MINERALOGY AND GEOCHEMISTRY OF RED AND BLACK SEDIMENTS OF THOOTHUKUDI DISTRICT, TAMILNADU, INDIA

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ABSTRACT

The coastal sedimentary belt between Kulathur and Surangudi villages of Thoothukudi district in South India, located within the latitudes $9^0 00' \text{ N} - 9^0 06' \text{ N}$ and longitudes $78^{\circ}16$ ' E – $78^{\circ}18$ ' E, is mainly covered by black soil sediments and detached outcrops of red (teri) sediments. The petrological and mineralogical study reveals that red (teri) sediments had originated within black sediments as in-situ deposits. The reddening may be due to leaching and oxidation under favourable climatic conditions of iron bearing heavy minerals like garnet, ilmenite, hypersthene etc., present in the sediments. The calcrete deposition by evapotranspiration of ground water process develops micritic calcite veins with nodular and mottled texture within the red sediments. The presence of angular, spherical and sub spherical quartz grains in compact red sandstone of bottom profile indicates fluvio-marine (coastal aeolian action) origin. The major element geochemistry of black and red sediments of the study area shows that both the sediment types have more or less similar distribution of major element oxides. The major SiO₂, Al₂O₃, Fe₂O₃ and TiO₂ oxides are in high concentrations (> 1%), whereas K_2O , Na_2O , MgO and P_2O_5 oxides have low concentrations (< 1%). The correlation study between the sources of elements of the sediments indicates their geochemical affinities during sedimentation. Further, the study of major elements helps to interpret provenance, depositional environment, classification, chemical maturity index and climatic attributes of the sediments of the study area.

Key Words: *red* (*teri*) *sediments, major element chemistry, provenance, chemical maturity index*

INTRODUCTION

The Sub – Recent red (teri) sand dune outcrops amidst black soil terrain occurring as detached patches in the coastal belt of Ramanathapuram and Tuticorin districts in South India are omnipresent. The top surface of the bed is generally loose and unconsolidated, whereas the subsurface beds below 1 m are very hard and compact, due to consolidation. Teri sand outcrops are groundwater potential zone which promote calcrete occurrence not only as veining, but also with nodular and mottled texture. The origin of red (teri) sediments in the coastal region is geologically under debate. Early researchers (Thiruvikramji *et. al.*, 2008) have discussed the teri sand of Sathankulam deposit in Tuticorin district as a Saga of Holocene climatic change. Teri deposit is highly enriched with minerals like - garnet, ilmenite, rutile, monazite and hypersthene etc. Due to mineral wealth of teri sand dunes, various companies such as Transworld Garnet, Beach Mineral Company (BMC), Indian Ocean Garnet Sand (IOGS), Tata etc., are concentrating their mining activities on these deposits. On support of their activities, for the welfare of the society, an attempt has been made in this paper to delineate the mineralogy, petrology and their depositional environments. Except for one or two minor reports, no research work has been carried out previously on the soil outcrops of Kulathur and Surangudi area to shed light on petro mineralogy, provenance, geochemical

implications and climatic significance of the depositional environment.

GEOLOGICAL SETTING

The Proterozoic hard basement rocks of the study area are located at depths of 25 m below ground level. The quartzite, calc - silicates and crystalline limestone, khondalite, charnockite and pink granite were observed from the adjacent hard rock terrains as well as from the deep well sections of the coastal study area. The basement rock is overlain by Tertiary calcareous sandstone and argillaceous limestone. They are followed by sub - recent black and red soils occurring as surface formations. The terrain is generally a plain formed with red dunes maximum elevation of 46 m above MSL. The overall drainage density of the study area is low and two ephemeral rivers, Vaippar and Vembar, are running within the study area. The annual rainfall of the study area is approximately 600 mm characterized by the tropical climatic conditions. The stratigraphic succession is shown in the Table 1. The study area covers the villages of Kulathur and Surangudi located at a

distance of 28 km and 45 km respectively from Tuticorin town. Further, it is well connected in the Tuticorin and Rameshwaram state highway.

METHODOLOGY

Ten samples of red and black soil including compact red sandstone were collected from different locations within the latitude from N9° 00' to N9° 06' and longitudes from 78° 16' E to 78° 18' E located between Kulathur and Surangudi villages (Figure 1). Both black and red sediments samples were analyzed for major elements geochemistry by X-Ray Fluorescence (XRF) method. The samples were analyzed at the XRF laboratory of National Geophysical Research Institute (NGRI), Hyderabad. The compact red sandstone was prepared for micro thin section analysis to study the petrological and mineralogical characters. They were then photographed under binocular petrological microscope.

 Table 1. Stratigraphy of Study Area

Age	Depth Below Ground Level (metres)	Lithology					
Recent		Soils (Black and Red sediments and compact					
to Sub –	10	Red Sandstone) with Calcrete					
Recent							
Tertiary	10-25	Hard compact calcareous sandstone and shell limestone					
Proterozoic	below 25	Hard basement rocks – pegmatite, granite, charnockite, khondalite, calc silicate, crystalline limestone and quartzite.					



Figure 1. Location map of the study area

FIELD OBSERVATIONS

The field observations indicate that the red sediments (teri sediments) occur as detached patches within the black soil. Both black and red soils contain calcrete deposits as granules, nodules, veins and chalk occurring within the sediments (Figures 2a - 2f). Such deposits have also been reported in the regolith deposits of Australia (Hill *et al.*, 1999). The gradation or mixing of red and black soils in the study area suggests that the red soil has originated as local deposit, and formed by leaching and oxidation of iron bearing minerals present in the black soil under alternating semi-arid and arid conditions.

MINERALOGICAL OBSERVATIONS

Mineralogical observations reveal the presence of minerals such as spherical, sub spherical and angular quartz, altered feldspar, perthite, hypersthene, garnet, ilmenite, rutile, magnetite and zircon in the sediments (Figures 3a - 3f). It appears that sediments have formed early as a fluvial black soil regolith deposit originating from source rocks such as khondalite, charnockite, quartzite and granite etc. They were deposited by the rivers Vaippar and Vembar. The iron-rich heavy minerals of garnet, ilmenite hypersthene, rutile etc, present in black soil have undergone leaching and oxidation processes insitu due to favourable climatic conditions, which have caused reddening within the black soil. The presence of spherical and sub spherical quartz indicate that the sediments have a long transport history due to fluvial action (Figures 3b & 3f). The presence of angular and sub angular quartz in the sediments reveals the lesser transport history of aeolian action of coastal winds (Figures 3c, 3e). The foregoing observations support the characterization of these sediments as fluvio - marine deposits. The calcrete deposition in the regolith part of the study area may be due to evapo-transportation of alkaline rich groundwater originated from the source rock of calcareous sandstone aquifer of Tertiary age found below the soil horizons. This had given rise to micritic calcite rimming, coating, microbial filament-rich stratification and veining structures around unaltered detrial quartz grains.

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Figures 2a-2f. (field photographs). (2a) A view of the contact between black soil and red soil occurrences at Kulathur village. (2b) A view of gradation of black and red soil occurrences with calcrete lining noticed in Melmanthai village. (2c) A view of compact red sandstone with calcrete layer at Surangudi village. (2d) A view of the Vaipar river at Melavaippar village. (2e) A subsurface argillaceous limestone outcrop in Pond section of the Surangudi village north. (2f) A view of Red (teri) sand elevated dunes outcrop, Surangudi village east.



Figures 3a-3f. Photomicrographs: 3(a) Micrite precipitation (calcrete vein) in teri and black soil with quartz, ilmenite and magnetite grains under reflected plane polarized light from Melmanthai village.; 3(b) Detrital spherical quartz surrounded by ferruginous cementing medium in red sand stone under reflected plane polarized light from Surangudi village; 3(c) Quartz, ilmenite, rutile, clay with calcification and red cement under reflected plane polarized light from Surangudi village; 3(d) Garnet with high relief and surrounded by ferruginous cement in red teri sandstone under reflected plane polarized light from Surangudi village; 3(e) Hypersthene and quartz in red sandstone under reflected plane polarized light from Surangudi village; 3(f) The black soil having quartz surrounded by micritic calcite rimming under reflected plane polarized light from Melmanthai village.

GEOCHEMICAL OBSERVATIONS

The distribution of major elements of both black and red sediments of study area shows more or less similar trend of major element oxides (Figure 4 and Table 2). The distribution of SiO₂, Al₂O₃, Fe₂O₃ and TiO₂ oxides are in elevated concentrations above 1%, whereas the other elements such as K₂O, MgO, Na₂O, MnO and P₂O₅ oxides are in low concentrations below 1%. The major element compositions of both black and red sediments are taken into account for geochemical correlation studies, as they show similar distribution trends.

The average SiO₂ content of black and red sediments is 58.89%, whereas the average distribution of Al₂O₃ is 11.33%. The Al concentration is attributed to a good measure of transported flux (Ramasamy *et al.*, 2007). The little variation in silica percentage in red (teri) sediments with the black sediment may be due to deposition of angular quartz grains by aeolian action on sand dune deposits. The distribution of Al₂O₃ shows an inverse relationship to that of

 SiO_2 and shows a low degree of negative correlation (r = - 0.3) suggesting that they could have derived from different sources. When compared to aluminum, the SiO_2 concentration is dominant in all the sediments. This may be due to the supply of more unaltered quartz from the adjacent quartzite terrain by fluvial action and the added source of coastal wind-blown quartz grains deposited on sand dunes. The availability of spherical and angular quartz grains in thin sections also supports their fluviomarine origin.

The K_2O/Al_2O_3 ratio of the sediments can be used as an indicator of their original composition. The K_2O/Al_2O_3 ratios for clay minerals and feldspars are different (0.00 to 0.3; 0.3 to 0.9) respectively (Cox *et al.*, 1995). The average K_2O/Al_2O_3 ratio for the studied sediments is 0.1 which is close to the limit of clay mineral range which suggests that kaolin or illite as the dominant clay mineral in the sediments. The higher SiO_2/Al_2O_3 coupled with SiO_2 and MgO in Proterozoic Pakhal shale in India suggest fairly good amount of felsic source in the provenance (Dayal and Moorthi, 2006). The SiO_2/Al_2O_3 coupled with SiO_2/MgO ratio in the sediments of the study area and is different from the condition of Pakhal shale, which suggests mixing of felsic and mafelsic sources.

Titanium is concentrated mainly in phyllosilicates (Condie et al., 1992; Ramasamy et al., 2007) and is relatively immobile compared to other elements during various sedimentary processes and may strongly represent the source rock (Mc.Lennan et al., 1993; Ramasamy et al., 2007). The black and red sediments of the study area show lower TiO₂ values with an average of 1.15%. The correlation study between TiO₂ and Al₂O₃ shows positive correlation (r=0.5). It indicates that these elements have concentrated from the similar sources. Most of the samples of the study area have low P₂O₅ contents. The deflection of P_2O_5 contents may be explained by presence of lesser amounts of accessory phases such as apatite and monazite minerals.



Figure 4. Distribution of major elements in red and black sediments of the study area

Element (%)	Red Sediments		Black Sediments			Red Sediments	Black Sediments	Red Sandstone		Avg. Sample	
	1	2	3	4	5	6	7	8	9	10	(%)
SiO ₂	61.39	60.21	59.07	57.06	51.87	53.61	61.32	60.83	63.10	60.43	58.89
Al ₂ O ₃	11.82	10.40	11.84	10.30	11.90	12.10	11.30	11.13	11.40	11.08	11.33
Fe ₂ O ₃	3.63	3.53	3.86	3.32	4.52	3.91	3.14	2.79	2.86	2.63	3.42
MnO	0.07	0.06	0.10	0.06	0.10	0.08	0.03	0.04	0.05	0.03	0.06
MgO	0.10	0.08	1.57	1.36	1.42	1.40	0.10	0.12	0.10	0.11	0.64
CaO	1.19	1.16	1.39	1.36	0.92	0.90	0.43	0.22	0.36	0.18	0.81
Na ₂ O	0.20	0.17	0.16	0.12	0.17	0.18	0.07	0.09	0.15	0.08	0.14
K ₂ O	1.15	1.12	1.25	1.21	0.96	0.92	0.83	0.81	0.84	0.80	0.99
TiO ₂	1.17	1.15	1.09	1.05	1.68	1.59	1.10	0.90	0.89	0.88	1.15
P_2O_5	0.06	0.04	0.10	0.06	0.05	0.04	0.03	0.03	0.02	0.02	0.05
K ₂ O/ Na ₂ O	5.75	6.58	7.81	10.08	5.64	5.10	11.85	9.00	5.60	10.00	7.74
SiO ₂ /Al ₂ O ₃	5.19	5.78	4.98	5.53	4.36	4.43	5.42	5.46	5.53	5.45	5.21
SiO ₂ /MgO	613.9	752.62	57.62	41.95	36.52	38.30	613.2	506.91	631	549.36	329.20
K ₂ O/Al ₂ O ₃	0.09	0.11	0.10	0.12	0.08	0.08	0.08	0.07	0.07	0.07	0.09
Al ₂ O ₃ /TiO ₂	10.10	9.04	10.86	9.80	7.08	5.61	10.27	12.36	12.80	12.59	10.25
Al ₂ O ₃ /K ₂ O	10.27	9.28	9.47	8.51	12.39	13.20	13.61	13.74	13.57	13.85	11.78

Table 2. Distribution of major elements in red and black sediments of the study area

PROVENANCE

The geochemical signature of clastic sediments is used to determine the source rock characteristics (Taylor and Mc Lennan, 1985; Ramasamy et al. 2007). The Al₂O₃/TiO₂ ratio of most clastic rocks is normally used to infer the source rock composition, because this ratio increases from 3 to 8 for mafic igneous rocks, from 8 to 21 for intermediate rocks and from 21 to 70 for felsic igneous rocks (Hayashi et al. 1997). The average Al₂O₃/TiO₂ ratio of sediments of the study area is 10.25 suggesting that basement rocks of granite, pyroxene granulite or charnockite, khondalite and quartzite rocks from the adjacent hard rock terrain of the study area are the probable source rocks for these sediments (Table 2).

DEPOSITIONAL ENVIRONMENT

The depositional environmental study through the standard diagram of geochemical plot of MgO/Al₂O₃ vs K_2O/Al_2O_3 (after Shehata and Abdou, 2008) points out that the study area sediments fall in both non marine and marine environment and give additional support for the same environment attributed in the petrographical interpretation (Figure 5).

CLASSIFICATION

The geochemical composition of samples of the study area plotted based on log (wt % SiO_2/wt % Al_2O_3) vs log (wt % Na_2O / wt % K_2O) (Fig 6) (after Pettijohn, 1975; Islam and Rahman, 2009) points out that they generally fall within lithic arenites fields (Figure 6). The geochemical classification of sediments plot diagram (after Madhavaraju and Lee, 2010) indicates that the sediments of the study area generally fall in the wacke field (Figure 7).

CHEMICAL MATURITY INDEX AND PALAEOCLIMATE

In deciphering the history of sedimentary rocks, Nesbit and Young (1982) proposed Chemical Index of Alternation (CIA) values using molecular proportion of some bulk sediments as given by the formula

 $CIA = (Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O) + K_2O) \times 100$

Where CaO* represents silicates phase value, CIA value of nearly 100 for kaolinite and chlorite, and 70 - 75 for average shale. The high values (76 - 100) indicate intensive chemical weathering in the source area, whereas low

values (50 or less) indicate unweathering source area. The average CIA values for the study area (85) indicate intensive chemical weathering and low Na₂O indicate high to moderate weathering of source rock (Figure 8).



Figure 5. Depositional environments based on MgO/Al_2O_3 and K_2O/Al_2O_3 (after Shehata and Abdou, 2008)



Figure 6. Geochemical classification of sediments (after Pettijohn, 1975; Islam and Rahman, 2009)



Figure 7. Geochemical classification of sediments (after Madhavaraju and Lee, 2010)

The higher Al_2O_3/Na_2O and K_2O/Na_2O ratio and low CaO contents in these sediments suggest that these fine grained clastic sediments are also chemically matured. Dayal and Moorthy (2006) and Suttner and Dutta (1986), proposed a classification plot of sediment partial – chemistry diagram based on ($Al_2O_3 + K_2O +$ Na_2O) % with the climatic boundaries (Figure 9). The study area sediments fall in the semi-arid to arid climate field with more maturity index.



CaO+ Na₂O

Figure 8. Chemical Index Alteration of weathering diagram (after Nesbit and Young, 1982)



 $(Al_2O_3+K_2O+Na_2O)$ % Figure 9. Climatic boundaries based on $(Al_2O_3+K_2O+Na_2O)$ % Vs SiO₂% (Dayal and Moorthy, 2006, Suttnev and Dutta, 1986)

CONCLUSIONS

The petro – mineralogical and major element geochemical studies reveals that the study area sediments of both black and red sediments were deposited as fluvio – marine deposits and are showing similar geochemical distribution trend of elements. The origin of red sediments amidst black soil is deposited as in situ deposit and its red coloration may be due to leaching and oxidation process of iron bearing heavy mineral present in sediment under favorable the climatic conditions. The source rocks for the sediments of the study area are granite, pyroxene granulite or charnockite, khondalite and quartzite as the sediment are showing intermediate sources (mixing of felsic and mafelsic). According to the geochemical classifications of sediments, the studied samples falls in the lithic arienite and wacke fields (Figures 6 &7). The chemical index of alternation analysis (Figure 8) study indicates moderate to high weathering rates from source rock and its fine grain characteristics reveals chemically matured in nature. The geochemical climatic classification study reveals that the sediments were deposited within the arid to semi-arid climatic boundary limits (Figure 9).

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