RESEARCH ARTICLE

Fluoride content of minerals in gneissic rocks at an area of endemic dental fluorosis in Sri Lanka: estimates from combined petrographic and electron microprobe analysis

H.A. Dharmagunawardhane^{1,*}, S.P.K. Malaviarachchi¹ and William Burgess²

¹Department of Geology, University of Peradeniya, Peradeniya, Sri Lanka

²Department of Earth Sciences, University College London, United Kingdom

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Abstract: A mass balance of the mineralogical sources of fluoride in charnockitic gneiss bedrock and regolith (weathered rock) in Sri Lanka has been undertaken, using optical petrography and Scanning Electron Microscopy (SEM) with energy dispersive X-ray spectrometry (EDX) to support development of a conceptual model of fluoride release to groundwater. Bedrock and regolith samples were collected in Polonnaruwa where there is a widespread occurrence of dental fluorosis attributed to excessive fluoride (up 5.25mg/L) in groundwater, while primary minerals of the gneissic bedrock are identified as the ultimate source of fluoride. Fluoride leaching related to long-term weathering of the bedrock and development of the regolith, control the occurrence of F in the groundwater system which is yet unresolved. In the study area, the charnockitic gneiss bedrock is mantled by a few meters thick regolith within which the groundwater table fluctuates seasonally.

Mineral abundance and mineral fluoride content were estimated using petrographic and SEM analysis. Plagioclase, hornblende, pyroxene, K-feldspar, quartz, biotite and titanite (sphene) were the major minerals of the rock though the mineral proportions vary widely over the area. Apatite and magnetite were present as accessory minerals. Fluoride concentrations obtained from SEM-EDX analysis were combined with the volume percentage of minerals from petrography to estimate the total rock fluoride concentration.

The order of fluoride abundance was apatite (highest), biotite, titanite, and hornblende. Plagioclase, K feldspar, pyroxene and magnetite did not have any noticeable fluoride concentrations. Loss of fluoride from the rock mass upon weathering was clearly evident and hornblende appeared to be the most significant fluoride releasing agent through weathering. Apatite, though present in accessory amounts, is distributed evenly in the rock and hence may be considered as a steady fluoride donor causing

elevated and uniform fluoride distribution in groundwater. On the other hand, hornblende and biotite though of irregular occurrence (area wise), may cause high fluoride anomalies in groundwater in areas of high abundance.

Keywords: Dental fluorosis, fluoride, groundwater, Sri Lanka.

INTRODUCTION

Among numerous health problems that Sri Lankan population is facing today, dental fluorosis among young children in the dry zone is an issue with growing concern. Endemic dental fluorosis in Sri Lanka was first described by Seneviratna *et al.* (1974). High fluoride content in groundwater in certain parts of the country and its relationship with dental fluorosis have been reported by several workers (Seneviratna and Seneviratne, 1975; Tillaivasam, 1988; Dissanayake, 1989; Dharmagunawardhane and Dissanayake, 1993). These studies have shown that fluoride bearing minerals such as mica, amphibole, apatite and titanite (Sphene) etc. are present in the majority of crystalline rocks of Sri Lanka and therefore can be considered as potential fluoride releasing agents to groundwater upon weathering and leaching. Dharmagunawardhane and Dissanayake, (1993) further revealed that there is a distinct influence by the climatic factors in dissolution chemistry of fluoride causing comparatively higher concentrations in the dry zone groundwater than that in the wet zone. Although the same geological formations extend from wet zone to dry zone of the country, groundwater in the dry zone has shown a remarkably high fluoride concentration. According to these investigators,

*Corresponding Author's Email: dharmag45@yahoo.com

this situation is at least partially explained by the fact that in the elevated wet zone areas with high rainfall, fluoride is leached out from primary and secondary minerals in rocks and soils whereas, in the dry zone, evaporation tends to bring soluble ions upward by capillary action. In the wet zone, the saturated zone is replenished by the downward infiltration through the capillary zone during a large part of the year than in the dry zone, thus diluting the saturated zone. The patterns of seasonal fluctuations of groundwater fluoride concentrations are complex and non uniform due to the complexities in lithology, terrain conditions, character of weathered profile of the rocks and the depth to the groundwater table. However, in areas of shallow groundwater table which occurs within the weathered material, groundwater fluoride concentration in general shows a slight decrease towards the end of the wet season and slight increase towards the end of the dry season before the monsoon rains start. The present study is a further development of the work emphasizing the potential of particular minerals contributing to the groundwater fluoride concentration. This study, attempted to quantify the fluoride concentration in a number of fluoride bearing minerals present in the metamorphic rock terrain of Sri Lanka.

Fluoride is a well known compound to occur in a number of rock types and weathering releases fluoride in to groundwater (Bailey 1976; Ramesham and Rajagopalan, 1985; Abu Rukah and Alsokhny, 2004; Edmunds and Smedliey, 2005; Saji *et al.*, 2007; Reddy *et al.*, 2010). Bailey (1976) reported fluoride contents of 0.87-11.32 % in apatite, 0.01-2.9 % in hornblende, 0.28-1.36 % in sphene and 0.08-3.5 % in biotite in granitic rocks. Tsunogae *et al.*, (2003) reported fluoride contents as high as 2.1 % in amphibole from the granulite rocks of east Antarctica. Sri Lankan basement was also a part of the Antarctica during the Cambrian times (Shiraishi *et al.*, 2004) and composed of similar granulite rock types formed at same pressure, temperature and tectonic conditions. Therefore, minerals of the basement rocks of Sri Lanka may also contain fluoride in similar levels.

Published work on the determination of fluoride in minerals in the Sri Lankan rocks is extremely limited except for few studies reporting fluoride contents in mica (biotite) from charnockite and biotite-gneiss from north western Sri Lanka (e.g. Perchuk *et al.*, 2000) and

in apatite from a carbonatite complex in the north central part of Sri Lanka (Jayawardena, 1976; Pitawala *et al.*, 2003 and Pitawala and Lottermoser, 2012). However, the fluoride availability in other minerals of the Sri Lankan rocks is unknown. Jayawardena, (1976) reported fluoride of 1.5 - 2.5 % while Pitawala, *et al.* (2003) and Pitawala and Lottermoser, (2012) found fluoride contents ranging from ~3 - 4.6 % in apatite from carbonate rocks and ~2.7 - 3 % in marble. Thus, fluoride present in the most common minerals like mica and apatite from the Sri Lankan rocks may invariably act as a direct source for high fluoride contents in groundwater.

Dharmagunawardhane, (2001) observed a comparatively higher concentration of fluoride in water supply boreholes drilled in gneissic rocks and charnockite compared to those drilled in quartzite and marble in the crystalline terrain of dry zone in Sri Lanka. This situation indicates the possible contribution of mica, amphibole, titanite and apatite that are of frequent occurrence in gneiss and charnockite. It is therefore important to estimate the potential contribution from individual minerals either in fresh rock or in the regolith to groundwater fluoride content for delineation of vulnerable areas of fluoride risk.

This paper presents determination of fluoride content of minerals in the gneissic bedrock and regolith equivalent at three sites at Polonnaruwa in the North Central province of Sri Lanka. A mass balance of mineralogical contributions to the overall F budget of the bedrock and the weathered regolith is presented. The implications of the study for the release of fluoride from primary bedrock minerals as a consequence of weathering, and the ultimate mobilization of fluoride to the present day groundwater system were also discussed.

MATERIALS AND METHODS

Geology of the study area

Based on type, structure and age, rocks of Sri Lanka have been subdivided into four major terrains (Cooray, 1994); the Highland (HC), Wanni (WC), Vijayan (VC) and Kadugannawa Complexes (KC) as shown in the Figure 1(a). These terrains are composed predominantly of metamorphosed crystalline rocks with sedimentary rocks occurring at the extreme north

and north western parts of the country (Figure 1a). These four rock units display a diversity of rock types such as gneisses, amphibolites, charnockites, quartzites, calc-silicates and marbles. The present study was carried out in Polonnaruwa, which belonged to the HC (Figure 1).

Polonnaruwa is, located in the north-central province of Sri Lanka. The area is mainly underlain by charnockitic gneiss. The bedrock has a general strike of approximately North-South with a moderate dip ($40\text{--}50^\circ$) towards west (Figure 1b). Although outcrops of the bed rock are present at some places, the residual weathered overburden of varying thickness (up to a maximum thickness of about 10 m) covers the bedrock almost everywhere.

The Mineralogical composition of charnockitic gneiss has been first described by Vitanage, (1959) and reported that the essential minerals of the rock are hypersthene, green amphibole, plagioclase, K-feldspar, quartz and biotite. The important accessory minerals are apatite and zircon. The relative proportions of these minerals especially hypersthene, hornblende and biotite vary at different locations indicating heterogeneity of the protolith, hence showing differential weathering conditions.

Collection of Samples

Bedrock samples were collected in the middle part of the charnockitic gneiss band at outcrops of three locations representing both fresh rock and the overlying faintly weathered (but not decomposed) rock. The locations were selected

considering the occurrence of best representative outcrops on quarry faces in the area.

Analysis of minerals

Identification of minerals and the estimation of their abundance in rock samples were determined by petrographic (polarizing) microscope and scanning electron microscope (SEM) using thin sections of rock samples. Determination of fluoride concentration in individual minerals was done as point elemental analysis using SEM Energy Dispersive Spectra (EDS) observations. The relative fluoride abundance among minerals was determined based on energy dispersive X ray (EDX) analysis of electron microprobe. A mass balance of fluoride was derived by combining the determinations of mineralogical abundance and F content of the F bearing minerals.

RESULTS AND DISCUSSION

Petrography and Mineralogy

Petrographical observations on thin sections of charnockitic gneiss from all sites revealed that they are more or less homogeneous in mineralogical composition. Plagioclase, K-feldspar, hornblende, clino-pyroxene (diopside) orthopyroxene (hypersthene), quartz and biotite were major minerals while apatite, magnetite, sphene, ilmenite and zircon (rarely) were present as accessory minerals (Figure 2). Highly variable mineral proportions and textural features among samples such as grain size and orientation were noteworthy

Figure 1: (a) Litho-tectonic units of Sri Lanka (after Cooray, 1994) showing the study area. b) Sample locations showing the three sites. c) Fluoride distribution in groundwater of the study area.

The microscopic observation on weathered rock sections revealed early stages of weathering, particularly in biotite, hornblende and clinopyroxene (diopside), as disintegration and discoloration were observed along cleavages and grain boundaries (Figure 3). However,

plagioclase showed disintegration along grain boundaries and cleavages without significant discoloration on the surface. No significant alterations were visible in apatite other than slight increase of cracks on the grains (Figure 4).

Figure 2: Photo micrographs showing major and accessory minerals in the charnokitic gneiss country rock under plane polarized light (a,c) and cross polarized light (b,d) . PL:plagioclase, KF: K-feldspar, H: hornblende, CP: Clinopyroxene (diopside),OP: orthopyroxene (hypersthene), B: biotite, Q: quartz, A:apatite, S: sphene.

Figure 3: Photo micrographs showing biotite (B), hornblende (H), diopside (D) and plagioclase in weathered rock under plane polarized light (a) and cross polarized light (b)

Figure 4: Photo micrographs showing apatite (A) in fresh (a; plane polarized light, b; cross polarized light) and weathered rocks (c; plane polarized light, d; cross polarized light) with less visible alterations.

Table 1: Relative abundance of minerals in fresh and weathered rock at different sites (%)

	FRESH ROCK				WEATHERED ROCK			
	SITE1	SITE2	SITE3	AVERAGE	SITE1	SITE2	SITE3	AVERAGE
Apatite	0.75	0.2	0.5	0.48	0.5	0.1	0.1	0.23
Biotite	8	0	3	3.67	0	0	5	1.67
Titanite	0	10	0	3.33	8	1	0	3
Amphibole	40	20	15	25	0	30	0	10
Ortho pyroxene	0	0	5	1.67	0	1	0	0.33
Clino pyroxene	3	45	5	18.33	35	30	0	21.67
K- feldspr	2	0	5	2.33	2	0	5	2.33
Plagioclase	40	10	55	35	45	25	75	48.33
Quartz	2	10	10	7.33	2	10	10	7.33
Undetermined estimate	4.3	4.8	1.5	3.5	7	2.9	4.9	4.93
Total	100	100	100	101	100	100	100	100

Mineral composition

The relative abundance of minerals in fresh rock and weathered rock samples taken from three sites were observed under the petrographic microscope and their volume percentages were estimated (Table 1). The mineral proportions were found to be highly variable among the three sites and even between the fresh and weathered rock samples collected from the same site. Plagioclase is the most abundant mineral at all locations. Amphibole (hornblende) and pyroxene are also present in higher amounts but were variable. Quartz was found in low to moderate concentrations with a rather uniform distribution between fresh rock and weathered rock at each location. Biotite, K-feldspar, orthopyroxene (hypersthene) and sphene (titanite) concentrations were generally low and also their occurrences were highly irregular. Apatite was found in accessory amounts at all locations. Magnetite, zircon, and ilmenite were also found in few thin sections in minor accessory amounts. These three minerals and unidentified minerals are included under “undetermined estimate” in the Table 1.

Electron microprobe analysis

Electron microprobe analysis was carried out on 12 thin sections of rock samples from all three sites in order to obtain F concentrations of the representative minerals that were pre-selected based on petrographic observations. These representative minerals were further confirmed prior to quantitative analysis by comparing $K\alpha$ peaks of the energy dispersive X-ray

spectrometry (EDS). Contents of F and associated elements in minerals were obtained by application of multiple point analyses using energy dispersive X-ray spectrometry (EDS) of electron microprobe analysis.

The concentrations of F and other elements obtained were given in the Table 2. The results (Figure 5) showed that the range of F content in apatite (1.2-3.94%), Biotite (0.04-0.43%), Sphene (0.18-0.43) and hornblende (0.08-0.29) with an average fluoride concentrations of 2.61, 0.40, 0.32, and 0.22%, respectively. Pyroxene (hypersthene and diopside), plagioclase, K-feldspar and magnetite did not have appreciable or any F in them. Thus, results revealed that the main sources of F in the charnockitic gneiss of the study area are apatite, biotite, sphene (titanite) and amphibole (hornblende).

Relative abundance of fluoride

X-ray elemental mapping using EDX was done on thin sections of polished rock samples to obtain relative concentration of F in minerals where the brightness of spots in digital images are proportional to the elemental concentration. This method provided a facility to make a visual comparison of the relative concentrations (Figure 6). Results from the samples studied clearly indicate the consistency of the relative concentrations with those obtained by direct measurements as shown in the Figure 5.

Table 2: Electron microprobe data for analysed minerals (in wt%)

MINERAL*	PARAMETER	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	Cr ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	F	Cl	Total
APATITE (49)	MIN	0.09	0	0	0.03	0.02	0	0	39.17	0	0	35.75	1.28	0.05	99.55
	MAX	1.48	0.05	0.46	1.5	0.25	0.03	0.35	57.34	0.32	0.08	45.18	3.94	4.1	
	AVERAGE	0.25	0	0.02	0.18	0.08	0	0.02	54.51	0.06	0.01	41.4	2.61	1.08	
	MEDIAN	0.19	0	0.01	0.12	0.06	0	0.01	55.35	0.03	0	41.56	2.65	0.17	
	STDV	0.21	0.01	0.07	0.22	0.06	0.01	0.05	2.83	0.08	0.01	1.56	0.75	1.22	
BIOTITE (33)	MIN	31.35	0.09	12.06	8.84	0.01	0	3.12	0	0.01	0.1	0	0.04	0.02	93.56
	MAX	41.59	5.4	28.91	19.16	0.36	0.08	14.53	11.49	1.88	9.77	0.1	0.54	0.82	
	AVERAGE	35.84	4.46	15.13	17.2	0.14	0.02	11.14	1.2	0.24	7.72	0.03	0.4	0.26	
	MEDIAN	35.73	4.91	14.78	17.79	0.13	0.01	11.45	0.04	0.08	9.26	0.02	0.43	0.09	
	STDV	2.16	1.16	2.83	2.12	0.08	0.02	1.81	3.3	0.52	3.04	0.03	0.11	0.28	
SPHENE (19)	MIN	27.47	35	1.5	0.87	0.04	0	0	27.31	0	0	0.08	0.18	0	96.43
	MAX	29.71	37.01	2.44	1.33	0.1	0.03	0.03	28.81	0.06	0.02	0.31	0.43	0.03	
	AVERAGE	28.92	35.9	1.98	1.05	0.07	0.01	0.01	27.98	0.01	0	0.19	0.3	0.01	
	MEDIAN	29.07	35.68	1.85	1.04	0.07	0	0.01	27.93	0.01	0	0.19	0.31	0.01	
	STDV	0.56	0.71	0.34	0.13	0.02	0.01	0.01	0.42	0.01	0.01	0.06	0.08	0.01	
AMPHIBOLE (35) (Hornblende)	MIN	36.43	1.5	8.15	13.51	0.2	0	6.75	9.27	1.35	0.92	0	0.08	0.08	97
	MAX	42.02	2.41	13.45	21.68	0.67	0.07	11.41	11.76	1.96	2.2	0.04	0.29	1.65	
	AVERAGE	40.21	2.08	11.88	17.44	0.32	0.03	9.65	11.41	1.74	1.65	0.02	0.22	0.43	
	MEDIAN	40.26	2.12	12.02	17.01	0.32	0.02	9.98	11.48	1.74	1.56	0.02	0.23	0.1	
	STDV	1.15	0.22	1.02	1.94	0.09	0.02	1.14	0.41	0.17	0.28	0.01	0.05	0.56	
ORTHOPYROXENE (22) (Hypersthene)	MIN	41.25	0.06	0.74	24.64	0.64	0	12.51	0.56	0.02	0	0	0	0	98.37
	MAX	52.12	0.13	1.6	29.39	1.29	0.03	20.22	1	0.18	0.18	0.04	0	0.12	
	AVERAGE	50.05	0.08	1.12	28.35	0.91	0.01	17.1	0.68	0.05	0.02	0.01	0	0.02	
	MEDIAN	50.15	0.07	1.08	29.01	0.89	0.01	17.06	0.66	0.04	0.01	0	0	0.01	
	STDV	2.17	0.02	0.24	1.44	0.14	0.01	1.36	0.1	0.03	0.04	0.01	0	0.03	
CLINOPYROXENE (30) (Diopside)	MIN	47.34	0.04	0.84	8.59	0.29	0	8.04	10.64	0.09	0	0	0	0	97.66
	MAX	54.86	0.54	4.68	17.63	1.12	0.04	13.67	23.32	0.9	0.14	0.04	0.05	0.08	
	AVERAGE	49.18	0.27	2.5	13.34	0.41	0.02	10.07	21.17	0.66	0.01	0.01	0	0.01	
	MEDIAN	49.01	0.26	2.47	13.01	0.38	0.01	10.26	22.17	0.68	0	0.01	0	0.01	
	STDV	1.31	0.13	0.98	2.21	0.15	0.01	1.49	2.93	0.19	0.03	0.01	0.01	0.02	
K FELDSPAR (18)	MIN	61.95	0	17.91	0.02	0	0	0	0.01	0.73	7.17	0	0	0	99.07
	MAX	67.29	0.02	20	2.62	0.02	0.02	0.06	1.1	2.16	15.22	0.06	0.03	0.93	
	AVERAGE	65.5	0.01	19.33	0.2	0	0.01	0.01	0.21	1.1	12.64	0.01	0	0.06	
	MEDIAN	66.05	0	19.46	0.06	0	0	0	0.05	0.91	14.1	0.01	0	0.01	
	STDV	1.61	0.01	0.6	0.6	0.01	0.01	0.01	0.35	0.38	2.74	0.01	0.01	0.22	
PLAGIOCLASE (28)	MIN	58.96	0	25.65	0.1	0	0	0	6.01	1.31	0.19	0	0	0	100.8
	MAX	64.24	0.04	28.24	0.6	0.03	0.02	0.03	7.12	6.22	0.59	0.03	0.02	0.38	
	AVERAGE	62.13	0.01	26.75	0.18	0.01	0	0	6.4	4.84	0.43	0.01	0	0.02	
	MEDIAN	62.38	0.01	26.8	0.16	0	0	0	6.27	5.01	0.47	0	0	0.01	
	STDV	1.11	0.01	0.68	0.09	0.01	0.01	0	0.34	1.01	0.11	0.01	0	0.07	
MAGNETITE (19)	MIN	0	0.01	0.04	84.5	0.01	0	0	0	0	0	0	0	0	93.49
	MAX	5.38	0.34	1.89	95.71	0.11	0.17	1.2	0.61	0.11	0.13	0.03	0	0.05	
	AVERAGE	0.5	0.14	0.42	92.14	0.04	0.06	0.1	0.05	0.02	0.01	0.01	0	0.01	
	MEDIAN	0.07	0.11	0.39	94.59	0.04	0.05	0.03	0	0.01	0	0	0	0	
	STDV	1.38	0.09	0.38	3.97	0.03	0.06	0.27	0.15	0.03	0.03	0.01	0	0.01	

* Number within brackets indicate the total number of grains analysed.

Figure 5: Fluoride concentrations in minerals

Figure 6: (a) Back scattered electron image (BSE) showing different minerals; apatite (A), biotite (B), hornblende (H), plagioclase (PL) and ilmenite (I). (b-g) EDS X-ray images showing relative abundance of elements proportional to brightness. Fluoride (F), phosphorus (P), potassium (K), aluminum (Al) sodium (Na) and titanium (Ti).

Variations of F content between fresh and weathered rock

Fluoride concentrations in minerals of fresh and weathered rock samples were also determined separately (Table 1). Fluoride concentrations in the weathered minerals were obtained only at points where the surface is smooth in order to avoid non uniform signal response due to morphological effects (Table 3).

Loss of fluoride due to weathering is clearly noted in all four fluoride bearing minerals

(Table 3). The loss of fluoride in apatite was 19% from the original amount, in biotite it was 13%, in titanite (sphene) 30% and in amphibole (hornblende) 26% despite similar weathering conditions available for all the minerals. However, their initial fluoride concentration, chemical composition and relative easiness for weathering can influence the amount of loss of fluoride upon weathering. The net fluoride loss from the whole rock mass depends also on the abundance of each mineral in the rock.

Table 3: Relative abundance of minerals in fresh and weathered rock at different sites (%)

	FRESH ROCK				WEATHERED ROCK			
	SITE1	SITE2	SITE3	AVERAGE*	SITE1	SITE2	SITE3	AVERAGE*
Apatite	2.79	2.57	nd	2.68	2.16	nd	nd	2.16
Biotite	0.42	na	0.32	0.37	na	na	0.32	0.32
Titanite	na	0.37	na	0.37	0.26	0.26	na	0.26
Amphibole	0.24	0.21	nd	0.23	na	0.17	na	0.17
Ortho pyroxene	0	na	0	0	na	0	na	0
Clino pyroxene	0	0	0	0	0	0	na	0
K- feldspr	0	na	0	0	0	na	0	0
Plagioclase	0	0	0	0	0	0	0	0
Total	100	100	100	101	100	100	100	100

*average of measured values only

na; mineral not available, nd: not measured, quartz was considered as fluorine free

Table 4: Calculated fluoride budget of the country rock of the study area

	FRESH ROCK				WEATHERED ROCK (OVERBURDEN)		
	Density* (g/cc)	Abundance (%)	F- Concentration (wt%)	F content in mineral	Abundance (%)	F- Concentration (wt%)	F content in mineral
Apatite	3.18	0.48	2.68	0.0129	0.23	2.16	0.005
Biotite	2.9	3.67	0.37	0.0136	1.67	0.32	0.0053
Titanite	3.523	3.33	0.37	0.0123	3	0.26	0.0078
Amphibole	3.08	25	0.23	0.0563	10	0.17	0.017
Orthopyroxene	3.209	1.67			0.33		
Clino pyroxene	3.277	18.33			21.67		
K feldspr	2.565	2			2.33		
Plagioclase	2.7	33.33			48.33		
Quartz	2.62	7.33			7.33		
Total Fluoride content in rock (in wt%)				0.09501 (950ppm)			0.0351 (351ppm)

*Source : Carmichael and Raton 1989

Fluoride budget

$$\sum [v_i d_i] [F_i] = F_R \quad (1)$$

Whole rock fluoride content could reasonably be estimated if the volume percentage of the mineral, density of each constituent minerals and the fluoride concentration of each mineral are known using the following equation,

where, v_i is volume percent of mineral i , d_i is density of the mineral i , F_i is fluoride concentration (wt%) in mineral i and F_R is the fluoride concentration (wt%) in the rock.

However, in weathered rocks, fluoride can be present in secondary minerals and grain boundaries in variable amounts and therefore may not be detectable accurately with the above method. Hence, lower estimates of fluoride can result in weathered rocks. In addition, density of individual minerals can vary over a wide range causing erroneous estimates.

close to 3.0 g/cm³ (Table 3). Therefore, the same density value for all minerals was used and hence density correction (in equation 1) was not considered in the calculation.

Fluoride budget of the country rock of the study area was estimated as mentioned previously (Table 4). Densities of the minerals were obtained from the standard tables of mineral physical properties (Carmichael and Raton, 1989). The densities are almost equal and

The estimated fluoride concentration in the fresh country rock is consistent with the values obtained for gneissic rocks in other parts of the world (Tsunogae *et al.*, 2003). The estimated fluoride content of the weathered rock could however be lower than what is actually present in the rock because some fluoride may be present in secondary minerals and oxides that were not accounted for in the present study. The net loss of fluoride from each fluoride bearing mineral as

a weight percent age of the rock can be obtained from the difference of total fluoride (wt%) in fresh and weathered rocks. Thus, estimated loss of F from apatite, biotite, titanite (sphene) and amphibole (hornblende) are 0.0079, 0.0083, 0.0045 and 0.0393 (as a wt%) respectively.

Although fresh apatite has the highest concentration of fluoride compared to the other three fluoride bearing minerals in the study area, amphibole and biotite appear to be the dominant fluoride releasing minerals. Higher occurrence of amphibole in the country rock and its relative vulnerability for weathering compared to other coexisting fluoride bearing minerals probably could release high fluoride fluxes into groundwater. Apatite, though present in accessory amounts, was found in all rock samples (Table 1) indicating its more even distribution across the crystalline country rock. Therefore, its area wise contribution to groundwater fluoride could be expected to be more uniform. On the other hand, spatial distribution of amphibole and biotite was rather variable even within the same rock and hence anomalously high fluoride fluxes to groundwater can be expected in areas where these two minerals are of high abundance.

CONCLUSIONS

In charnockitic gneiss country rock in Polonnaruwa, Sri Lanka, fluoride was present in number of minerals including apatite (average 2.61%), biotite (average 0.40%) titanite (average 0.30%) and hornblende (average

0.22%). Plagioclase, K-feldspar, orthopyroxene-clinopyroxene and magnetite did not show any significant fluoride concentrations.

Loss of fluoride from individual fluoride bearing minerals and hence, from the whole rock mass as a result of weathering were evident. Amphibole (hornblende) which was present in high concentrations in the country rock appeared to be the most potential fluoride releasing agent through weathering. Biotite can also be considered as a significant fluoride source due to its comparatively high fluoride content, significant abundance and weathering prone nature.

Apatite, though present in accessory amounts, owing to its high fluoride content and uniform spatial distribution in country rock, may be considered as a steady fluoride donor to groundwater. This may cause elevated but more uniform fluoride distribution in the groundwater. On the contrary, amphibole and biotite may cause high fluoride anomalies in groundwater in areas of their high abundance. Since amphibole and biotite are found in a large number of crystalline rocks in Sri Lanka, they must also be considered as significant fluoride donors to groundwater.

Since mineral separation from rock mass is often not possible for wet chemical analysis in order to determine fluoride in minerals and rocks, *in situ* analysis by electron microprobe combined with petrography provide a rapid method of estimating the fluoride mass balance in any rock accurately.

REFERENCES

- Abu Rukah, Y., Alsokhny, K. (2004). Geochemical assessment of ground water contamination with special emphasis on fluoride concentration in North Jordan. *Chemie der Erde* **64**: 171-181.
- Bailey, J. C. (1977). Fluorine in Granitic Rocks and Melts: A Review. *Chemical Geology* **19**:1-42.
- Dharmagunawardhane, H.A., and Dissanayake, C.B., (1993). Fluoride Problems in Sri Lanka. *Journal of the Environmental Management and Health* **4**(2): 9-17.
- Dissanayake, C. B., (1989). Deep wells and Rural Development. *Journal of the Geological Society of Sri Lanka* **2**:1-4.
- Edmunds, W.M., Smedley, P.L. (2005). Fluoride in natural waters. In: Selinus, O. (Ed.), *Essentials of Medical Geology*. Elsevier Academic Press, London, 301-329.
- Fan, X., Parker, D. J., Reddy, D.V., Nagabhushanam, P., Skhija, B.S., Reddy, A.G.S., Smedley, P.L. (2010). Fluoride dynamics in the granitic aquifer of the Wailapally watershed, Nalgonda District, India. *Chemical Geology* **269**:278-289.
- Perchuk, L.L., Safonov, O.G., Gerya, T.V., Fu, B., Harlov, D.E. (2000). Mobility of components in metasomatic transformation and partial melting of gneisses: an example from Sri Lanka. *Contributions to Mineralogy and Petrology* **140**: 212-232.
- Pitawala, A., Schislowksi, M., Dahanayake, K., Hofmeister, W. (2003). Geochemical and petrological characteristics of Eppawala phosphate deposit, Sri Lanka. *Mineralium Deposita* **38**: 505-515.

- Pitawala, A., Lottermoser, B. G. (2012). Petrogenesis of the Eppawala carbonatites, Sri Lanka: A cathodoluminescence and electron microprobe study. *Mineralogy and Petrology* **105**: 57-70.
- Ramesham, V., Rajagopalan, K., 1985. Fluoride ingestion into the natural waters of ardrock reas, Peninsular India. *Journal of the Geological Society of India* **26**: 125–132
- Seneviratne, B. and Seneviratne, K. (1975), The distribution of Fluoride containing water in Ceylon. *Indian Journal of Medical Research* **63**:302.
- Seneviratne, B., Tambapillai, S., Hettiarachchi, J. and Seneviratne, K., (1974). Endemic Fluorosis of Ceylon. *Transactions of the Royal Society of Tropical Medicine and Hygiene* **68**(1) :105-103.
- Shaji, E., Bindu, Viju, J., Thambi, D.S. (2007). High fluoride in groundwater of Palghat district, Kerala. *Current Science* **92**: 240-245.
- Tsunogae, T., Osanai, Y., Owada, M., Toyoshima, T., Hokada, T., Crowe, W. (2003). High fluorine pargasites in ultrahigh temperature granulites from Tonagh Island in the Archean Napier Complex, East Antarctica. *Lithos* **70**: 21-38.
- Vitanage, P. W (1959). Geology of the country around Polonnaruwa. *Geological Survey of Ceylon* **1**: 75-79pp
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