METAMORPHISM OF COAL MACERALS

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ABSTRACT

The chemical, structural and optical changes undergone by the coal macerals with increasing rank or metamorphism have been discussed in this paper. When properties of macerals are plotted against rank, it is found that the different macerals follow separate path. Abrupt and significant change in the properties of the macerals takes place at about 82-83, 89-90 and 92 percent carbon levels. At about 89-90 percent carbon content the track of exinite merges with the track of vitrinite and with further progress in rank at about 92 percent carbon content the latter meets the track of inertinite. At about 92 precent carbon level the chemical and structural differences between the macerals become almost negligible. Though fusinite attains a more or less stable chemical composition and structure in the early stage of coalification (diagenetic phase), other macerals of inertinite group show changes in the later stage (geochemical phase) of coalification. The difference in the chemical composition of the macerals decreases with increasing reflectance and becomes nil or negligible when reflectance (in oil) of vitrinite of coal reaches a value of about 1.80 or more. Present study also reveals that an estimation of chemical composition of pure macerals can be made from their reflectance values.

INTRODUCTION

It is well known that the coal macerals differ in their physical, chemical and optical properties. The differences are significant in low rank coals and the individual maceral follow different metamorphic paths which ultimately merge at higher rank. In an earlier paper the present author (Ghosh, 1971) discussed certain changes in the properties of the macerals with rank. Some more significant facts regarding metamorphism of coal macerals, encountered in course of further studies, have been discussed in this paper.

The present study is based on the data obtained on the chemical composition, structural and optical properties of macerals isolated from Indian coals and the data published by several other workers (referred to with the explanation of figures) of the different countries on coal macerals. Properties of the macerals isolated from Indian coals are given in tables 1 and 2.

RESULTS

Elementary composition: The primary difference in chemical composition of macerals is in their carbon, hydrogen and oxygen contents. With increasing rank carbon content of the macerals increases and oxygen and hydrogen content decreases. In a coal inertinite contains maximum carbon followed successively by exinite and vitrinite. Hydrogen content is maximum in exinite and minimum in inertinite.

Sulphur and nitrogen contents of the macerals do not show any appreciable change with rank. Usually nitrogen is maximum in vitrinite and followed by exinite and inertinite. Sulphur content of Tertiary coals of Assam and Jammu is higher than that recorded in Lower Gondwana (Permian) coals of India. From the studies of Roy (1963) as well as from

Table—1
Ultimate composition, aromaticity, hydroaromaticity, distribution of reactive oxygen groups and reflectance of coal macerals.

Coal and its Geological age	Maceral*	Ultimate composition (D.A.F.)					Aromaticity	Hydroaromaticity	Reactive oxygen groups			R_o (Reflectance)
		C	H	N	S	O			O(OH)	$O_{(CO)}$	$O_{(COOH)}$	
1	V	76.2	5.7	1.0	3.2	13.9	0.70	0.22	8.65	2.11	0.23	0.48
Daranggiri	E	78.5	10.3	0.7	4.5	6.0	0.65	0.28	2.48	2.38	0.25	0.15
Assam, Eocene	I	88.5	3.2	0.6	1.3	6.4	0.88	0.06	2.06	3.33	0.21	1.70
2	V	78.2	5.4	1.9	0.8	13.7	0.72	0.23	9.43	1.30	0.20	0.55
Tandur	E	82.5	7.4	1.5	0.7	7.9	0.66	0.26	2.93	3.42	0.21	0.18
Permian	I	88.1	4.2	1.2	0.8	5.7	0.90	0.06	1.67	3.19	0.20	1.75
3	V	80.8	5.3	2.1	0.7	11.1	0.74	0.22	6.52	2.65	0.22	0.55
Samla	E	82.3	6.9	1.8	0.7	8.3	0.65	0.27	2.89	3.37	0.19	0.20
Permian	I	86.6	4.7	1.3	0.7	6.7	0.88	0.07	2.12	3.40	0.20	1.67
4	V	84.7	5.4	1.6	0.6	7.7	0.76	0.18	3.72	3.04	0.15	0.87
Sanctoria,	E	88.6	5.8	1.3	0.7	3.6	0.74	0.20	1.08	1.73	0.14	0.40
Permian	I	89.3	4.2	1.1	0.8	4.6	0.91	0.05	0.95	2.73	0.10	1.81
5	V	85.8	5.3	1.8	0.7	6.4	0.78	0.17	2.55	3.17	0.14	0.52
Ramnagar,	E	89.2	6.9	1.3	0.7	1.9	0.76	0.19	0.52	1.19	0.06	0.92
Permian	I	91.0	4.2	1.2	0.8	2.8	0.91	0.05	0.71	1.48	0.10	2.13
6	V	86.6	5.3	1.5	0.8	5.8	0.82	0.14	1.91	2.77	0.08	1.02
Laikdih,	E	88.2	6.5	1.3	0.6	3.4	0.80	0.15	0.94	1.81	0.10	0.55
Permian	I	91.8	4.0	1.0	0.8	2.4	0.93	0.03	0.52	1.53	0.08	2.25
7	V	89.4	5.5	1.6	0.5	3.0	0.82	0.14	0.83	1.83	..	1.28
Ghanuadih	E	89.7	5.7	1.2	0.6	2.8	0.80	0.15	0.64	1.79	..	0.77
Permian	I	91.8	3.6	1.1	0.7	2.8	0.93	0.03	0.53	2.05	..	2.88
8	V	91.1	4.4	0.8	2.0	1.7	0.91	0.05	0.43	1.19	..	1.80
Chakkar,	I	93.2	2.8	0.6	1.7	1.7	0.98	..	0.31	1.37	..	4.02
Jammu, Eocene												

*V—Vitrinite; E—Exinite; I—Inertinite.

Table 2**—Ultimate composition and reflectance of macerals from Tindharia coal, Darjeeling District, Eastern Himalaya.

Sample No.	Maceral*	Ultimate composition (D.A.F.)					Ro (Reflectance)
		C	H	N	S	O	
D—12	V	78.3	5.1	1.4	0.4	14.8	0.65
	I	87.8	3.8	1.3	0.5	6.6	1.81
D—13	V	86.9	4.9	1·0	0.5	6.7	1.10
	I	89.8	3.7	1.0	0.5	5.0	2.12
D—14	V	88.0	4.9	1.4	0.5	5.2	1.44
	I	90.3	3.5	1.2	0.4	4.6	2.60
D—15	V	89.0	5.0	1.1	0.5	4.4	1.57
	I	90.9	3.5	0.9	0.6	4.1	3.12

*V—Vitrinite; I—Inertinite.
** Data not plotted in the figures of this paper.

the present investigation it is seen that the sulphur content is maximum in exinite and is minimum in inertinite. Organic sulphur constitutes the major part of the total sulphur of the Tertiary coals of India (Table 3).

Table 3—Total and organic sulphur content in coal macerals.

Coal	Maceral*	Total sulphur	Organic sulphur
1	V	3.16	2.63
Daranggiri	E	4.51	4.24
	I	1.26	0.64
8	V	2.04	1.03
Chakkar	I	1.67	0.37

*V—Vitrinite; E—Exinite; I—Inertinite.

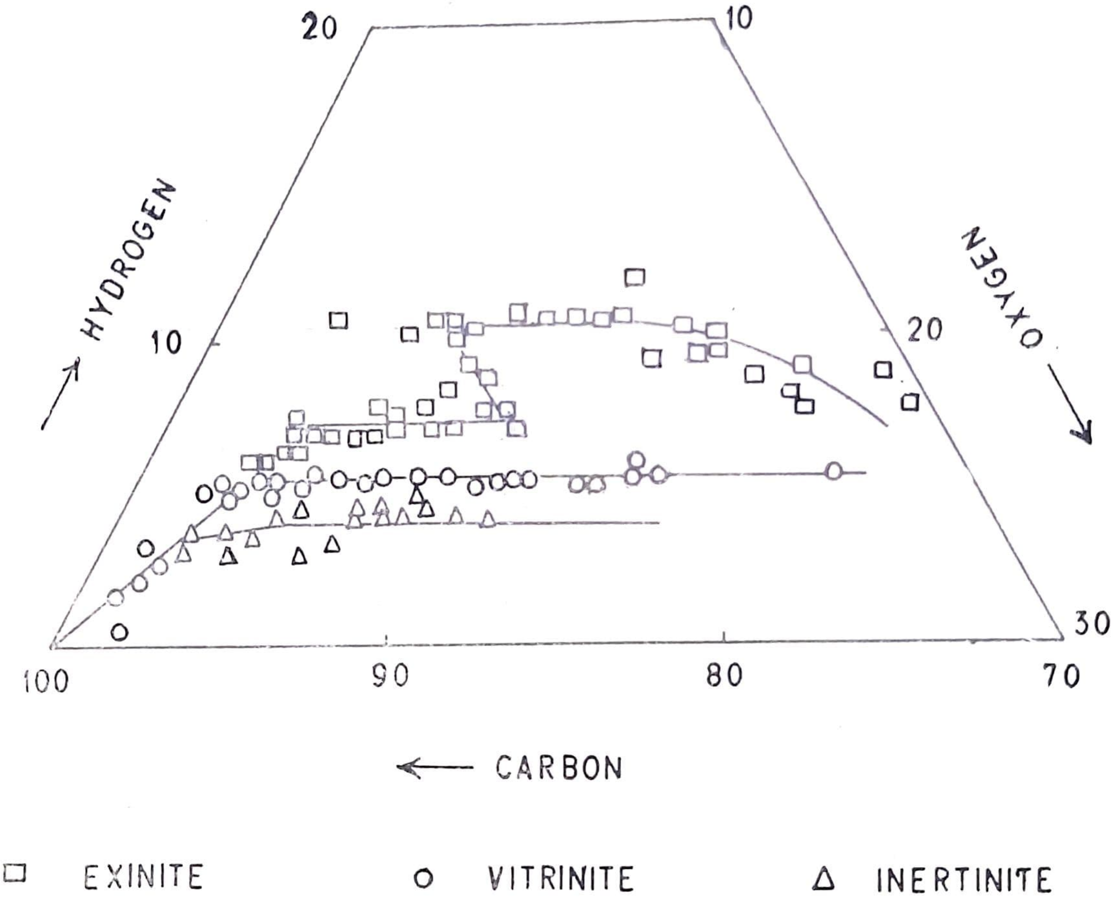
Reactive oxygen groups: Reactive oxygen constitutes a significant part of the total oxygen content of the macerals. The total reactive oxygen content (as percent of total 0) of the macerals increases with rank. Amongst the macerals, it is highest in exinite and lowest in inertinite. Of the reactive oxygen groups, the (OH) groups decrease and the (CO) groups increase with rank. In a coal both the (OH) groups and (CO) groups are maximum in vitrinite and are minimum in inertinite.

Structural parameters: Aromaticity of macerals increases from exinite to inertinite and also with rank. The hydroaromaticity increases in the reverse order to that of aromaticity. In the same rank coal hydroaromaticity as well as distribution of hydrogen decrease in the order of exinite, vitrinite and inertinite. From the IR and PSR studies TSCHAMLER *et al.* (1966) have proved that the "exinite possesses the biggest aliphatic position with highest relative amount of CH_2 groups and micrinite possesses the smallest aliphatic position with lowest relative amount of CH_2 groups."

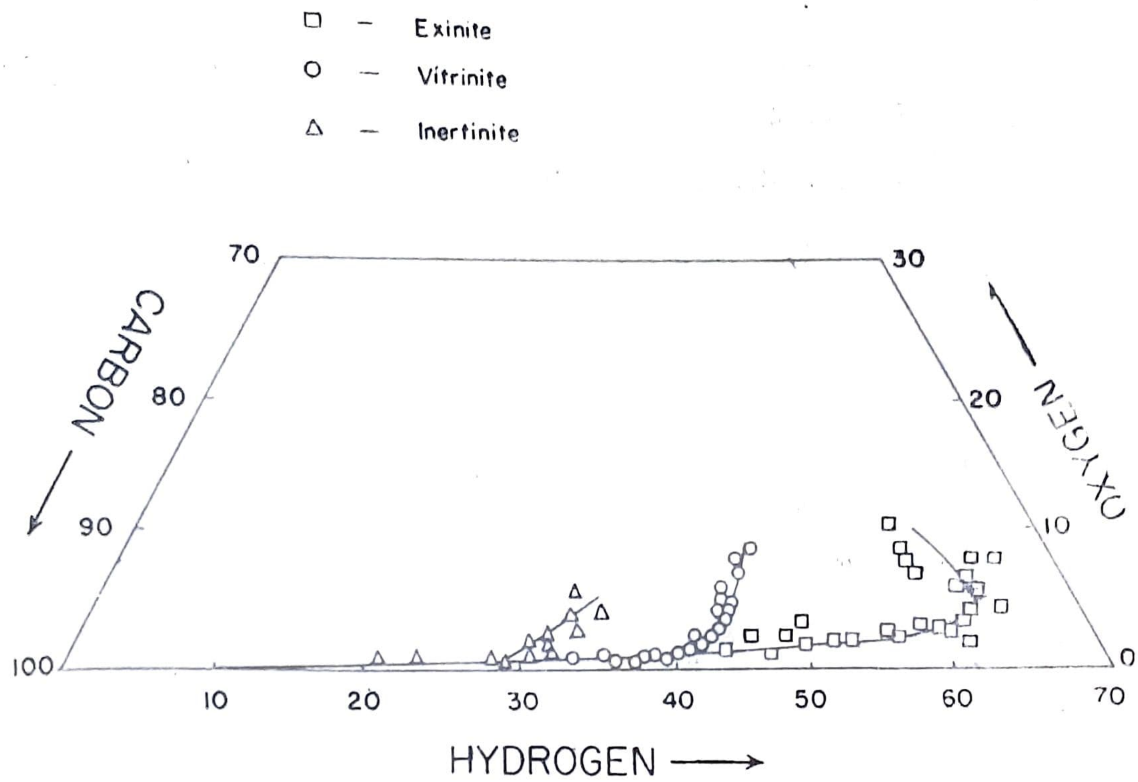
DISCUSSION

The nature of the metamorphic changes undergone by the coal macerals has been shown in figures 1 to 5. The difference in the properties of the macerals is significantly high in low rank coals and decreases with increase in rank and ultimately merge together at higher rank. This shows that in low rank coals the relative proportion of the different macerals can considerably influence the bulk chemical composition of a coal and therefore the average analyses of coal sample can not be used in ascertaining its rank and properties. This is particularly true in case of many low rank Indian coals which are rich in inertinite (SEN, 1968; GHOSH, 1969).

The constituent macerals of the exinite group differ from each other in chemical composition particularly below the bituminous rank level. In the same level of carbon content, sporinite contains more H and less O compared to resinite, cutinite and alginite. The macerals semifusinite and fusinite of inertinite group also differ in chemical composition. The inertinite starts its track at considerably higher C level compared to the other two groups of macerals. This reflects that inertinite undergoes the major metamorphic



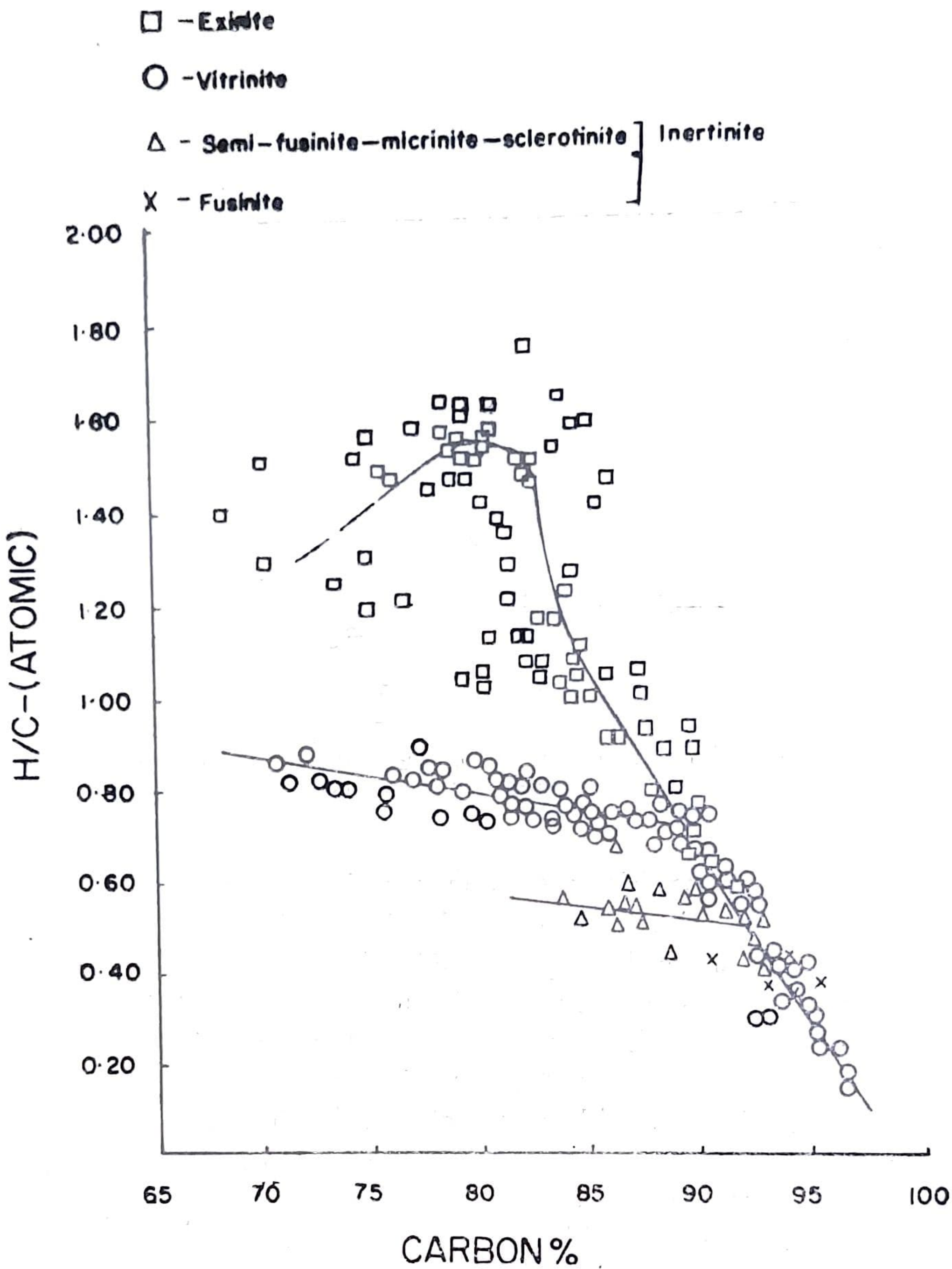
Text-fig. 1. Relationship between C, H and O (D. A. F.—basis, C+H+O=100 percent by weight) Based on the data of MACRAE (1943), CRICK (1951), KUHLWEIN (1951), KROGER *et al.* (1956), ALPERN (1956), DORMANS *et al.* (1957), MURCHISON (1957), ERGUN *et al.* (1959, 1960), FRIDEL & QUEISR (1959), GIVEN *et al.* (1960), FRANCIS (1961), LADNER & STAGNY (1963), MURCHINSON & JONES (1964), TSCHAMLER *et al.* (1966), AUSTEN *et al.* (1966) and present author.



Text-fig. 2. Change of carbon, hydrogen and oxygen content (on atomic percentage basis) of coal macerals with rank (C+H+O=100 atoms). Based on the data used in Text-fig. 1.

change in the diagenetic phase. However, from the chemical and reflectance data of the macerals isolated from the Tindharia coal (Darjeeling District, Eastern Himalaya) it appears that the macerals of inertinite group suffer changes in the geochemical phase due to tectonism (Table 2). It is also evident from the text-figures 1 to 4 that the rate of chemical change with rank of the different macerals is distinctly different.

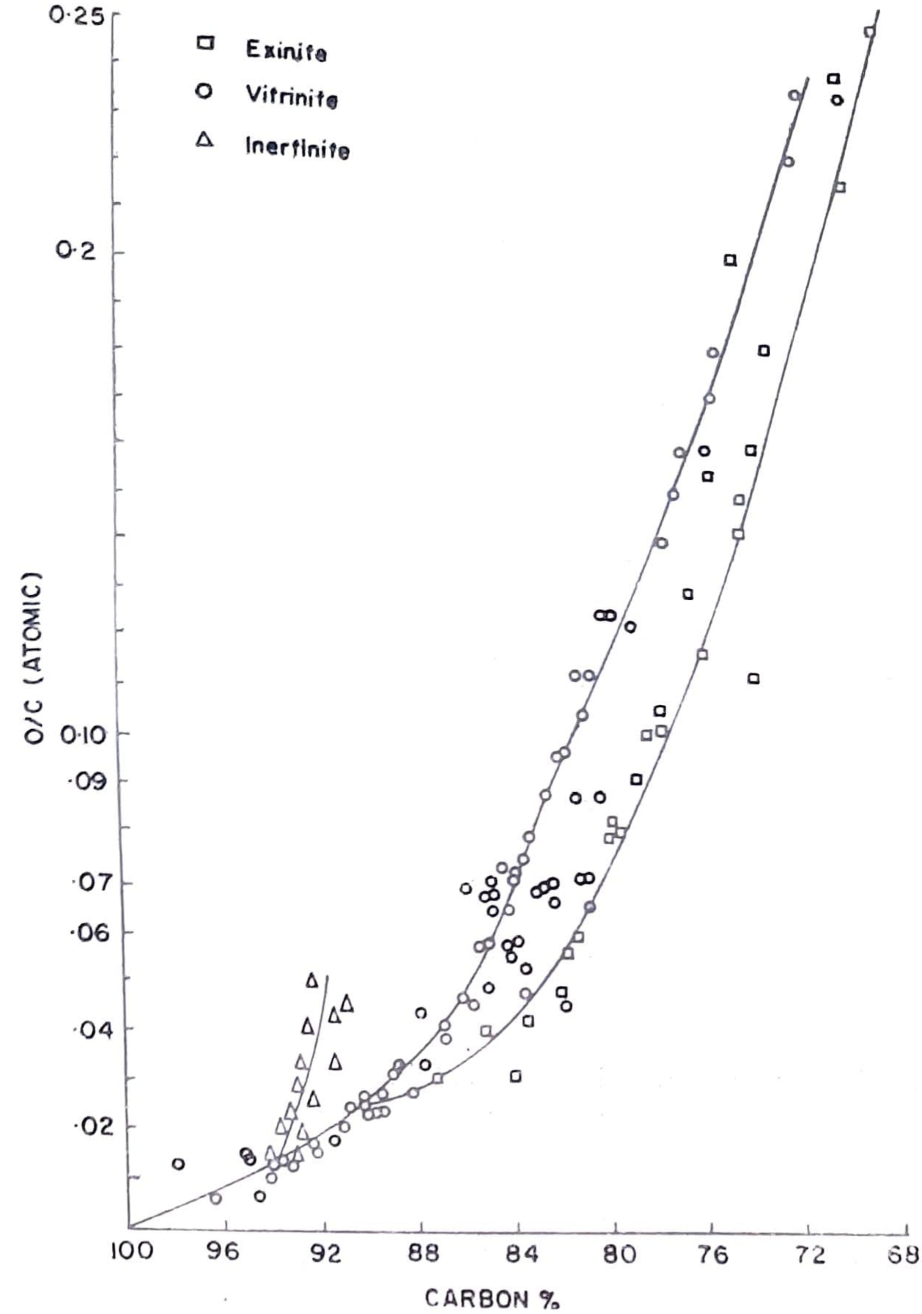
It is mentioned earlier that nitrogen and sulphur contents of macerals do not show any systematic change with rank. Therefore change in the quantitative distribution of the three major chemical elements, carbon, hydrogen and oxygen, of the macerals with rank has been examined by plotting the data on a triangular diagram (Text-fig. 1) (basis C+H+O=100 percent by weight). The net change in the macerals with rank is removal of H and O and enrichment in C. Though oxygen is removed throughout the entire range of rank increase, however, major part of it is removed at the first stage (Text-figs. 1 and 2). Hydrogen content of macerals remains almost constant over certain rank ranges and dehydrogenetation takes place abruptly and in steps. The rank level for the initiation of dehydrogenation is not same for all the macerals. Dehydrogenation of exinite starts first at 82-83 percent carbon level and is followed by vitrinite (91 percent carbon level) and inertinite (94 percent carbon level). Hydrogen content of exinite remains steady (H-10.2 percent) between 76 and 82-83 percent carbon content and below 76 percent carbon content the exinite track shows increase in H and decrease in O with increase in carbon content (Text-fig. 1.). Furthermore, at 82-83 percent carbon content exinite track also shows an increase in O and decrease in H. After having a drastic increase of oxygen and decrease of hydrogen at 82-83 percent carbon content, hydrogen content of exinite once again remains constant (H=7.2 percent) up to 89 percent carbon content and thereafter falls again till it meets the track of vitrinite. Hydrogen content of vitrinite (H=5.3 percent) and inertinite (H=3.8 percent) also remains almost constant up to 91 and 94 percent carbon contents respectively. Deoxygenation of macerals takes place through the removal of reactive oxygen groups and



Text--fig. 3. Relationship between C (D.A.F.) and H/C (atomic) of coal macerals. Based on the data used in Fig. 1. (Basis C+H+O+N+S=100 percent by weight).

during dehydrogenation the hydroaromatic and/or aliphatic side chains or side groups are removed. Dehydrogenation of inertinite takes place through demethanation.

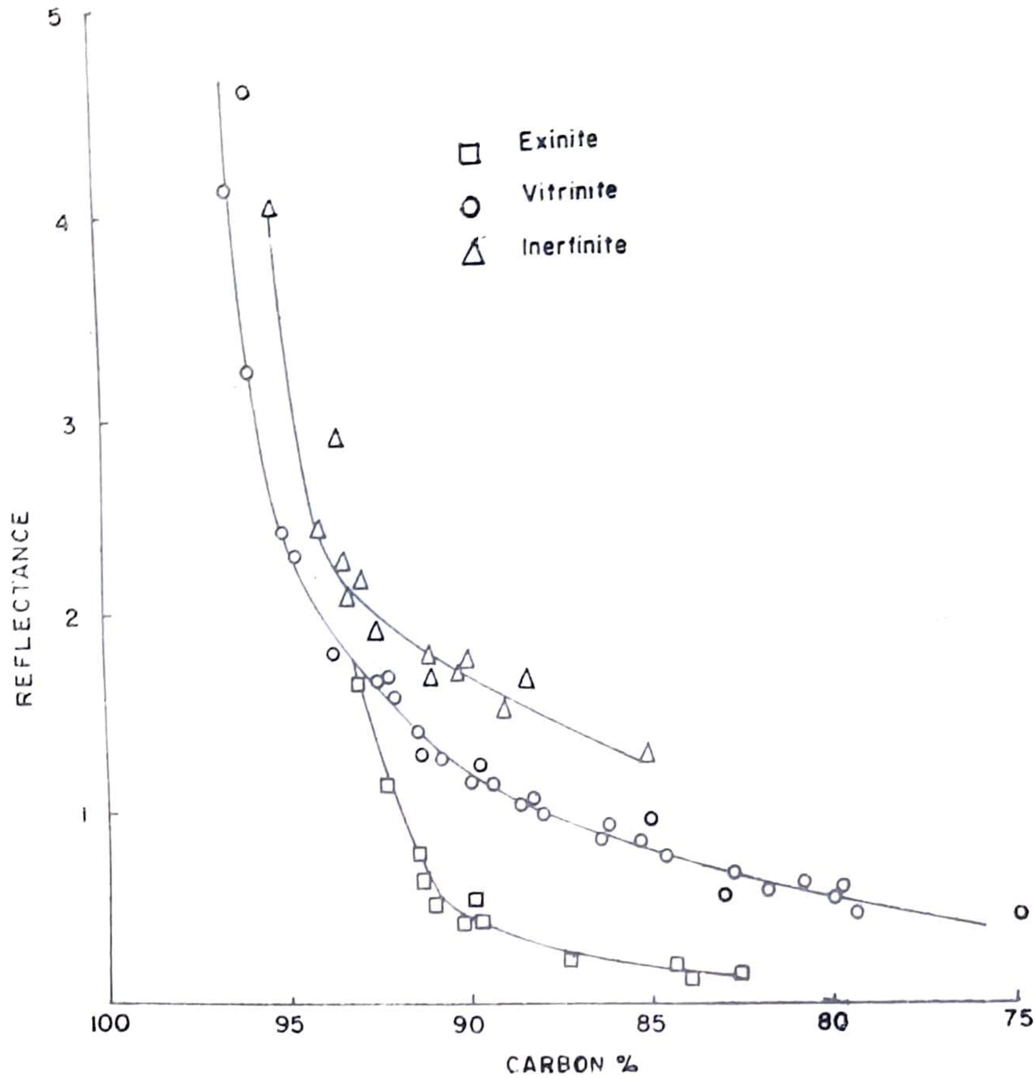
The changes in the atomic hydrogen-carbon (Text-fig. 3) and oxygen-carbon (Text-fig. 3 & 4) with C or rank (calculated on the basis of C+H+O+N+S=100 percent by weight) have also been studied to get an idea about the nature of the structural changes undergone by the macerals with rank. The line of best fit of exinite shows an increase in H/C with increasing C up to 82-83 percent carbon level. Upto this carbon level O/C falls significantly till it reaches a value of about 0.06. Thereafter exinite track takes a sharp bend and H/C begins to fall rapidly with rank till it reaches the metamorphic track of vitrinite at about 89-90 percent carbon content. At this carbon content the track of exinite also takes a sharp bend and follows that path till the end. Prior to this vitrinite track shows a gradual fall in H/C though O/C falls steadily. The inertinite track meets track of vitrinite at about



Text-fig. 4. Relationship between C (D.A.F.) and O/C (atomic) of coal macerals. Based on the data used in Fig. 1. (Basis C+H+O+N+S=100 percent by weight).

92 percent carbon content which corresponds with H/C=0.30 and O/C=0.015. It is evident from the above findings that abrupt change in the chemical structure of the macerals takes place at 82-83, 89-90 and 92 percent carbon contents.

Reflectance of macerals also increases with rank. Text-figure 5 shows that the difference in the optical property of macerals decreases with rank and the track of exinite merges with the track of vitrinite at about 1.80 Ro. From the nature of the tracks of the macerals it is evident that the difference in the chemical composition of the macerals becomes nil or negligible when reflectance (in oil) of vitrinite of a coal becomes 1.80 or more. In other words Ro value alone is sufficient in ascertaining the chemical composition of overall sample when Ro of vitrinite of the coal sample is 1.80 or more. An estimation of chemical composition (C, H and O on D.A.F. basis) of pure macerals can be made from their reflectance with the help of the text-figures 1 and 5.



Text-fig. 5. Relationship between reflectance and carbon content (D.A.F.,—basis, C+H+O=100 percent by weight) of coal macerals. Based on the data of DORMANS *et al.* (1957), ERGUN *et al.* (1959, 1960), and present author.

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