



REDISTRIBUTION AND MASS CHANGE GEOCHEMISTRY DURING WEATHERING OF LATERITES FROM THE SWARNAGADDE PLATEAU, UTTAR KANNADA DISTRICT, KARNATAKA, INDIA

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ABSTRACT

The granite/granitic gneiss weathering in Swarnagadde plateau occurs in Uttar Kannada district of Karnataka state, forming low altitude flat topped laterite hills and plateaus adjoining part of Central Western Ghats, in the western continental margin of India. The laterite samples were highly weathered with chemical index of alteration ca.98.92%, nearly complete loss of Na, Ca, Mg and K in the ferruginous/aluminous zone. The alumina content mainly occurs as gibbsite, boehmite, diaspor and secondary clay minerals (kaolinite), where as iron content mainly occurs as goethite, and hematite in aluminous and scarce amount in ferruginous and lithomarge zone. Mineralogy and geochemistry study is the basis for the classification of these deposits, as aluminous laterites, ferruginous laterites and lithomargic clay. The major, trace elements, and mineralogical characteristics of laterites, these were formed in situ by the alteration of parents rocks of granite/granitic gneiss compositions. Significant depletion of base cations and Si, coupled with enrichment of Fe and Al, reveal that intense leaching of cations, kaolinization, desilication and ferruginization took place in lateritic deposits during weathering and lateritization. The study uses the geochemistry of immobile elements to trace the precursor rock of the laterite deposits and calculate the mass changes that took place during the weathering and lateritization processes. Plot of chemical data and calculation of correlation coefficients show that Al and Zr were immobile during the lateritization process and were used for mass change calculations. Mass changes were calculated from the concentration ratio of immobile elements for the different lateritic rocks and the granitic gneiss (parent). As only one linear trend is evident in the Al-Zr binary diagram and granitic gneiss coincides with this trend, on the basis of mass change and correlation coefficients analysis that the source of the Swarnagadde lateritic deposit was the underlying granitic gneiss.

KEYWORDS : mass change, correlation coefficients, immobile, concentrations, laterite.

1.INTRODUCTION

Laterites and aluminous laterites are the residual products mainly derived from a wide variety of parent rocks by intense chemical weathering under strongly oxidizing and leaching conditions of the area. Chemical weathering of rocks is one of the major processes which modify the Earth's surface and is one of the major processes in the geochemical cycling of elements [2]. As a result, the mobilization and redistribution of elements in weathered products is much different from that of parent rocks [18, 22]. The rate and nature of chemical weathering is controlled by various factors such as parent rock type, topography, climate and biological activities and, mainly the residual accumulation of aluminium ore, aluminium is considered to be an immobile element during weathering that is concentrated in situ as inert lateritization residue [1, 6, 14]. During chemical weathering the elements Al, Fe and Ti tend to combined with secondary minerals and retained in the weathering profile [4, 19, 20], on the other hand, the elements such as Na, K, Mg and Ca do not react with other elements and are removed in the percolating groundwater (lower pH) through the fissures and fractured zones.

Kaolinite, gibbsite and other oxides are formed in these bleached or oxidized zones, because all dissolved salts are removed [27]. The behaviour of trace elements during weathering is complicated because these elements are affected by various processes such as dissolution of primary minerals, formation of secondary minerals, redox processes, transport of material, coprecipitation and ion exchange on various minerals [4, 5, 7, 8, 10, 18, 22]. On the contrary elements that are predominantly hosted in highly resistant minerals, such as Ti, Ta, Cr, Nb, Zr and Hf in granitic rocks are believed to be immobile [5, 14, 19]. The study uses the geochemistry of immobile elements to trace the precursor rock of the laterite deposits and calculate the mass changes that took place during the weathering and lateritization processes. Plot of chemical data and calculation of correlation coefficients show that Al and Zr were immobile during the lateritization process and were used for mass change calculations. Mass changes were calculated from the concentration ratio of immobile elements for the different lateritic rocks and the granitic gneiss (parent). As only one linear trend is evident in the Al-Zr binary diagram and granitic gneiss coincides with this trend, on the basis of mass change and correlation coefficients analysis that the source of the Swarnagadde lateritic deposit was the underlying granitic gneiss.

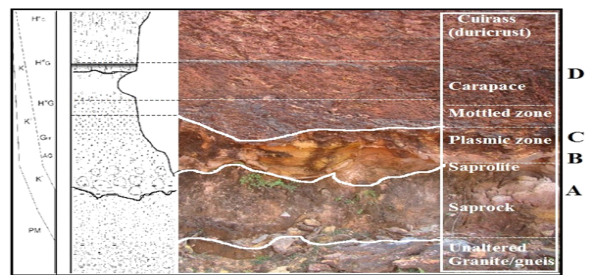


Figure 1 Field photograph of complete weathered lateritic profile of the study area showing different zones from protolith to top duricrust.

2.GEOLOGICAL SETTING

The investigated area comprises the coastal margin of western peninsular India between 14° 18' to 14° 24'N and 74° 24' to 74° 30'E of the India Toposheet No-47J/7. The coastal lowlands of western India lying between the Arabian Sea and the foot of the Western Ghats escarpment are known as Konkan in Maharashtra, Kanara in Karnataka and Malabar in Kerala States. However, occurrence of these lateritic deposits as clusters of plateaux over large tracts of lowlands. The most widespread occurrences of laterites within the Western India have been recognized in a series of different geological-geomorphological settings, and are found in two distinct geomorphological zones: (i) capping the elevated basalt mesas of the Western Ghats, where they are developed upon the Deccan lavas [25, 29, 30] and (ii) an extensive, semi-continuous belt lying to the west of the main Western Ghats escarpment between Bombay and Mangalore capping the coastal plateaux of the outer Konkan plain [28]. The Western Ghats escarpment is preceded by a ramp of dissected laterite-capped mesas which slope gently from altitude of ca. 180 to 200m in the east of the coastal plain, to ca. 80 to 100m adjacent to the coast. A second generation of laterite mesas is particularly prominent in estuarine regions and occupies a lower elevation of 60 to 70m. The study area is characterized by Precambrian crystalline rocks (Granites, Granitic gneisses and Schists), laterites and basic dykes. The oldest rock of the study area is granitic gneiss and these are predominantly of tonalite in nature and are comparable to similar early Precambrian

granitic gneiss of other shield areas of the world. Granitic gneiss/granites cover major portion of the coastal tract, which is the North-Western coastal continuation of peninsular gneisses or Northern continuation of South Kanara gneisses/granites. The gneisses form prominent hills and headlands along the coasts, however, the granites are present as patches within gneisses.

3.MATERIALS AND METHODS

In order to understand geochemical characteristics of major and trace elements of laterite deposits from Swarnagadde plateau, Uttara Kannada district, a complete weathering profile was selected. Geological field mapping was carried out between April and May, 2010 and 2011, nearly 30 representative samples were collected from different profiles (at the interval of 0.25 to 0.5 m and 1 m) in vertical section of laterite mining quarries and recent road cuttings of the study area. Sampling of weathered crust began from the protolith (parent

rock) and the interval within profile was determined based on the lithological, mineralogical and physical characters. The colour of the weathered material is brown to reddish brown or brown to yellowish brown which is mainly due to hard bed rock.

Determination of chemical composition, fourteen samples were selected and analyzed by using inductively coupled plasma optical emission spectroscopy (ICP-OES for major and minor oxides) and inductively coupled plasma mass spectroscopy (ICP-MS for trace and rare earth elements) with fusion opening (lithium borate) and, with 4-acid digestion. Loss on ignition (LOI) values was measured by weight reduction of the samples after 1 hr heating at 1,000° C. detection limit for SiO₂, Fe₂O₃, CaO, MgO, Na₂O, K₂O, TiO₂, P₂O₅ are 0.01 wt. %; Cr₂O₃ 0.002 wt%. Detection limit for trace elements is 0.5 ppm and for rare earth elements 0.1 ppm. The results of the chemical analysis are presented in the Table.1.

Table 1 Concentration values of Major, Minor (wt %) and Trace (ppm) elements in samples taken from the lateritic deposit of the study area.

Sample	BS-18	BS-11	BS-10	BS-22	BS-06	BS-08	BS-32	BS-36	BS-46	BS-25	BS-42	BS-33	BS-53	BS-56	BS-60	Gr.Gn Ave(6)
Depth (m)	0.5	1.5	2.5	3.5	4.5	5.5	6.5	7.5	8.5	9.5	10.5	11	12	12.5	13	14
SiO ₂ (%)	8.55	12.76	15.21	18.45	11.90	12.29	12.48	14.22	41.29	48.17	45.32	58.29	54.10	59.73	62.31	71.99
TiO ₂	1.66	1.12	1.10	1.70	1.79	1.79	1.80	1.81	1.75	1.38	1.86	1.58	1.71	1.41	1.12	0.35
Al ₂ O ₃	24.92	23.66	25.53	22.14	39.67	41.13	41.86	48.43	38.61	36.14	33.56	24.18	24.80	23.27	20.63	15.22
Fe ₂ O ₃	48.44	47.11	41.58	44.17	22.66	20.06	18.76	7.06	2.85	2.53	3.25	2.97	3.60	2.92	3.01	2.40
MnO	0.03	0.01	0.08	0.01	0.14	0.15	0.13	0.17	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05
CaO	0.09	0.07	0.07	0.06	0.07	0.06	0.06	0.05	0.21	0.05	0.05	0.05	0.05	0.12	0.27	0.81
Na ₂ O	0.05	0.01	0.05	0.01	0.02	0.11	0.02	0.01	0.09	0.06	0.05	0.11	0.13	0.79	2.16	5.06
MgO	0.08	0.13	0.12	0.13	0.02	0.02	0.02	0.01	0.36	0.37	0.21	0.68	0.46	0.69	0.64	0.78
K ₂ O	0.31	0.21	0.24	0.07	0.02	0.02	0.02	0.01	0.15	0.24	0.38	0.31	0.21	0.44	0.66	1.17
P ₂ O ₅	0.14	0.86	0.19	0.07	0.13	0.13	0.13	0.13	0.06	0.56	0.08	0.17	0.16	0.16	0.12	0.06
LOI	15.25	13.51	15.34	12.76	22.94	23.71	24.09	27.55	14.56	10.25	15.18	11.65	14.67	10.40	8.84	1.75
Total	99.61	99.63	99.58	99.64	99.55	99.55	99.54	99.57	100.83	99.88	100.05	100.09	100.19	100.02	99.89	99.49
(ppm) Ag	1.07	0.03	0.65	0.88	1.47	1.47	1.48	1.49	0.79	2.44	1.53	1.57	1.16	0.03	1.16	0.59
Be	0.57	1.20	0.67	0.03	1.10	0.28	0.57	0.03	0.64	0.90	0.37	0.03	0.03	0.03	1.45	1.03
Co	3.07	9.42	7.72	3.14	26.68	29.03	30.21	40.79	21.48	66.60	41.87	42.95	31.81	37.83	24.85	2.84
Cr	61.60	123.20	54.70	47.90	74.41	75.69	76.33	82.10	39.36	114.68	80.41	78.71	59.67	<0.05	59.67	41.10
Cs	0.68	1.09	1.09	0.03	0.34	0.31	0.29	0.14	0.06	0.17	0.13	0.13	0.10	0.16	0.23	0.37
Cu	42.16	52.10	27.74	25.95	28.45	26.94	26.19	19.43	9.17	26.42	18.88	18.34	13.96	17.26	14.15	7.74
Ga	45.67	28.95	35.77	30.09	57.41	58.65	59.28	64.87	31.08	90.53	63.52	62.16	47.13	57.40	44.47	21.34
Hf	3.61	2.84	2.49	2.74	4.57	4.66	4.71	5.11	2.33	6.56	4.89	4.67	3.58	4.24	3.12	1.19
Li	3.05	7.27	6.50	1.99	2.70	2.52	4.47	3.41	3.64	6.44	6.69	6.93	4.68	7.12	6.78	8.66
Mo	9.50	13.51	5.72	13.23	7.87	7.68	7.59	6.73	3.57	11.11	6.93	7.13	5.27	6.48	4.76	1.18
Nb	16.76	8.77	10.91	13.39	19.72	20.03	20.18	21.57	11.17	34.29	21.96	22.35	16.62	19.83	13.40	2.09
Ni	40.86	101.69	61.57	88.89	46.49	47.04	47.31	49.77	23.10	65.72	47.98	46.19	35.32	40.93	27.70	4.82
Pb	21.46	27.58	22.31	18.15	29.83	30.61	31.00	34.51	15.78	44.39	33.04	31.56	24.23	29.49	23.71	11.07
Rb	11.97	11.50	12.22	2.52	5.69	5.05	4.73	1.85	0.77	2.00	1.69	1.54	1.21	6.75	17.08	37.77
Sb	5.56	9.28	3.64	2.13	3.78	3.62	3.54	2.83	1.29	3.62	2.71	2.58	1.98	0.03	1.98	0.03
Sc	34.85	28.86	23.35	20.50	25.49	24.50	24.01	19.59	9.03	25.57	18.82	18.06	13.83	16.02	10.90	1.69
Se	3.27	2.87	1.28	3.43	1.75	1.63	1.57	1.04	0.51	1.50	1.02	1.01	0.76	1.09	1.15	1.20
Sn	0.03	0.03	0.03	0.03	1.78	1.65	1.62	1.76	0.77	2.09	1.65	1.54	1.20	0.03	1.20	0.71
Sr	30.68	17.58	18.05	13.45	31.88	31.96	32.00	32.37	15.52	45.25	31.71	31.05	23.53	113.10	274.84	605.49
Ta	1.07	0.59	0.76	0.88	1.27	1.29	1.30	1.38	0.62	1.74	1.31	1.25	0.96	0.03	0.96	0.03
Th	19.59	13.71	17.22	11.13	23.25	23.60	23.78	25.37	11.70	33.13	24.38	23.40	17.92	20.83	14.35	2.93
U	4.66	6.08	3.81	2.16	4.77	4.76	4.76	4.73	1.76	4.08	4.13	3.53	2.87	3.16	2.24	0.74
W	1.77	1.35	1.30	1.08	1.96	1.98	1.99	2.09	1.03	3.05	2.08	2.06	1.55	0.03	1.55	0.03
Y	6.87	4.73	4.29	3.82	7.11	7.12	7.13	7.17	3.34	9.53	6.93	6.68	5.10	6.71	6.29	4.48
Zn	32.55	41.57	29.29	17.58	33.40	33.56	33.65	34.39	18.31	57.16	35.51	36.62	27.05	40.95	46.63	63.61
Zr	84.44	97.34	89.07	62.26	73.48	77.03	78.80	94.77	73.28	71.63	70.67	66.56	88.96	75.37	86.41	73.50

4.RESULTS AND DISCUSSION

Results of Major and Trace elements geochemistry:

The results of chemical composition of the lateritic deposits across the studied profile and granite/granitic gneiss parent rocks shows SiO₂, Al₂O₃ and Fe₂O₃ domain (Table. 1). The concentration of silica content ranges from 8.55 to 62.31%, decreasing from the base parent granitic rock (average 71.99%) towards the top of the weathered profile, which corresponds to the transition from the aluminous/ferruginous crust to the covering soil (Fig. 1). The content of Al/Fe reflects the variable kaolinite content, which is more at the base and absent near the top of the profile indicating formation of secondary minerals with the increase intensity of weathering. The concentration of Fe₂O₃ ranges from 2.53 to 48.44% (average 2.40%), which is typical of lateritic profile and is higher than the aluminous crust. The Al₂O₃ content is slightly enriched comparatively Fe₂O₃ and ranges from 20.63 to

48.43% (average 15.22%) increasing upward over the lithomargic clay horizon. Al and Ti are strongly enriched in the weathered lateritic deposit of the study area. The Fe content reaches a maximum in the ferruginous laterites indicating further there is no development of bauxitization course. Concentration of MgO (0.01-0.69%), CaO (0.05-0.27%), Na₂O (0.01-2.16%) and K₂O (0.1-0.66%) are dramatically lower than in the fresh granite/granitic gneiss. Loss on ignition (LOI) ranges from 8.84 to 27.55% of the weathering products, and LOI in the lower sections is generally higher than the upper section of the profile. In general Al, Ti and trace elements Zr, Cr, Co, Hf, Ga, Mo, Th, Nb, and Y get enriched through all parts of the lateritic profile. The highest amount of Sr is observed in the granite/granitic gneiss of the Swarnagadde plateau (Table 1), probably because of the same ionic radius (charge) as Ca²⁺ [11]. The content of Sr depleted in the ferruginous/aluminous and lithomargic clay zone.

4.1 Mobilization and redistribution of elements using mass change calculation method

Though there are several indexes, such as chemical index of alteration (CIA) and intensity of chemical weathering (CIW) have been proposed to evaluate the intensity of chemical weathering [9, 18, 23]. In general these indices are calculated mainly from concentrations of mobile elements, such as CaO, Na₂O and K₂O, these indexes are suitable only for incipient to moderate weathering, and inappropriate use for intensive (strong) chemical weathering [12, 13, 20, 24]. These oxides are even considerably lower than those reported from the advanced zone [16]. The CIA values of lateritic profile are greater than 99%, and very high concentrations of Al₂O₃, Fe₂O₃ and TiO₂, with maximum values up to 48.43%, 48.48% and 1.86% respectively, suggesting that the chemical weathering intensity in this profile could be categorized as extreme [20]. According to MacLean et al [14] use of immobile elements that are suitable to trace the source of the Al to a particular rock type or unit. In general, some chemical elements, particularly Zr, Ti and Cr are strongly immobile [14] during weathering and diagenesis of laterite. Mass changes coupled with lateritization can be estimated by comparison of the concentrations of immobile elements relatively fresh granite/granitic gneiss and weathered lateritic rock samples. Estimating the gains or losses of mass are based on the relative abundance of immobile elements remaining unchanged when other more mobile elements are lost or gained. Thus, it is possible to calculate precursor compositions for laterites, and to deduce the amount of mass changes during lateritization.

4.2. Mass change calculation.

Mass changes can be calculated from the following relations of MacLean and Kranidiotis [12] and MacLean [12]. An enrichment factor (EF) first calculated for each sample, followed by obtaining reconstructed composition (RC), based on the EF, and finally obtaining mass change based on reconstructed composition (RC):

- 1) $EF = \frac{Zr \text{ in precursor rock}}{Zr \text{ weathered sample}}$
- 2) $RC = \% \text{ component in altered rock} \times EF$ and
- 3) $MC = RC - \text{precursor composition}$

The immobile element selected for evaluating element mobilization may vary in different profiles. K has been used to evaluate the mobility of alkali and alkaline earth elements during incipient weathering processes [22], and Zr is used in granitic weathering profiles [19]. The order of major and some trace elements mobility in profiles are Ca > Na > Mg > Fe > K > Si > Al > Ti > Zr. In our study Zr is selected as an immobile (monitor) element to trace the precursor rock, mobility and redistribution of individual elements during the chemical weathering of the profile.

5. DISCUSSION.

The mass change values of the lateritic profiles shows that Al₂O₃, Fe₂O₃, TiO₂ are enriched in laterites, where as other major oxides such as SiO₂ and MgO are depleted relative to the parent rock, Si decreases with an increasing degree of alteration. The downward movement of a small amount of Al within the lateritic profile is seen in fig. 2 & 3. The maximum amount of Al is concentrated in aluminous laterite, this may be because of Al was leached from the upper layers. Since Al is least soluble in neutral pH groundwater, the downward migration in solution is due to seasonal fluctuation in pH of the saline groundwater [3]. In some profiles P₂O₅ and MnO are enriched. Both Al and Fe are considered to be immobile during weathering, the observable profiles (Fig. 3) shows that these elements are not mobilized [15]. In general, major elements such as Na, Ca and K are concentrated mainly in feldspars. The significant decrease trends for Na, Ca and K in the weathering profile reflect the alteration of feldspars (Fig. 2 & 3). Both Ca and Na decreases more rapidly than K, these trends reflect primarily from the greater alteration rate of plagioclase compared to K-feldspar.

Figure 2 Mass changes in the Swarnagadde lateritic deposits relative to the granite/granitic gneiss. The mass changes can be considered as enrichment and depletion in wt. % or grams per 100g of the granitic gneiss precursor.

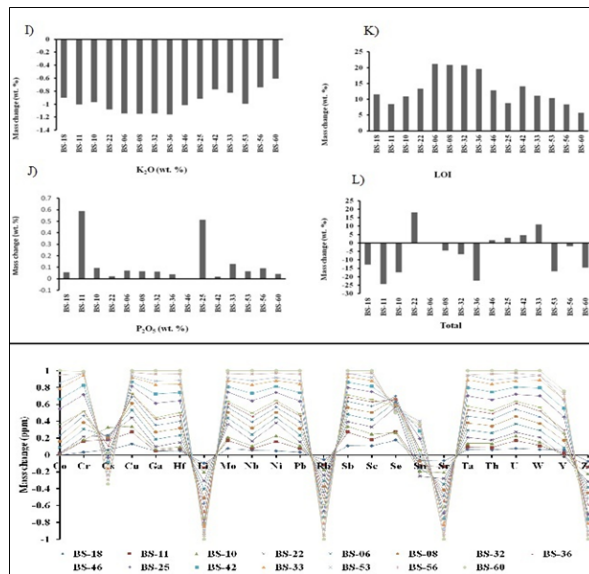


Figure 3 Mass changes in the Swarnagadde lateritic deposits relative to the granite/granitic gneiss. The mass changes can be considered as enrichment and depletion in wt. % or grams per 100g of the granitic gneiss precursor.

Alkali and alkaline earth metals like Cs, Li, Rb and Sr are removed from the aluminous and ferruginous laterite profiles of the area. On the other hand elements such as Zr, Hf, Th, Nb, Sc and REE are remained immobile during incipient to moderate stages of weathering [15]. However, Zr and Hf and Ta were the only elements that showed no mobility under extreme alteration stages.

The mass change values support the general observation that during chemical weathering of virtually all types of rocks, loss of elements rather the gain are more prevalent because most of the elements are leached during weathering [15]. A critical assessment of the loss or gain of the studied lateritic profile show that Al₂O₃, TiO₂ and Fe₂O₃ are enriched in the laterite indicating probable iron and alumina enrichment.

6. CONCLUSIONS

Mass change calculations have been used to determine elements mobility in granite/granitic gneiss during weathering. Mobilities are calculated from geochemical data normalized with respect to Zr in the fresh parent rock. Kaolinite, gibbsite and quartz are the most important minerals in the aluminous laterites of the Swarnagadde area. Whereas, hematite, goethite, kaolinite and scarce amount of anatase is present in top layer of the ferruginous laterite. These minerals are scarce except kaolinite in lithomargic clay zone of the weathering profile.

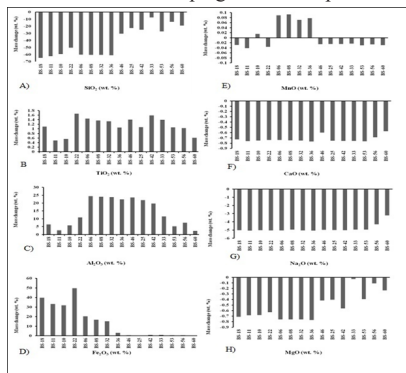
Weathered profile overlying granite/granitic gneiss in the Swarnagadde plateau show three distinct horizons; top ferruginous laterite, aluminous laterite and lithomargic clay (saprolite) based on their colour, textures and structures. The mineralogy along the profile shows moderate to extreme (strong) weathering; it is confirmed with the CIA values. The trend of weathering and lateritization is towards enrichment of aluminium and progression towards the formation of lateritic bauxite.

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