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Case Study of Paleo-Weathering, Paleo Environment, and Paleoclimate Analysis in Rocks of Eastern Ghat, Deccan Trap, and Rajahmundry Sandstone Near Rajahmundry Area.

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ABSTRACT

The paleo weathering, paleoclimate and paleoenvironment of the rocks of Deccan trap, Rajahmundry sandstone and eastern ghat at have been evaluated based on geochemical data. The Chemical Index of Alteration (CIA), Chemical Index of Weathering (CIW), Plagioclase Index of Alteration (PIA), Mineralogical Index of Alteration (MIA) and the indicates intense weathering. Also, Rb/Sr, Al/K, Rb/K ratios are high while Sr/Ba is low indicating that the sediments were derived during intense chemical weathering of the source area. The Th/U-Th plot suggests that weathering conditions were not constant during sedimentation. There is negative correlation between CIA with K and Na+Ca; as weathering intensity increases, these elements are depleted, while there is a linear negative correlation between CIA and Al which implies high intensity of chemical weathering and subsequent formation of clay minerals. The paleo environmental indices (U/Th, Ni/Co, Cu/Zn, (Cu+Mo)/Zn, V/Sc, V/Ni, V/Cr the ratios, plot of Ni versus V, plot of V/Cr against Ni/Co, Mo concentrations and Ce/Ce*) and paleoclimate results suggest that the rocks were weathered under oxic to Anoxic conditions with a humid climate on low relief in a non-marine deltaic environment and the paleosalinity based on low Sr/Ba ratio indicates low saline water a during deposition in a continental environment.

Keywords: Rajahmundry, paleoclimate, weathering, paleoenvironment, Index of Alteration

INTRODUCTION

One method of reconstructing climate in the rock record is the application of physical, mineralogical, and chemical relationships observed between modern soils and their corresponding climates and the application of these "climofunctions" to fossil soils, or paleosols. Paleosols are particularly useful climate indicators because they initially form at the nexus of the atmosphere, biosphere, lithosphere, hydrosphere, and cryosphere (i.e., Critical Zones, Ashley, 1998). As a result, paleosols have the potential to record and preserve relevant climate information such as paleo-pCO2, paleotemperature (Gallagher and Sheldon, 2013), paleoprecipitation, and paleohumidity (Gulbranson et al., 2011). Many recent studies have focused on the creation of new proxies that are empirically derived from the bulk geochemistry of modern soils and the application of these proxies to paleosols. Some of these studies are rooted in chemistry and soil science, and others are based on statistical correlations without a process-based mechanistic approach to pedogenesis. No matter what type of chemistry-to-climate correlation is observed in modern soil systems, all of these proxies assume little or no diagenetic alteration of the original soil composition. The implications of diagenetic modifications for paleoclimate reconstructions, specifically how the addition of calcite during the lithification process may modify soil chemistry and related weathering index values, remain unexplored. Calcite is one of the most common cements in paleosols. Paleo-environment and paleo-climatic study of 18 R&C soil profile samples was done to decipher the environmental condition of the geological past in which weathering took place in rocks of Eastern ghat, Deccan trap, and Rajahmundry sandstone, and several paleo-environment indices were used such as (U/ Th, Ni/Co, Cu/Zn, (Cu+ Mo)/Zn, V/Sc, V/Ni, V/Cr Plot of V/Cr Against Ni/Co, and Ce-Anomaly to understand the environment of weathering in detail. The Chemical Index of Alteration (CIA), plagioclase Index of Alteration (PIA), and other weathering indices were studied thoroughly to understand the Intensity of weathering and established a relation between the paleo-environment and the intensity of weathering. The Paleosalinity of the sediments was studied by the Sr/Ba indices to understand the salinity level of the geological past and its role in sedimentation.

The area is bounded by latitude N 17° 00' 00" to 17° 15' 00" and longitude 81° 45' 00" to 82° 00' 00" E. covers the upland area North of Godavari delta in East Godavari District of Andhra Pradesh. It is well connected by metalled roads. National Highway 5 passes through the Toposheet, it connects Rajahmundry to Bhubneshwar. Rajahmundry is the major town on the left bank of Godavari. Other important towns include Rajanagaram and Korukonda. The nearest Railway station and Airport is Rajahmundry Physiographically, the area in general exhibits a rolling topography with isolated hills The northern part of the area is covered by strike ridges and denudational ridges. The area south of Kolukumela is plain land with a southerly slope dotted by inselbergs of low relief. The highest elevation of 249 m above MSL is marked by Jarurayi Konda hills and the lowest elevation is 26.8 m marked by Rajahmundry Township. The area is drained by many streams. R & C soil samples were collected from 9 different locations within the quadrant which represent the overall chemistry of the Soil samples of the study area. R & C soil samples were collected in a 5' x 5' grid pattern



Fig 1: Sample location map of Study Area, showing locations of R&C soil samples

2. Geology of the Study Area

The area is occupied by the rocks of Khondalite, Charnockite and Migmatites Groups of Eastern Ghats Supergroup in the north, overlain by Tirupathi Formation of East Coast / Gondwana of Gondwana Supergroup, DeccanTrap, Rajahmundry Sandstone towards southern part and Krishna-Godavari Formation towards southwest The Khondalite Group is represented by khondalite, which occupies the northern part of the area. Khondalite is observed around Mellisala, Gopalpuram and Tirumalayyapalem. It is chiefly of garnet-sillimanite + graphite gneiss and contains a few thin persistent bands of quartzite at places. Intermediate charnockite and hypersthene granite/acid charnockite comprising the charnockite Group occur as minor bodies. The Migmatite Group is made up of garnetiferous quartzo feldspathic gneiss and manganiferous quartzo-feldspathic rocks which are derived from the former due influx of quartzo feldspathic injections and observed near Rajavaram, korukonda, and Srirangapatam. The Tirupathi Formation of the upper Gondwana Group overlies the Eastern Ghats Supergroup in the central and is overlain by floodplain deposits of the Krishna-Godavari Formation in the west. It is composed of a ferruginous boulder conglomerate at the base followed by sandstone with interbedded clays. The sandstone is ferruginous and the ferruginous content increases progressively from bottom to top. Basalts of the Deccan trap are recorded on the eastern bank of the Godavari River.

Methodology

Major oxides, Cr, Rb, Sr, Y, Zr, Nb, Ba, Ga, Sc, V, Th, Pb, Ni, Co, Cu and Zn were analysed by XRF (Make and Model: Malvern Panalytical; Axios mAX4KW WD-XRF Spectrometer). REE's, As, Sn, In, Hf, Ta, U were analysed by ICPMS (Make and Model: ICPMS - Agilent make, 7700X). Standard reference material GSD and GSS series, IGGE China with known element concentrations was analysed after each batch of 20 samples for accuracy and duplicate samples after each batch of 10 samples was analysed for repeatability. In addition, repeated analysis of 5% of stream sediment samples were carried out to validate unambiguously the consistency in sampling and the accuracy in the analytical procedures

Result & Discussion

1. Weathering Indices

1. Chemical Index of Alteration (CIA)

Soil is the surface layer of the mantle of rock waste in which the physical and chemical processes of weathering cooperate in intimate association with biological processes and along with the climate play a vital role in its formation. This is the reason why the nature of soil varies both laterally as well as vertically with depth. Topsoil or R (in NGCM terms) experiences more alteration history than the subsoil or C horizon which is a partly weathered portion with vestiges of bedrock, as rain leaches the soluble materials like alkalis of the soil profiles leaving behind the resistant minerals. The chemical index of alteration also known as CIA (McLennan, 1985) is a well-established parameter for determining the degree of weathering. During the degradation of feldspars, Ca, Na, and K are removed and clay minerals with a higher fraction of Al are formed. CIA is estimated. from the proportion of Al2O3 vs. the weathering-prone oxides. The formula used for the calculation CIA is given below:

$$CIA = \frac{(Al2O3) \times 100}{(Al2O3 + CaO * + Na2O + K2O)}$$

Where CaO* represents the amount of CaO incorporated in the silicate fraction. Unaltered feldspars have a CIA of 50, whereas kaolinite has a value of 100 (total removal of alkali elements).

2. Plagioclase Index of Alteration (PIA)

PIA is plagioclase index of alteration. This modification of the CIA equation is equivalent to projecting the solid circles onto the A-CN join from the K-feldspar composition. The equation yields values of 50 for fresh rocks and values close to 100 for clay minerals such as kaolinite, illite, and gibbsite, consistent with values derived from the CIA equation.

$$PIA = \frac{(Al203 - K20) \times 100}{(Al203 + Ca0 * + Na20 + K20)}$$

From the plot between CIA and PIA it is quite obvious they throw light upon the intensity of Silicate weathering and decipher the paleoclimate and Availability of CO_2 or in better words P_{CO_2}

3. Index of Lateralization

A different approach is required that is suited to the chemical changes in laterite or bauxite profiles. During lateralization, the dissolution of quartz and kaolinite (congruent or incongruent) and the enrichment of Fe oxides are the dominant processes, resulting primarily in a loss of Si relative to Al and Fe in the weathered residue. chemical classification of laterites based on the SiO2/(Al2O3 + Fe2O3) ratio and the SiO2–Al2O3– Fe2O3(T) (SAF). ternary plot to distinguish between kaolinized, lateritised, and bauxitised weathering residues. First, a notional 'limit of kaolinitisation' for the early to intermediate stages of weathering can be calculated, which is associated with relatively minor Si loss. Desilication begins to dominate beyond this limit and a quantitative tripartite progression of the 'degrees' (i.e., weakly, moderately, and strongly) of lateralization or bauxitisation can be made. This chemical classification, however, is not unanimously accepted

$$IOL = \frac{(Al203 + Fe203) \times 100}{(Si02 + Al203 + Fe203)}$$

4. MgI (Magnesium Index)

$$MgI = \frac{(Al) \times 100}{(Al + mg)}$$

5.CALMag : CAL-MAG weathering Index is best suited for the vertisol which is mainly clay-rich soils that shrink and swell with changes in moisture content. During dry periods, the soil volume shrinks, and deep wide cracks form. This indices also helps in calculation of paleoprecipitation

$$CALMAG = \frac{(Al) \times 100}{(Al + Ca * + mg)}$$

6. MIA

The mafic index of alteration (MIA) is proposed here as a chemical weathering index that extends the equation of the CIA to include the mafic elements Mg and Fe. Many of the mafic minerals (pyroxene, olivine) are susceptible to chemical weathering, resulting in the loss of Mg from weathering profiles.

MIA (O)When the alteration environment is oxidizing and Fe is retained, total Fe is considered an immobile element along with Al (Al2O3), and the MIA calculation is

$$MIA (0) = \frac{(Al203 + Fe203 T) \times 100}{(Al203 + Fe203 T + Mg0 + Ca0 + Na20 + K20)}$$

MIA(**R**) When the alteration environment is reducing and Fe is leached along with Mg, total Fe is considered a mobile element along with Mg, Ca, Na, and K and the MIA calculation is

$$MIA (R) = \frac{(Al203) \times 100}{(Al203 + Fe203 T + Mg0 + Ca0 + Na20 + K20)}$$

8. CIA-K

$$CIA - K = \frac{(Al) \times 100}{(Al + Ca * + Na)}$$

9.MIA(O)-K

$$\mathbf{MIA}\left(\mathbf{0}\right) = \frac{(\mathrm{Al} + \mathrm{Fe}\,\mathrm{T}) \times 100}{(\mathrm{Al} + \mathrm{Fe}\,\mathrm{2T} + \mathrm{Mg} + \mathrm{Ca} + \mathrm{Na}\,\mathrm{2} + \mathrm{K})}$$

10. MIA(R)-K

$$\mathbf{MIA}\left(\mathbf{0}\right) = \frac{\mathrm{Al} \times 100}{(\mathrm{Al} + \mathrm{Fe2T} + \mathrm{Mg} + \mathrm{Ca} + \mathrm{Na2} + \mathrm{K})}$$



Figure1 : Relative study of weathering indices in C horizon and regolith of soil profiles collected from study Area

the mafic index of alteration (MIA). The MIA adds the elements Fe and Mg to the Al–Ca–Na–K system, allowing the mafic mineral component of rock weathering to be quantified. The MIA is most suitable for, but not restricted to, studying mafic rock weathering. The study of chemical weathering of mafic substrates, compared to felsic substrates, provides many advantages from a geological and chemical perspective

- a) the parent rock is often fine-grained and typically quite homogeneous
- b) the substrate is rich in redox-sensitive elements, such as the transition metals

c) basalt or its metamorphosed/ altered equivalent are ubiquitous throughout the known geological record,

Silicate weathering is perhaps the most important removal mechanism of CO_2 from the atmosphere, with the weathering of mafic substrates often being cited as especially important in the regulation of global climatic changes. Although the major elements closely reflect the mineralogical transformations during weathering, understanding the cycling of certain minor and trace elements has the potential to provide further insight into pedogenetic processes, such as biological activity or the oxidation state of a profile. Comparative weathering indices studies indicate moderate to extreme weathering in the soil profiles. this also indicates that different climate condition and intensity of weathering

Intensity of weathering

Regolith and C-horizon samples were collected from different suitable sites in the study area. chemical index of weathering alteration was calculated and plotted against Al₂O₃ from the distribution of R and c horizon locations we can infer that most of the samples were weathered to their extreme level, however, the trend of weathering is moderate to the extreme. this also emphasizes that paleoclimate was favorable for the formation of Clays. The presence of smectite in the clay composition indicates Arid to semi-arid conditions.







Figure 3: Fractionation of Sm/Nd ratio as a function of the CIA during the weathering stages

These observations suggest that Sm/Nd and Nd isotope systematics of altered rocks and derived sediments are sensitive to pedogenetic fractionation. This would not alter the Nd isotope composition of modern profiles or sediments, but fractionation in Sm/Nd would manifest as variations in the Nd isotope composition in ancient weathering profiles. In this sense, the more weathered material would be less radiogenic as a result of the lower Sm/Nd generated during LREE enrichment. This has been exploited to crudely date the age of paleosols since an isochron develops that is proportional to the age of pedogenesis

In case of Rb/Sr systematics with weathering the enrichment of Rb can lead to pegoneic fractionation and this will shift the Rb /Sr systematics. Weathered material will be more radiogenic .



Figure 4: Fractionation of Rb/Sr ratio as a function of the CIA during the weathering stages

Paleo Environment Analysis

Table 1: Look up table for several Paleo-environment Indices

Fe/Al	V/Cr	Ni/Co	V/Sc	U/Th	Cu/Zn	(Cu+Mo)/Zn	Th/U	Sr/Ba	Rb/K	Ce-
										Anomaly
0.30	1.94	1.40	9.10	0.07	1.74	1.75	14.16	0.18	0.49	0.79
0.26	1.33	1.77	12.71	0.07	1.04	1.06	13.48	0.09	0.58	1.07
0.28	1.61	1.61	11.78	0.05	1.15	1.21	20.31	0.19	0.53	1.18
0.20	2.25	0.73	17.78	0.05	0.86	0.91	21.04	0.16	0.36	0.91
0.30	1.68	1.58	8.33	0.05	1.17	1.19	21.52	0.16	0.49	0.87
0.26	1.31	1.94	8.25	0.08	0.67	0.70	11.91	0.26	0.61	0.99
0.21	1.20	1.50	8.20	0.06	0.37	0.37	17.31	0.07	0.70	0.88
0.25	1.23	1.41	8.95	0.06	0.77	0.79	17.06	0.09	0.60	0.95
0.23	1.13	1.37	7.68	0.06	0.53	0.54	17.43	0.09	0.62	0.89
0.71	3.00	1.47	9.00	0.06	1.28	1.29	17.75	0.20	0.35	0.78
0.22	1.61	1.65	12.41	0.06	1.05	1.05	16.78	0.12	0.48	0.98
0.25	1.83	1.53	10.80	0.04	1.08	1.08	23.75	0.18	0.51	1.03
0.18	2.35	0.70	17.14	0.05	0.61	0.64	22.04	0.13	0.35	0.90
0.30	1.77	1.25	9.76	0.05	1.21	1.23	20.92	0.16	0.45	0.89
0.25	1.29	1.90	8.81	0.09	0.69	0.70	10.54	0.24	0.54	1.05
0.26	1.48	1.00	13.36	0.05	0.38	0.40	18.58	0.11	0.49	0.87
0.27	1.43	1.33	15.83	0.05	0.47	0.48	20.08	0.11	0.37	0.91
0.21	1.32	0.93	10.33	0.05	0.38	0.39	21.35	0.09	0.46	0.94

Oxidation and reduction states are significant for identifying sediment deposition in marine or non-marine environment. The accretion of some trace metals in sediments is directly or indirectly constrained by redox conditions via either a change in redox state and/or speciation (McKay *et al.*, 2007). U/Th, Ni/Co, Cu/Zn, (Cu+Mo)/Zn, V/Sc and V/ Cr ratios have been utilized to assess paleo-redox conditions (Bjorlykke, 1974; Hallberg, 1976; Dypvik, 1984; Dill, 1986; Shaw *et al.*, 1990; Brumsack, 2006; Nagarajan *et al.*, 2007; Hetzel *et al.*, 2009. U/Th ratios below 1.25 suggest oxic conditions of deposition, while values above 1.25 indicate suboxic and anoxic conditions (Hallberg, 1976; Jones & Manning, 1994). The U/Th values for sediment in the study area is between 0.04 and 0.09, which indicates an oxic environment.

V accumulates relative to Ni in reducing environments, where sulfate reduction is more efficient. Ni is mainly enriched in organic-rich sediments where these metals are trapped with organic matter (Leventhal & Hosterman, 1982; Gilkson *et al.*, 1985). The proportionality of these two elements V/(V+Ni) is significant to outline evidence on Eh, pH and sulphide activity in the depositional environment (Madhavaraju & Lee, 2009). V/(Ni+V) ratios below 0.46 indicate oxic environments, but ratios between 0.54 and 0.82 suggest suboxic and anoxic environments (Hatch & Leventhal, 1992). According to Jones & Manning (1994), Ni/Co ratios below 5 indicate oxic environments, while ratios above 5 indicate suboxic and anoxic environments.

The ratio (Cu+Mo)/Zn is shown to be a relevant paleo redox indicator for bottom water and sediment surface. The (Cu+Mo)/Zn values for which suggests an oxic to the suboxic environment of deposition. High Cu/Zn ratios indicate reducing depositional conditions, while low Cu/Zn ratios suggest oxidizing conditions (Hallberg, 1976); the Cu/Zn ratios for the studied samples is between 0.37 - 1.74 (average = 0.86), indicating oxic to suboxic; but more oxidizing conditions. According to Lewan (1984). V/Cr ratio has been utilized as an index of paleo oxygenation due to the incorporation of Cr in the detrital fraction of sediments and its possible substitution for Al in the clay structure (Kimura & Watanabe, 2001). Vanadium solubility in natural waters, its extraction from seawater, and absorption into sediments are predominantly affected by redox conditions (Bellanca *et al.*, 1996). Vanadium may be bound to organic matter by the addition of V4+ into porphyrins and is generally found in sediments deposited in reducing environments (Kimura & Watanabe, 2001). V/Cr ratios above 2 indicate anoxic conditions, while values below 2 suggest more oxidizing conditions (Jones & Manning, 1994). The V/Cr values for sandstone under investigation range between 1.13 and 3 (average = 1.65), which points to deposition in an oxic environment.







Figure 6: K vs Al plot from weathering plot

From above diagram its quite visible that weathering of feldspar is prominent in regolith C horizon and due to leaching of Al_2O_3 , Al content is more in the C horizon due to illuviation effect



Figure 7: Soil sample shows enrichment effect of U and Th in weathering profile



Figure 8: Soil sample depicting environments of weathering on Fe/Al ratios



Figure 9: V and Ni plot depicts different environment of weathering



Figure 10: V/Cr and Ni/Co plot depicts different environment of weathering



Figure 11: K and CIA plot shows relationship between different degree of weathering and release of potassium



Figure 12: different rate of weathering and release of Na +Ca

Cerium Anomaly



Figure 13: plot for different Cerium anomaly for different Samples



Figure 14 : Relationship between CIA and Ce -anomaly in different sample



Figure 15 : Relationship between PIA and Ce -anomaly in different sample

Cerium can track redox-related transformations during pedogenesis in modern and ancient weathering profiles as a result of the potential oxidation of Ce3+ to Ce4+ (e.g., Middelburg et al., 1988; Braun et al., 1990; Mongelli, 1993; Gallet et al., 1996; Murakami et al., 2001; Patinoet al., 2003)

From the above figures the Ce anomaly show trend with weathering indices CIA (chemical index of Alteration) and PIA. the trend is more prominent with PIA (plagioclase index of Alteration). since rocks were formed and weathered in different geological periods so the Ce* values show a different level of redox conditions during the process of pedogenesis. In oxic marine environments, Ce4+ preponderates and is utilised by strongly reactive Fe-Mn-oxyhydroxides, leading to depletion of Ce in oxic seawater. Cerium anomaly (Ce/ Ce*) may be utilised to determine the paleoenvironmental of deposition. Values >1 suggests an oxidizing environment (Piper, 1974; Milodowski & Zalasiewicz, 1991; McDaniel *et al.*, 1994). The samples in study area has Ce/Ce* values ranging between 0.78 and 1.18 with an average of 1.72 indicating an oxic environment of deposition.

Paleo precipitation:



CAL-MAG and CIA-K are the two weathering indices that talk about paleo precipitation. Here CALMAG was used to throw light upon the paleo precipitation conditions during the weathering episodes

Figure 16 : plot for pale oprecipitation estimation with the help of CALMAG indices value

Paleo salinity Interpretation

The salinity of water mass has an impact on its paleo-environment and paleo ecological reconstruction but the field of paleo-salinity determination or interpretation is untouched. In this study, Sr/Ba is used as a geochemical proxy for paleosalinity interpretation. Sr/Ba <0.2 in freshwater, 0.2–0.5 in brackish, and >0.5 in marine facies (Thomas J. Algeo et al ,2020). From the element ratio of Sr/Ba it is quite evident that weathering condition was fresh water to brackish in nature.



Figure 17 : plot for Paleosalinity estimation through Ba/Sr ratio

Conclusion

This study clearly showed that climatic conditions strongly affect the soil physicochemical, mineralogical and morphological properties, either directly or indirectly, in the local area. These results were supported by the application of the chemical weathering indices, namely CIA, CIW, Base/R2O3 (Al2O3 + Fe2O3 sesquioxide or R2O3) and PIA, in this study. They are commonly used for characterizing weathering profiles by incorporating bulk major element oxide chemistry

Distribution of Elemental ratios in the soil profiles can help in estimation of Paleoenvironment and paleosalinity

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