, "black sand" type of placers containing euxinite and similar species were noted. According to Goldschmidt,³ during the processes of weathering and sediment evolution, a small fraction of Nb remains in resistant minerals like cassiterite, columbite and rutile, and as such is arrested in residual sediments such as sands and sandstones. Most of the Nb however, is fixed in hydrolysate sediments such as clays and bauxites, along with most of the Ti and Zr.

Figure 1 illustrates the geochemical separation of some elements on the basis of their ionic potential.⁷ Apart from Nb and Ta, the rare-earth elements and economically useful elements such as Th and U are found in the hydrolysate group and it is of interest to note that these elements are abundant in the gem-bearing sediments of the Highland and Southwest Group of Sri Lanka.

In general, the chemical properties of yttrium, and the occurrences of yttrium in minerals are nearly identical with those of the rare earth elements of atomic numbers from 64 (gadolinium) to 71 (lutetium). During the process of weathering, soil formation and sedimentation, all the rare-earth elements are again fixed nearly completely in the hydrolysate minerals, eg. the various clay and shale components, the bauxite minerals and the oxides of iron and manganese.³

2. Areas of Study

Figure 2 (see inset) illustrates the locations of the areas of study with respect to the major geological divisions of Sri Lanka. Precambrian metamorphic rocks form the greatest part of the geology of Sri Lanka and are subdivided into the following major divisions.¹ (a) Highland Group (pyroxene — granulite facies) consisting of charnockites, quartzites, marbles, garnetiferous gneisses, hornblende gneisses, granulites and pegmatites, (b) Vijayan Complex (amphibolite — granulite facies) consisting of hornblende biotite gneisses, migmatites and granites, (c) Southwest Group (cordierite — granulite facies) composed of cordierite gneisses, wollastonite scapolite rocks and calc gneisses.

Figure 2. The geology of the Ratnapura area showing the sampling locations. The inset shows the locations of the areas of study with respect to the main geological divisions of Sri Lanka VC - Vijayan Complex; HG - Highland Group; SWG - Southwest Group.

Figure 2 illustrates the lithology of the Ratnapura, Rakwana and Balangoda areas. Except for scattered patches of alluvium, the areas included in the Ratnapura and Rakwana topographic sheets consist of Precambrian metamorphic rocks of the charnockite–metasedimentary type. The major rock types are charnockites, garnet–sillimanite granulites, amphibolite and perthite–bearing garnet–biotite granulitic gneisses. Of these charnockites and pelitic garnet – sillimanite granulites are dominant. Also of importance are intrusive rocks of the zircon granite type and also vein quartz and pegmatites.

The Ratnapura and Rakwana gem fields are an expanse of Pleistocene or sub–recent alluvium containing patches or streaks of gravel of heavy minerals laid down in the beds of streams, flood plains, in the beds of abandoned tributaries or in talus fans at the foot of steep slopes of hill–sides.¹⁷ During periods of intense flooding, lenses or layers of gravel are deposited and contain numerous heavy minerals including gems denuded from a large catchment area.

Figure 3 shows the lithology of the Elahera gem field situated in the north–east of Sri Lanka and characterized by ridge and valley topography in a plunging synclinal structure. Silva¹⁵ reported the occurrence of granites and pegmatites in the area. The general rock types consist of quartzites, marbles, garnet–sillimanite–biotite gneisses with tourmaline and charnockites. Tourmalinization of the garnetiferous gneisses is especially prominent. The gem bearing surficial material in the area are laterites, sandy clay, sandy gravel with laterite being the most conspicuous.

3. Materials and Methods

The samples were collected from locations as shown in Figures 2 and 3. All sediment samples were taken from existing gem pits from layers of gem-gravel generally of lenticular shape termed “illam” in Sinhalese. This is usually composed of rounded or sub–angular pebbles or boulders of quartz and heavy minerals including gemstones. Sampling was carried out at depths varying from 5m to 30m. Approximately 7 kg of sediments were taken, dried and sieved in the laboratory. The fraction less than 0.63 μm was selected for elemental analysis. The rock samples collected from fresh outcrops were crushed in the laboratory. About 5 grams of the homogenized size fraction 0.63 μm of sediments and powdered rock samples were made into pellets, mantled by 1 : 1 mixture of boric acid and bakelite employing a pressure of about 160 kg/cm^2 . In the samples with low plasticity which can produce cracks in pellets after preparation, 5–6 drops of a tertiary alcohol (moviol) is added. These tablets were then analysed by X-ray fluorescence spectrometry using a Siemens SRS 200 instrument. The reader is referred to Laskowski⁶ for details of the analytical method.

Figure 3. The geology of the Elahera gem-bearing area showing the sampling location.

Table 2. The Nb and Y contents of the sediments and rocks from the Ratnapura and Elahera gem fields of Sri Lanka.

RATNAPURA SEDIMENT			RATNAPURA ROCKS		
Sample Nr.	Y ppm	Nb ppm	Sample Nr.	Y ppm	Nb ppm
4	55	47	D	7	18
5	51	26	G	24	12
6	71	6	J	7	10
7	48	12	i M	39	20
8	68	21	N	6	5
9	40	22	O	15	8
10	56	16	S	186	47
11	35	27	C	18	14
12	40	13	E	16	5
13	73	17	ii K	28	9
14	37	24	L	32	9
15	105	24	Q	34	5
16	132	13	R	30	16
18	318	19	iii I	21	11
19	80	30	P	14	13
20	12	38	A	23	21
21	18	36	iv B	4	16
22	44	31	T	50	15
23	17	20	v F	3	5
24	67	17	H	8	4
25	111	27			
26	49	24	i — acid charnockite		
27	5	16	ii — basic charnockite		
28	24	7	iii — intermediate charnockite		
29	32	12	iv — Biotite Gneiss		
30	17	21	v — Qtz. Fsp.		
ELAHERA SEDIMENT			ELAHERA ROCKS		
31	20	21	u	38	14
32	21	19	n	—	—
33	16	16	s	32	21
34	21	34	r	6	2
35	29	17	t	2	1
36	31	36	o	25	9
			m	—	—
in washed gem gravels					
Ratnapura	122	112	i	18	6
Rakwana (i)	118	158	c	—	—
Rakwana (ii)	254	229	d	132	33
Elahera	11	98	e	—	—

4. Results and Discussion

Table 2 shows the Nb and Y contents of the sediment and rock samples from the Ratnapura and Elahera gem fields. The Nb contents of the Ratnapura sediments range from 6 to 47 ppm, and in the Elahera sediments, they range from 16 to 36 ppm. In the residual material used for panning of gemstones, the Nb content reaches 229 ppm. When compared to the 11 ppm Nb for average shales,¹⁶ there is a definite enrichment of Nb in the gem-bearing sediments of Sri Lanka. The analysed gem-bearing sediment fraction of 0.63 μm compares with the particle size of shale and average shale is therefore considered as a useful reference for trace metal concentrations. The rocks of the Ratnapura gem field, namely charnockites, biotite gneisses, and quartz-feldspar gneisses, contain an average of 12 ppm Nb, and in the Elahera gem fields, the rocks contain nearly identical average of 10 ppm. The enrichment of Nb during sedimentation can be put into perspective as shown in Figure 1, where the ionic potentials of the elements are shown. The hydration of an ion is proportional to its charge (Z) and inversely proportional to its radius (r). The factor Z/r is known as the ionic potential and is of great significance not only for the hydration of an ion, but for many of its properties in the presence of water. As Mason,⁷ has shown, the ionic potential of an element largely determines its place of deposition during the formation of sedimentary rocks and is significant in all mineral forming processes in the aqueous medium. As shown in Figure 1, Nb, with its intermediate ionic potential of 7.5 is classed under hydrolysates. Along with Nb, a number of less common elements are generally concentrated in hydrolysates. Along with Nb, a number of less common elements are generally concentrated in hydrolysate sediments. The elements Ti and Zr are associated with Nb as hydrolysates during weathering and sedimentation.

Figures 4 and 5 illustrate the Ti-Nb and Zr-Nb variations respectively for the Ratnapura and Elahera sediments and rocks. The Ti-Nb ratio varies from 1 to 15 and it is apparent that the enrichment of Ti relative to Nb is greatest in the Ratnapura gem fields. Zr on the other hand, shows a much greater degree of enrichment relative to Nb as shown in Figure 5. The Ratnapura sediments in particular show a Zr/Nb ratio greater than 20 in most cases. It is apparent from Figures 5 and 6 that there is a relatively large scatter indicating an incomplete fractionation of the elements concerned, in the rocks as well as in the sedimentary environment.

When Nb occurs in solid solution in the chemically resistant titanium and zirconium minerals (titanomagnetite, ilmenite, sphene, zircon, etc.,) it accumulates in placer deposits. More Nb passes into the aqueous phase as a result of the decomposition of rock-forming minerals such as biotite, muscovite, amphibole, and pyroxene, in which Nb is found.¹¹ Fergusonite and columbite are known to contain Nb and Y.

Figure 4. Diagram showing the variation of Ti with Nb in the sediments and rocks of the gem fields.

Figure 5. Diagram showing the variation of Zr with Nb in the sediments and rocks of the gem fields.

Figure 6. The variation of the SiO_2/Nb ratio with the Al_2O_3 content in the sediments of the gem fields.

Figure 6 illustrates the variation of Nb in sediments with respect to SiO_2 and Al_2O_3 . In general there appears to be a decrease in the SiO_2/Nb ratio with increasing Al_2O_3 content of the sediments, particularly in the case of the Ratnapura sediments. Grimaldi and Berger,⁴ who studied the niobium content of soils from west Africa reported that as Al_2O_3 increases, the SiO_2/Nb ratio decreases. They concluded that with increase in aluminium Si is being replaced faster than Nb from soils, and that both Si and Nb are being depleted faster than Al, the sequence for depletion being $\text{Si} > \text{Nb} > \text{Al}$.

In the case of rocks from the gem fields of Ratnapura and Elahera, the variation of the SiO_2/Nb ratio with increasing Al_2O_3 content is better defined (Figure 7). In the Elahera rocks in particular, the SiO_2/Nb ratio drops very sharply within a narrow range of about 2% Al_2O_3 . When compared to the variation of the SiO_2/Nb ratio with Al_2O_3 in the sediments, it is seen that the variation of Al_2O_3 percentage in the rocks has a much greater effect on the Nb content, than in these case of the sedimentary environment.

Yttrium, usually associated with the rare-earth elements, ranges from 5 to 318 ppm in the Ratnapura sediments, and 16 to 30 ppm in the Elahera sediments. When compared to the average value of 26 ppm Y for shales,¹⁶ the Ratnapura sediments show an enrichment by a factor of two. As given in Table 2, the sediments in the region around Karawita and Weddagala (Figure 2) show strong enrichment in yttrium. This element, which has an ionic potential of 3.3, also falls in the class of hydrolysate elements and is generally included with the rare earth elements. The rocks of the Ratnapura and Elahera gem fields contain on the average 28 ppm Y and show no enrichment when compared to the average crustal abundance of Y. Figure 8 illustrates the variation of Y with Nb in the sediments and rocks of Ratnapura and Elahera areas. In general, the Y/Nb ratio varies between 0.5 and 4 with an average ratio of about 2. The marked contrast in the relative geochemical behaviour of Y with Nb in the sediments when compared to rocks is shown in Figure 9, where the parameter SiO_2/Zr is plotted against the Y contents of the sediments and the rocks. The fields for the sediments and the rocks are clearly defined.

5. Geochemical Implications

Figure 10 illustrates in a schematic form, a genetic overview of Nb and Ta deposits and can be applied to the geological situation of Sri Lanka.

The geochemical history of Nb and Y in sedimentary processes depends on a number of factors, but primarily on the mode of their occurrence in the source rocks. Nb which occurs in solid solution in the chemically resistant Ti and Zr minerals such as titanomagnetite, ilmenite, sphene,

Figure 7. The variation of the SiO_2/Nb ratio with the Al_2O_3 content in the rocks of the gem field.

Figure 8. Variation of Y with Nb in the sediments and rocks of the gem fields.

Figure 9. The different fields of Y for sediments and rocks of the gem-fields with respect of SiO_2/Zr .

zircon, etc. accumulates in the placer deposits along with these minerals. When these minerals are only partially decomposed, a small fraction of Nb passes into the aqueous phase. In the case of the less resistant rock forming minerals such as biotite, muscovite, amphibole and pyroxene, Nb is known to be found in significant concentrations, in solid solutions. Very often these minerals carry a greater part of the Nb contents found in the rock.¹¹

When compared to the average concentration of 20 ppm Nb for the lithosphere, 21 ppm Nb in granites, 14 ppm Nb in basic rocks and 24 ppm Nb for igneous rocks in general,¹² no significant enrichment is seen in the Nb contents of the rocks and sediments from the gem fields of Sri Lanka. However, some of the washed gem gravels from the gem pits of Rakwana and Elahera (Table 2) show enrichments of Nb and Y. As reported by Von Gies and Kasper,² (Figure 10), Nb is particularly enriched in carbonatites and roof regions of normal granites and syenites. In later stages, i.e. pegmatitic, greisen and albitization, there is a strong enrichment of Nb along with many other trace elements.

In the case of Sri Lanka, the source of Nb and Y could well be traced to granites, later pegmatites as well as possible carbonatites. It is of interest to note that in the north central part of Sri Lanka is an apatite deposit considered to be a carbonatite, with the presence of Martite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). In view of the recent observations made by Munasinghe and Dissanayake,⁸ that the Highland Group of Sri Lanka is a volcano-sedimentary sequence, later magmatic differentiates, could well be the source of Nb and Y.

Rupasinghe and Dissanayake¹⁴ studied the REE from the gem-bearing sediments in Sri Lanka and noted that chondrite-normalized REE plots showed a marked similarity with those for charnockites in Sri Lanka as well as for charnockite-granite rocks in other parts of the world. They considered the progenitors for the REE to be the charnockite-granite association prevalent in the Highland Group in which most gem fields of Sri Lanka are found. It is also of interest to note that Nb-bearing rutile has been observed in some gem fields, associated with such rocks, and possibly with post tectonic pegmatites.

As reported by Von Gies and Kasper² tectonic boundaries, grabens and rift zones are possible locations for Nb and Ta. The eastern boundary of the Highland Group of Sri Lanka is known to be such a tectonic boundary⁹ and magmatic activity associated with such tectonism could also bring about Nb and Y enrichments.

Higher Nb and Y concentrations could therefore be expected in the deeply eroded charnockitic-granitic regions of Sri Lanka, specially when rare earth minerals are abundant.

6. Conclusion

From the study of Nb and Y abundances in the gem-bearing alluvial placers of Sri Lanka, situated in the Highland Group consisting of gneisses and charnockite-granite type rocks, the following conclusions can be drawn. Nb and Y appear to be enriched in some of the gem gravels possibly associated with the Ti and Zr — bearing minerals. Being elements of hydrolysates, Nb and Y show a tendency to enter the aqueous phase. The actual release of the elements into the aqueous phase however depends on the degree of weathering of the minerals in which Nb and Y are present. The actual sources of Nb and Y appear to be the granites and pegmatites related to the charnockite-group of rocks, particularly in the Highland Group. This magmatic activity associated with the tectonic boundary of the Highland Group-eastern Vijayan Complex may well have brought about the Nb and Y enrichments. More analytical data and further investigations are however necessary to support this view. The trace element characteristics show that the Ratnapura sediments have been derived from wide areas or varying source rocks as compared to Elahera sediments. The Nd/Sm ratios appear to indicate that the age of the original material that formed the sediments are the same for the two gem fields.

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