Trans. Inst. Indian Geographers
Vol. 13, No. 2 July 1991

GEOCHEMISTRY OF SOILS OF THE INDRAYANI RIVER BASIN, WESTERN MAHARASHTRA, INDIA.

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ABSTRACT: Ths Indrayani river basin of the western part of Maharashtra has developed two contrasting soil types from the parent rock basalt of more or less uniform chemical and mineralogical composition. The ferralitic soils of the western part of the basin have developed under free drainage conditions which is evidenced by the presence of kaolinite group of clay minerals, and iron and aluminium minerals. On the contrary, presence of the smectite group of clay minerals in the margalitic soils has been attributed tc restricted drainage conditions developed due to level topography of the eastern part of the basin.

Geochemical data of the soil profiles representing eastern and western parts of the basin, have shown that the chemical weathering has resulted in general increase in the concentration of Al_2O_3, Fe_2O_3 and TiO_2 on one hand and depletion of bases ($CaO + MgO + Na_2O + K_2O$) and silica (SiO_2) on the other. Triangular plots of Bases ($CaO+MgO+Na_2O + K_2O$), Silica (SiO_2) and R_2O_3 ($Al_2O_3 + Fe_2O_3 + TiO_2$) and plots of concentration ratios against depth for the soils under study, also indicate similar trends of chemical weathering.

INTRODUCTION

The Indrayani river basin (Fig. 1) situated on the eastern flanks of the Western Ghats, forms a part of the Deccan Volcanic Province, which is constituted chiefly of basaltic lava flows. The basalts with more or less uniform chemical and mineralogical composition have undergone chemical weathering that has resulted in the development of two contrasting soil types. The reddish brown coloured lateritic to semi-lateritic (ferralitic) soils are observed in the western part of the Indrayani river basin; while its eastern part shows the presence of grayish black coloured margalitic or black cotton soils (Fig. 1). In the present paper an attempt has been made to discuss the evolution of the soils in the light of the chemical and clay mineralogical data.

PHYSIOGRAPHIC SETTING

The Indrayani river basin experiences a tropical wet-dry climate with alternating wet and dry spells. It receives heavy rains during the period from June to September, the mean annual rainfall being 3129 mm. The rainfall gradually decreases eastwards and it amounts only to 605 mm at Alandi, located in the eastern part of the basin. The mean maximum annual temperature is 32°C. However, the temperature may rise to 42°C or more in summer and may fall down to 3°C during winter.

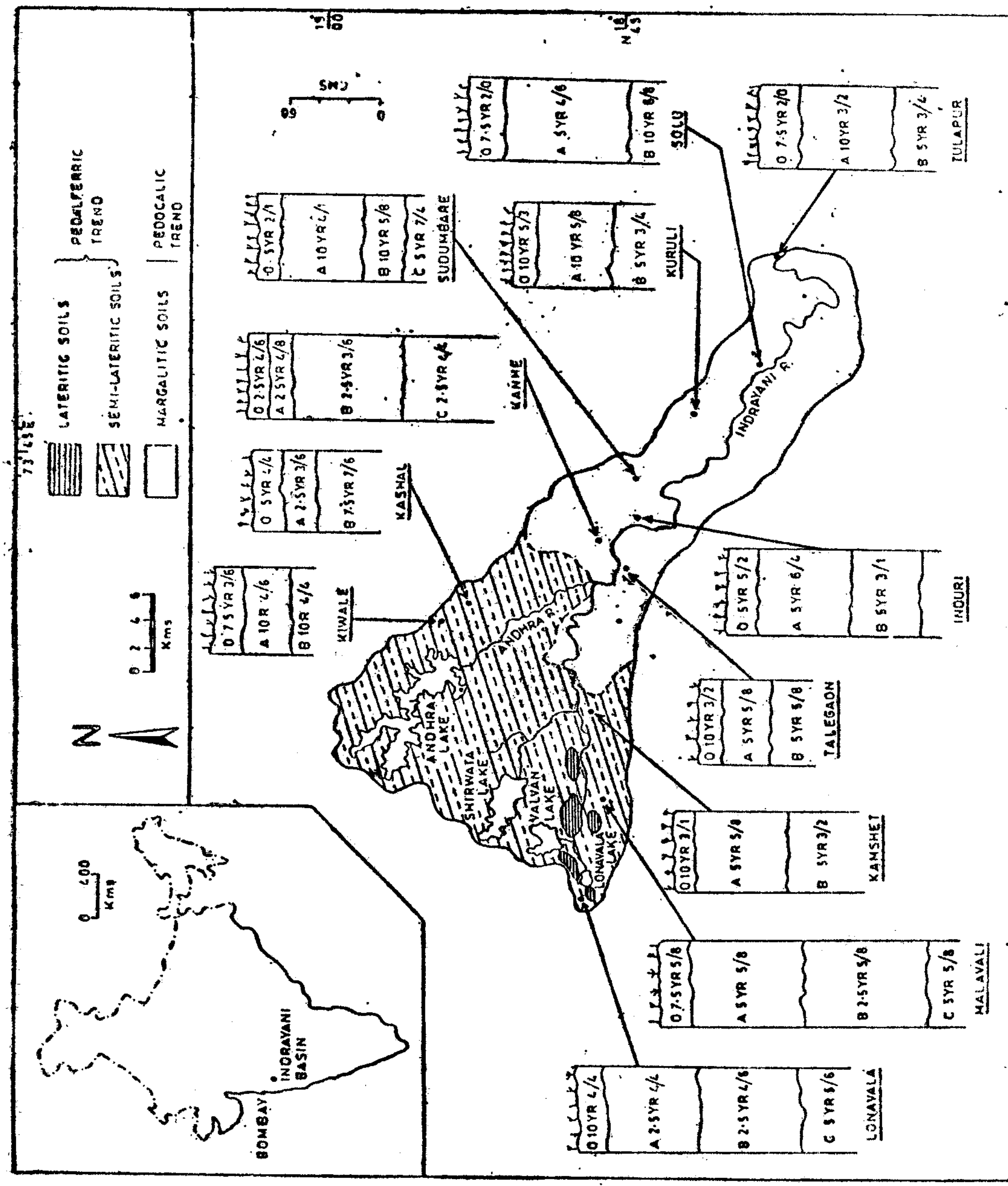

Fig. 1 : Soil map of the Indrayani river basin showing locations of soil profiles.

The area under study is drained by the Indrayani river and its tributaries, the most prominent being the Andhra, Kundali and Sudha. The Indrayani and Kundali rivers display flat-floored valleys in their upper reaches, where narrow discontinuous patches of thin alluvial cover occur. The Andhra valley is narrow and gorge-like and displays a bad-land topography. The lower reaches of Indrayani river basin are characterised by flat-floored very broad 'U' shaped valley with low and rolling interfluves.

The Indrayani river basin exhibits a rugged topography with moderate (5° to 10°) to moderately steep (10° to 28°) slopes in its western parts. However, valley flats and hill tops in this part of the basin display level (0° to 2°) to gentle (2° to 5°) slopes. On the other hand, the flat featureless and undulating topography in the eastern part of the basin is characterised by level to moderate (0° to 10°) slopes.*

THE SOILS

The Indrayani river basin shows an extensive development of soil cover. Field surveys have shown that red to reddish brown coloured lateritic to semi-lateritic soil indicating 'pedalferric' (al: aluminium; fer: iron) trend and grayish black coloured margalitic or black cotton soils suggesting 'pedocalic' (cal:calcium) trend (Mohr and van Baren, 1954) respectively occur in the western and eastern parts of the basin under study. In order to characterise these soils, twelve soil profiles (Fig. 1) representing western and eastern parts of the basin, were systematically sampled.

It is observed that the thickness of soil cover varies from place to place, as it is a direct function of slopes and vegetation cover. The areas with level to gentle slopes representing valley flats and hill tops show thick soil cover with well developed horizons. A thin soil cover with poorly defined horizons has been characteristic of the moderate to moderately steep sloping grounds. As soils are derived from basalt, they usually have gradational contact with it. At places, however, they are seen to rest directly on a fresh and unaltered basalt with an abrupt or a sharp contact. In an ideal soil profile in the Indrayani river basin, the humus rich 'O' horizon rests over highly leached 'A' horizon followed downward by a dark and dense 'B' horizon; partly to fully weathered, highly oxidised mineral rich 'C' horizon that gradually passes into fresh and unaltered basalt. The 'B' horizon of the soil profiles in the western part of the basin shows accumulations of aluminium and iron oxides; while concretions of calcium carbonate are recorded in this horizon of the soil profiles from the eastern parts. At places, in the western part of the basin, laterite showing red to reddish brown or yellowish brown colours and porous character has been observed (Fig. 1). It occurs in narrow tracts margining the valley sides. A typical lateritic profile shows an upper 1.0 to 1.5 m thick lateritic duricrust which follows downward by a 5.0 to 8.0 m thick mottled horizon of lithomarges showing variegated colours. This horizon grades into a 1.0 to 2.0 m thick pallid horizon overlying the bed rock basalt.

CHEMISTRY OF SOILS

In order to understand the chemical changes that the parent rock basalt has

* Slope classification after Young (1972).

undergone during its chemical weathering, chemical analysis of the soils was undertaken with the help of a 1275 Varian Atomic Absorption Spectrophotometer. Major element concentration as oxide, has been obtained for the soil samples from different horizons of the representative soil profiles shown in Fig. 1. Due to constraint of space, chemical data are presented only for the Malavali (Table 1) and Sudumbare (Table 2) soil profiles, which respectively represent the western and eastern parts of the basin under study. The loosely held water ($H_2\bar{O}$) is lost at temperature less than 105°C, therefore, it is not reported. The crystal lattice water ($H_2\overset{+}{O}$) which is actual weight loss at higher temperature due to conversion of crystal lattice OHs to water vapour and oxygen gas, is reported in the chemical analysis.

The vertical variation of each of the constituent oxides presented in Tables 1 and 2, respectively for the Malavali and Sudumbare profiles, has indicated that the bases (CaO, MgO, Na_2O and K_2O), silica (SiO_2) and ferrous iron (FeO) have been depleted on weathering. Alumina (Al_2O_3) and ferric iron (Fe_2O_3), however, show general increase in their concentration on weathering.

Since, the chemical weathering process is complex one and is more active at the surface, it follows that the decomposition of homogeneous parent rock is accompanied by progressive enrichment of the most immobile elements as the surface is approached. However, complete homogeneity is rarely encountered in nature and consequently to alleviate difficulties arising in this respect, an immobile element like aluminium is used as an internal standard as it is the most stable element in nature (Birkeland, 1984). Taking aluminium as an internal standard, concentration ratios (C.R.) for various oxides have been calculated as per the following formula given by Monro, **et al,** (1983):

$$C.\ R. = \frac{\%\ \text{oxide (d)}}{\%\ \text{oxide (ref)}} \times \frac{\%\ Al_2O_3\ \text{(ref)}}{\%\ Al_2O_3\ \text{(d)}}$$

where, C. R. : Concentration Ratio of oxide

d : sample at a specific depth

ref : reference parent material

The concentration ratios obtained for various oxides from the different horizons of the Malavali and Sudumbare profiles are respectively presented in Tables 1 and 2. The plots of concentration ratios against depth (Figs. 2 and 3) suggest that greater enrichment relative to that of Al_2O_3 is indicated by values more than unity; while those less than unity. Show relative depletion. As Na_2O and K_2O are readily mobile, they show marked decline in the zone of weathering relative to Al_2O_3. Silica, which is also a potentially mobile constituent, is depleted from the altered product. FeO being highly unstable, is converted into Fe_2O_3, hence, shows depletion on weathering. TiO_2 and Fe_2O_3 are stable in most weathering environments, therefore, their plots of concentration ratios coincide with that of Al_2O_3 or sometimes, they show gain in their concentration during chemical weathering. Calcium and magnesium behave similarly as that of alkalies (Na_2O and K_2O) during chemical weathering and their concentration ratios are usually less than unity.

Table 1 : Chemical data for Malavali Profile, Indrayani River Basin, Maharashtra, India.

Oxide %	Fresh Rock	'O' horizon	C. R.	'A' horizon	C. R.	'B' horizon	C. R.	'C' horizon	C. R.
SiO_2	50.61	49.00	0.71	48.16	0.78	48.10	0.74	49.40	0.75
Al_2O_3	13.58	18.50	1.00	16.60	1.00	17.40	1.00	17.58	1.00
Fe_2O_3	3.19	9.88	2.27	12.19	3.13	12.39	3.03	10.16	2.46
FeO	9.92	1.89	0.13	2.52	0.21	2.68	0.21	1.28	0.10
MgO	5.46	0.85	0.11	1.49	0.22	1.90	0.27	3.31	0.47
CaO	9.45	3.09	0.24	2.04	0.18	2.24	0.18	2.38	0.19
Na_2O	2.60	1.62	0.45	1.24	0.39	0.30	0.24	1.50	0.45
K_2O	0.72	0.42	0.43	0.18	0.20	0.18	0.20	0.30	0.86
TiO_2	1.91	1.85	0.71	1.70	0.73	2.05	0.84	2.52	1.02
MnO	0.16	0.19	0.87	0.19	0.97	0.26	1.27	0.13	0.63
H_2O^+	1.70	9.65	4.17	11.71	5.64	11.97	5.50	1.70	0.77

C. R. : Concentration Ratio

Table 2 : Chemical data for Sudumbare Profile, Indrayani River Basin, Maharashtra, India.

Oxide %	Fresh Rock	'O' horizon	C. R.	'A' horizon	C. R.	'B' horizon	C. R.	'C' horizon	C. R.
SiO_2	50.61	47.50	0.89	46.50	0.86	47.50	1.02	49.50	1.17
Al_2O_3	13.58	14.30	1.00	14.50	1.00	12.50	1.00	11.40	1.00
Fe_2O_3	3.19	10.34	3.08	8.98	2.64	9.48	3.23	8.44	3.15
FeO	9.92	1.52	0.15	1.12	0.11	1.64	0.18	1.12	0.13
MgO	5.46	5.28	0.92	5.23	0.90	5.16	1.03	5.65	1.23
CaO	9.45	6.35	0.64	6.83	0.68	6.88	0.79	6.88	0.87
Na_2O	2.60	1.75	0.64	1.75	0.63	1.82	0.76	1.50	0.69
K_2O	0.72	0.50	0.66	0.57	0.74	0.56	0.84	0.43	0.71
TiO_2	1.91	2.43	1.21	1.90	0.93	1.75	1.00	1.65	1.03
MnO	0.16	0.13	0.77	0.13	0.76	0.13	0.88	0.18	0.97
H_2O^+	1.70	7.77	4.34	10.68	5.88	11.94	7.63	13.25	9.28

C. R. : Concentration Ratio

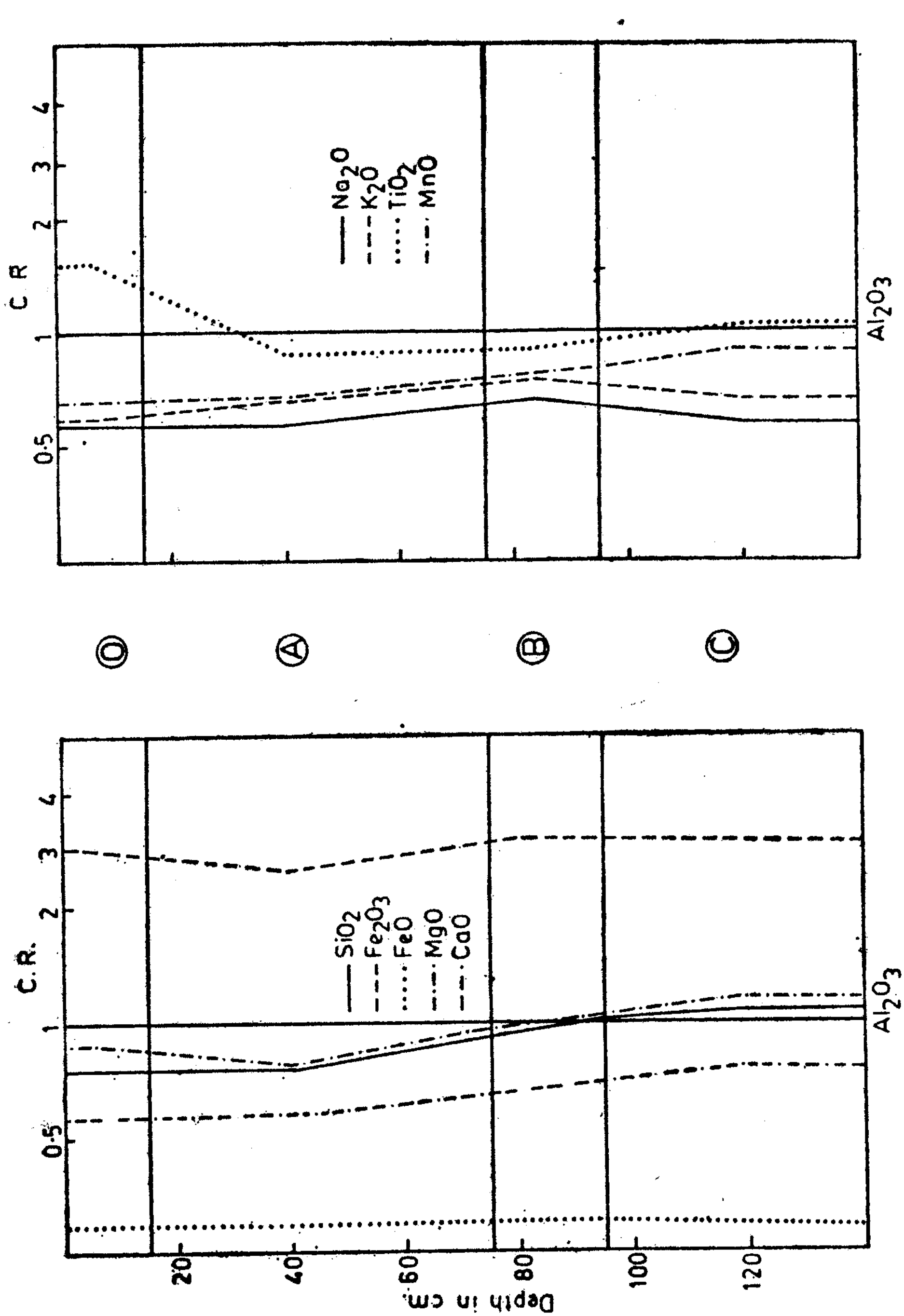

Fig. 2 : Plots of Concentration Ratios (C. R.) against depth for Malavali profile.

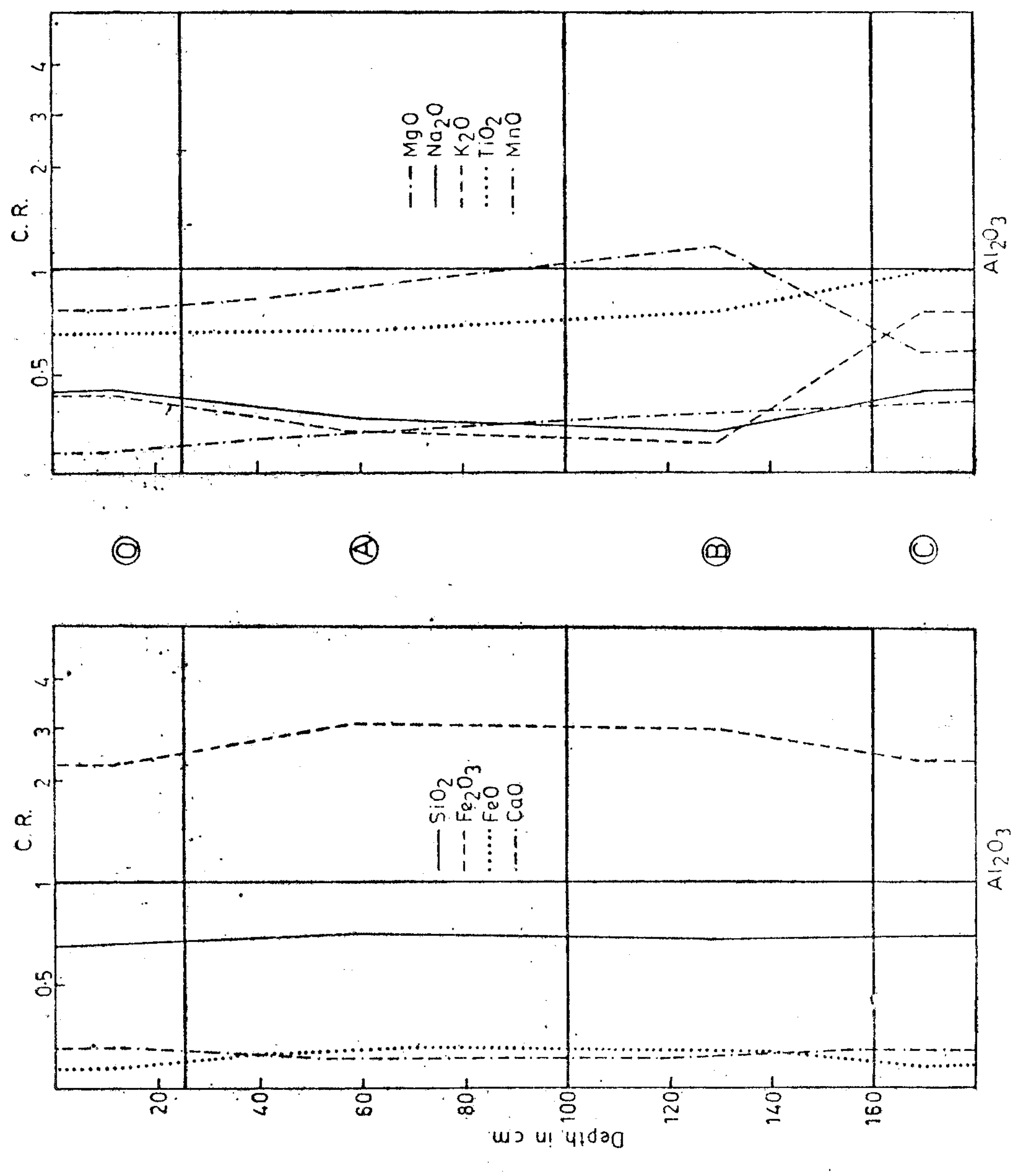

Fig. 3 : Plots of Concentration Ratios (C. R.) against depth for Sudumbare profile.

CLAY MINERAL ASSEMBLAGE

The clay mineral assemblage (Table 3) of soils of the Indrayani river basin has been obtained from DTA, XRD and IR spectroscopic studies (Patil, **et al**, 1990). It is observed that the soil profiles from the western part of Indrayani river basin have shown the predominance of the minerals of kaolinite group, the most common being kaolinite, fire-clay kaolinite, and halloysite. Upper horizons of these profiles, however, show the appearance of iron and aluminium minerals like goethite, limonite, gibbsite, boehmite, etc. Montmorillonite and other smectite group of clay minerals have been recorded in smaller quantities in the lower horizons of these soil profiles.

Soil profiles of the eastern part of Indrayani river basin, on the contrary, have shown the predominance of the minerals of smectite group, the most prominent clay mineral being montmorillonite. Halloysite along with kaolinite occur in the upper horizons of these soil profiles. Chlorite and vermiculite have also been recorded. Quartz and calcite are the two non-clay minerals present in the lower horizons of soil profiles of the eastern part of the basin.

Table 3 : Clay and related mineral assemblages of the soils of Indrayani River Basin, Maharashtra, India

Horizon	Western part (Malavali profile)	Eastern part (Sudumbare profile)
'O'	GI, BO, LI, KA, FC, HA, MO, VR.	MO, VR, KA, HA, FC. FC.
'A'	KA, FC, LI, GI, HA, MO, VR.	MO, VR, HA, KA, FC. FC.
'B'	HA, KA, MO, GI, VR, LI.	MO, VR, HA, KA, SI, CA. SI, CA.

Aluminium Minerals

GI : Gibbsite
BO : Boehmite

Clay Minerals

KA : Kaolinite,
HA : Halloysite
FC : 'Fire Clay' kaolinite
MO : Montmorillonite
VR : Vermiculite

Iron Minerals

LI : Limonite or Soil-goethite

Non-clay Minerals

SI : Silica (chert and flint)
CA : Calcite

The lateritic profiles in the western part of the basin, have shown the presence of iron and aluminium minerals including goethite, hematite, limonite, gibbsite, bayerite, boehmite, diaspore along with traces of kaolinite and halloysite in their upper horizons; while lower lithomargic horizons are dominated by the minerals of the kaolinite group (Patil, et al, 1991).

DISCUSSION

On the basis of data on clay mineral assemblage and chemistry of soils presented earlier, trends of chemical weathering of basalt as well as genesis and evolution of soil can be visualised. It is observed from the clay mineral assemblage that the soils in the western part of Indrayani river basin are dominated by the presence of minerals of kaolinite group; while those in the eastern part of the basin show the dominance of the minerals of smectite group.

A review of literature on chemical weathering processes and clay minerals (Hay and Jones, 1972; Colman, 1982a, b: Cawsey and Mellon, 1983) has revealed that the formation of clay minerals has been a function of climate and topography. The climate has two major controls on chemical alteration of parent material, namely, the temperature – controls the rate of transformation and the rainfall – controls availability of moisture along with rate of flow of water. Both the external and internal drainage conditions are controlled by topography. Under free drainage conditions defined both by rugged topography and high rainfall, the rate of transformation would be accelerated. As a result, only the most immobile constituents like Al and Fe would remain in the weathered products which would show characteristic assemblage of clay minerall.

Experimental studies carried out by different workers (Pedro, 1961; Pickering, 1962; Wollast, 1967; Berner, 1971; White and Sarcia, (1978) have shown that the rate of chemical reaction is a direct function of pH of solution which, in turn, is controlled by the rate of flow of water. In an experiment involving chemical weathering of albite under various flow rate conditions of water, Berner (1971, p. 173) has shown that at higher rate of flow of water albite altered to gibbsite; at little lower flow rate conditions kaolinite was formed and when the flow rate conditions approached stagnation, formation of montmorillonite took place. This suggests that the formation of various clay minerals is controlled by the rate of flow of water that, in turn, defines pH of the solution.

In a natural environment the trend of chemical weathering can be predicted on the basis of the clay mineral assemblage. In this regard, a general sequence of mineral alteration during the progressive chemical weathering of rock, as suggested by Carrol and Hathaway (1963) is given below :

progressive weathering

$$FM \longrightarrow M \longrightarrow H \longrightarrow K \longrightarrow G$$

Where,

FM : Fresh Mineral

M : Montmorillonite

H : Halloysite

K : Kaolinite

G : Gibbsite

This implies that the presence of montmorillonite in a weathered product is indicative of an early stage of chemical weathering; while an advanced or an ultimate stage is indicated by the presence of kaolinite and/or gibbsite. However, full sequence of alteration appears most commonly during the weathering of ferromagnesian minerals. The plagioclases in some cases may alter directly to halloysite (Bates, 1962) or to gibbsite (Swinedale, 1966).

The environment of formation of clay minerals can be predicted from the study of the abrasion pH of the constituent minerals of basalt. According to Stevens and Carron (1948), the abrasion pH of fresh rock ranges from 9.0 to 10.0, while that of completely altered rock (clay) is commonly between 5.0 and 6.0. The weathering of silicate minerals commences due to action of meteoritic waters which usually have initial pH in the range of 5.5 to 6.5. The initial pH may be further lowered to 3.5 by incorporation of CO_2 (Norton, 1973). At pH 5.5 to 6.5, the basaltic minerals breakdown and highly soluble constituents like Ca, Mg, Na and K are taken into solution. As a result, the waters in the near surface environment become alkaline which favours the mobilisation of silica as compared to iron and aluminium (Eswaran and Coninck, 1971). The acidic conditions with pH 3.5 favour the mobility of aluminium and iron (Patersen, 1971) which usually have relatively low solubility over a wide range of pH. Under acidic environment in the presence of organic matter and impeded groundwater circulation, iron and aluminium taken into solution, are retained at site in the form of hydroxides. Ca, Mg, Na and K, being major exchangable cations are removed from the weathered product by excessive groundwater circulation. Highly unstable ferrous iron is converted into ferric state and retained in the weathered product. Silica being required for the formation of clay minerals and which exists in far greater amounts in parent rock than what is required for the formation of clay minerals, is commonly depleted. On the other hand, aluminium is essential for the formation of clay minerals, it is retained in the altered product (Birkeland, 1984). Silica obtained from the breakdown of basaltic minerals, if retained at site for longer time, recombines with aluminium hydroxides in solution to from clay minerals.

The trends of chemical weathering of basalt can also be visualised from the comparison of chemical composition of weathered product with that of fresh unaltered basalt. Triangular plots (Fig. 4) of Bases ($CaO + MgO + Na_2O + K_2O$), R_2O_3 ($Fe_2O_3 + Al_2O_3 + TiO_2$) and SiO_2 for the soil profiles of the Indrayani river basin indicate that the trend of weathering is towards the concentration of oxides of iron, aluminium and titanium and depletion of bases and silica. However, for the lower horizons of a few soil profiles of the eastern part of the basin, the trend is towards the concentration of SiO_2 and $CaCO_3$. This has been due to poor drainage and low rainfall conditions prevailing in this part of the basin. Similar trends of chemical weathering have also been obtained from the study of the concentration ratios (Figs. 2 and 3).

An optimum two dimensional portrayal of chemical weathering can be obtained by plotting Weathering Potential Index (WPI) against Product Index (PI). Reiche (1943, 1950) has proposed these two indices which incorporate the major

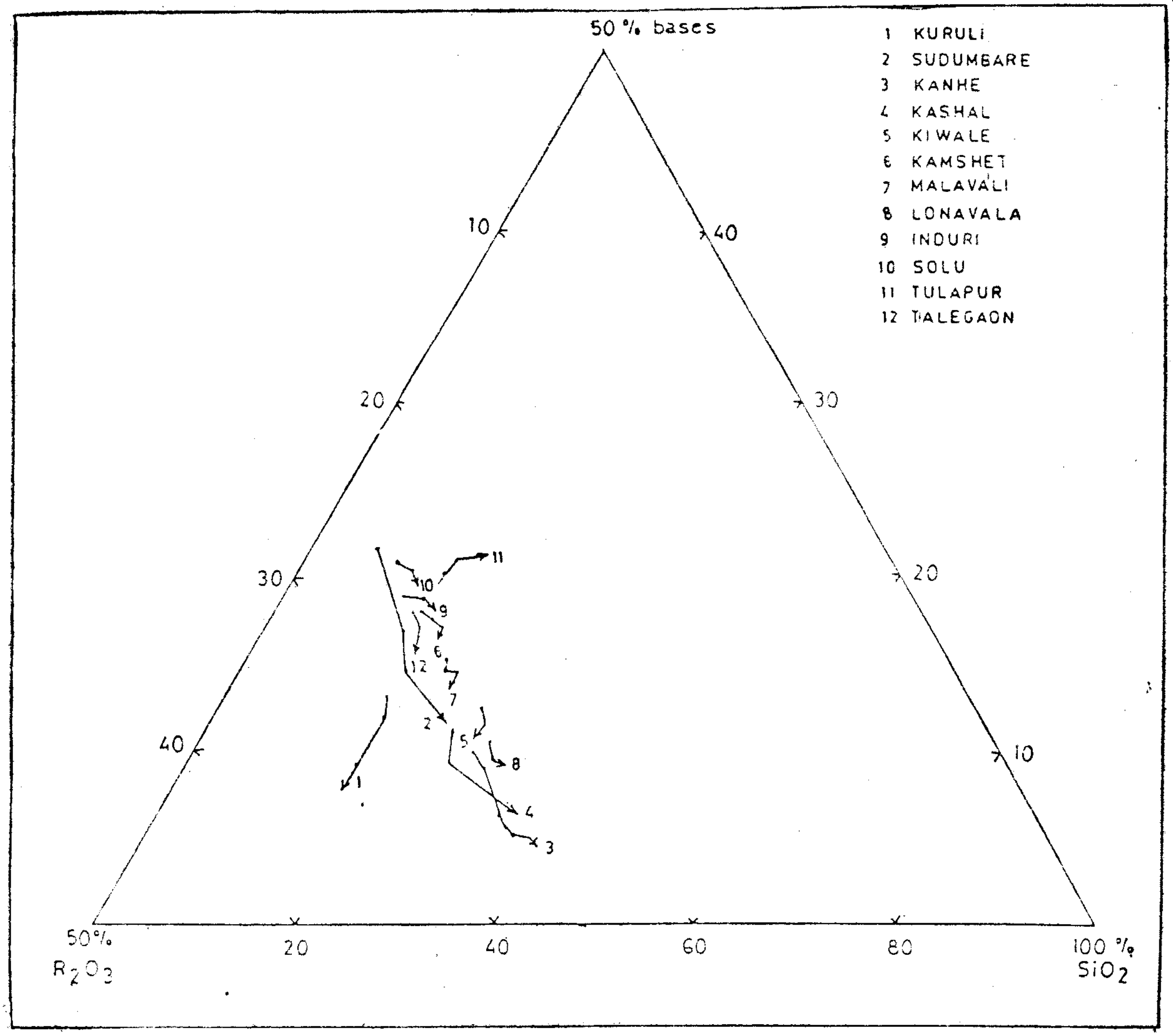

Fig. 4 : Triangular plots of SiO_2, R_2O_3 and Bases for the soils of Indrayani river basin.

elements involved in chemical weathering. The plots WPI against PI, neither show changes in an individual element nor do they account for compensative changes in the element or their groups (Colman, 1982a). However, from these plots the amount of chemical weathering can be visualised. In unaltered rocks, these indices have higher values. With progressive weathering WPI decreases rapidly due to loss of bases, while the PI decreases more slowly as silica is lost. The plots WPI against PI for the soil profiles of Indrayani river basin (Fig. 5) indicate that the chemical weathering has reached the kaolinite and halloysite fields and in some cases, it has crossed these fields suggesting still more advanced or ultimate stage, especially for the soils of the western part of the basin.

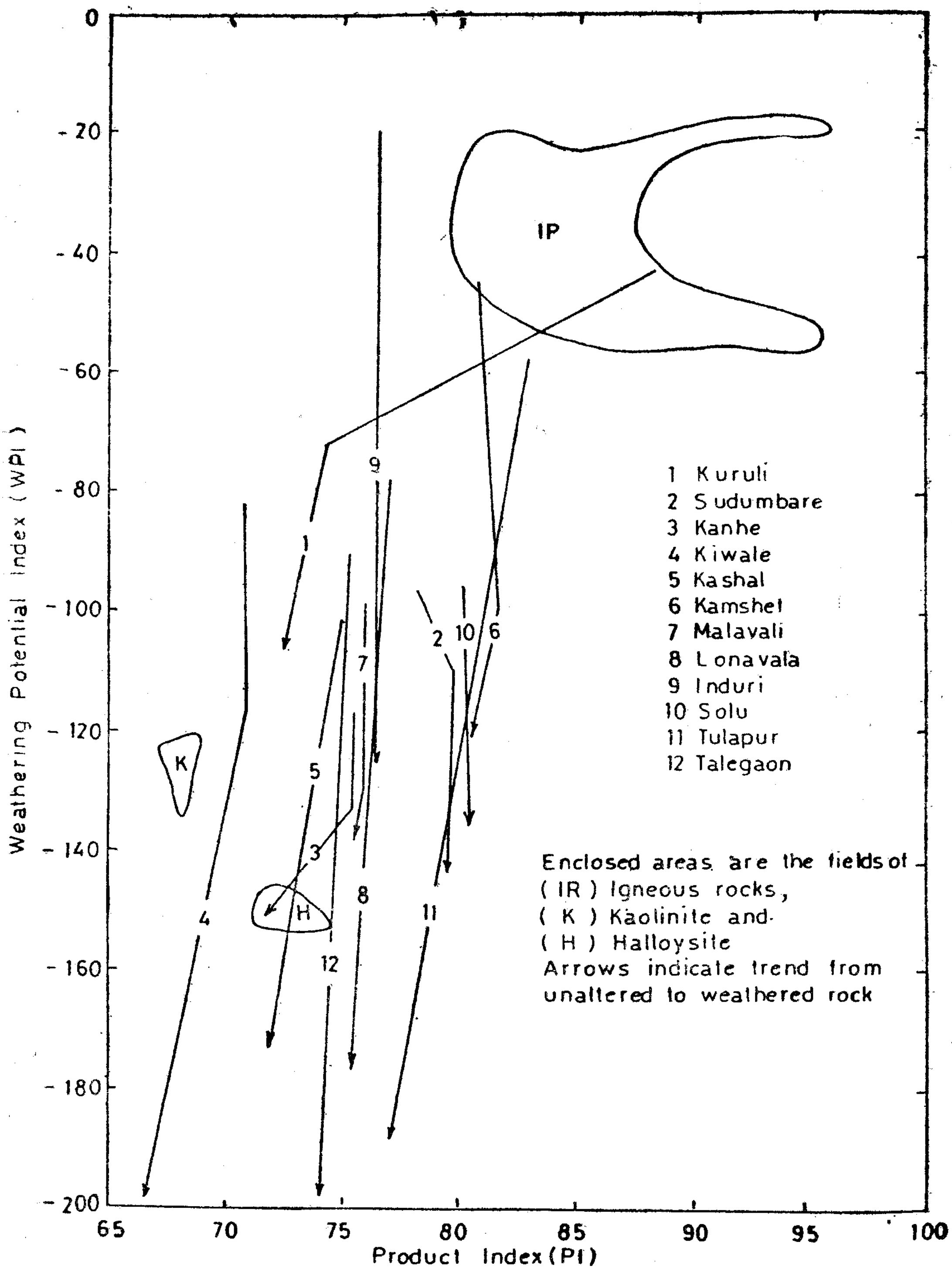

Fig. 5 : Plots of WPI versus PI for the soils of Indrayani river basin (after Reiche, 1943).

The development of laterite in the western part of Indrayani river basin has been attributed to selective accumulation of elements. The upper lateritic duricrust rich in iron has been formed by an absolute accumulation of iron; while the lower lithomargic horizon (saprolite) has been developed due to relative accumulation of aluminium (McFarlane, 1983). Iron in weathering profile may produce complex molecules with combined ferrous and ferric hydroxides in solution or in collatial suspension. On weathering particle size of the parent material becomes more finer. This promotes capillary action that brings molecules of ferrous and ferric hydroxides upward towards the more aerated oxidising environment of near surface during dry season. On oxidation, ferrous and ferric hydroxides in solution, are precipitated as ferric hydroxide in the top layer. The ferric hydroxide on dehydration gets hardened to form ferricrete. This process is repeated for several times and ultimately results in the concentration of iron in the top horizon and depletion of it from the lower horizon of the profile. Thus, ferricretes are formed by absolute accumulation of iron, while alumina gets accumulated in the lower horizon by relative enrichment resulting in lithomarges.

From the foregoing discussion it is evident that the level topographic and low rainfall conditions of the eastern part of the Indrayani river basin promoted the formation of margalitic or black cotton soils; while the rugged topography and high rainfall conditions favouring free drainage conditions developed lateritic to semi-lateritic soils in its western part.

ACKNOWLEDGEMENTS

The authors are thankful to Professor S. C. Gupte, Vice-Chancellor, University of Poona and formerly the Co-ordinator, School of Environmental Sciences, University of Poona, Pune, for providing facilities. They are also thankful to Professor K. B. Powar, Vice-Chancellor, Shivaji University, Kolhapur, for his constant support, encouragement and guidance.

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