SOME VARIATIONS IN PROPERTIES OF COAL MACERALS ELUCIDATED BY DENSITY GRADIENT SEPARATION*

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INTRODUCTION

Our recent development of a new procedure for the density separation of macerals offers a method for obtaining high resolution separation of the maceral groups: exinite, vitrinite, and inertinite, and can further resolve individual maceral types, e.g., sporinite (1,2). The procedure utilizes well-known techniques of density gradient centrifugation (DGC) to separate the coal into its components in a continuous aqueous CsCl density gradient. This results in a series of bands representing the density variations in maceral groups and maceral types. The gradient is then divided into convenient size fractions, the coal in each fraction is isolated and micropetrographic analyses are performed on selected fractions. In addition to providing pure materials for further work, a density fingerprint of a coal is produced. The observed changes in density are related in a complex way to the chemical structure of the coal or maceral (3). In order to better understand the chemical variations occurring in coal macerals we have examined the ultimate analysis of selected density fractions separated from the same coal.

EXPERIMENTAL

Separation

The basic procedures for DGC separation of macerals with advantages and disadvantages has been discussed previously (1,2). To summarize, the coal is ground to ~3 micron average particle size, chemically demineralized and separated on a density gradient. The gradient is then divided into fractions of ~0.01 g/cc range and each fraction is then filtered, washed, and dried.

Analysis

Because of the small samples often generated, ultimate analysis of selected density fractions was performed with a Perkin-Elmer 240 C, H, N Analyzer using a modified burn procedure which includes increasing the time of burn and the amount of O_2 used in the burn. Good correlation (r^2 = .98) with ASTM methods was found for a range of coals from sub-bituminous to anthracites.

RESULTS AND DISCUSSION

All the coals used here were obtained from the Pennsylvania State University Coal Data Base. The data for the coals are given in Table I. The separation of all these coals was performed in the same way and all the coals were resolved to the same degree. We have previously published detailed separation data on the high volatile B bituminous coal, PSOC-106, which gave good yields of all three maceral groups (1,3). The exinite in this coal is mainly sporinite, while the inertinite is mainly semi-fusinite. Figure 1a shows the distribution of the pure maceral particles as a function of density for PSOC-106. Pure maceral particles refer to those particles which by optical microscopy are composed of only one maceral species. Figure 1b shows the corresponding atomic ratios H/C, S/C, N/C,and O/C.

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The selected fractions analyzed represent density fractions consisting of at least 88% (vol.) of a single maceral species. The lines connecting sets of points between maceral groups must not be taken literally. These intermediate regions consist of particles with two or more macerals composing a single particle or two distinct populations of pure maceral particles. Thus, whether or not the connecting lines between maceral groups represent the atomic value in that region, their only purpose for this discussion is to aid the eye in following trends between maceral groups.

The H/C ratio exhibits a very large range of values over the entire coal: from 1.13 at the lowest density monitored to 0.48 at the highest density. The S/C ratios follow a similar trend: with the highest sulfur values in exinites and the lowest in inertinites. These sulfur values represent almost all organic sulfur since pyritic sulfur has been eliminated by the separation procedure. The S/C data is consistent with data found by an 'in situ' method of sulfur analysis in coal (4). Because of the nature of the separation method we can also see significant variations not only between maceral groups, but within each maceral group. Figure 2 is an attempt to provide some idea of the magnitude of variation that exists in the H/C ratio in the three maceral groups. The distributions are incomplete because of overlapping of maceral bands or composite maceral particles which give unreliable data. Table II represents the range of H/C values for each band and combined with previous ^{13}C with solid probe nmr data for f_a, shows the ring index or number of rings per 100 carbon atoms. The data for 50% of the coal refers to the coal centered around the peak value. The ring index includes all aromatic, aliphatic, and heterocyclic rings. The number of rings per 100 carbons is roughly the same for all the maceral groups and indicates, as expected, that they are all highly condensed species. However, the ratio of aromatic to aliphatic rings increases dramaticallly from exinites to inertinites. Exinite tends to exhibit wide variations in its composition, while vitrinite and inertinite are somwhat less variable. In all cases, though, the indications are that substantial variations in each maceral group are being observed by the density separation method. The oxygen and nitrogen data also show strong variations within the exinites and vitrinites, while inertinites do not.

In Figure 3 we have used the graphical densimetric method to show how the ring index varies with the density of the macerals (5). As can be seen the data parallels the increase in aromaticity.

The change in atomic ratios are not unique to the particular coal PSOC-106. Figures 4a and 4b show data on three more bituminous coals which contain substantial amounts of all three maceral groups. (The very high H/C value of 1.4 for PSOC-297 is due to alginite in this coal.) Although all the coals exhibit their own character in the magnitude and range of the H/C values, they all show significant chemical changes across each maceral band in a similar manner to PSOC-106. Similar data also holds for coals that contain ±95% vitrinite.

What do these variations represent? There are a number of factors which can be invoked to explain the changes observed. Each of the three major maceral groups is composed of sub-macerals (maceral types). Exinite is composed of the maceral types: sporinite, resinite, alginite, cutinite. Since the source materials for each maceral type had different chemical structures some artifact of these differences would be expected to remain. This is one source of variation. Moreover, within a single maceral type itself significant petrographic changes can be observed. For example, different spore species show different fluorescence color, and collinite and semi-fusinite can have broad reflectance ranges within a coal. All these microscopically observable changes suggest differences in chemical structure. Qualitatively, we do see regular variations in fluorescence and reflectance across the maceral bands. It is apparent that density gradient centrifugation can, to some extent, isolate these physical and chemical variations and, in a sense, provide more

homogeneous materials. However, the chemical variations we see by DGC have to be considered as lower limits of the chemical heterogeneity expected for coal. Since we are still dealing with discrete particles, its density may still be a weighted average of the maceral variants comprising the particle, even though these variants are below optical resolution. Further grinding may separate these variants, but problems of mechanochemistry and surface problems may then become significant.

CONCLUSIONS

Substantial variation in the chemical behavior of macerals has been shown for a number of coals. Density gradient techniques can provide better defined, more homogeneous materials as well as provide a lower limit on the heterogeneity.

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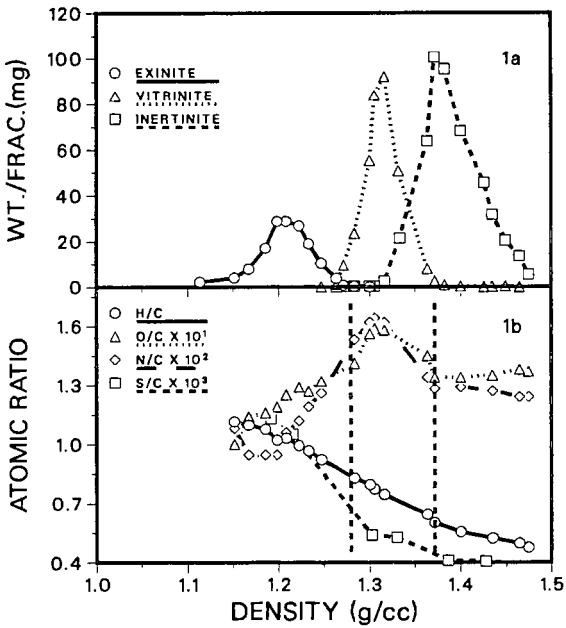

Figure 1a. Pure maceral distribution of PSOC-106.
1b. Variations of atomic parameters.

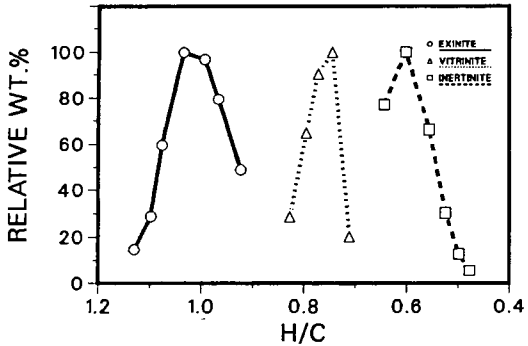

Figure 2. Distribution of coal macerals in PSOC-106 as a function of H/C ratio.

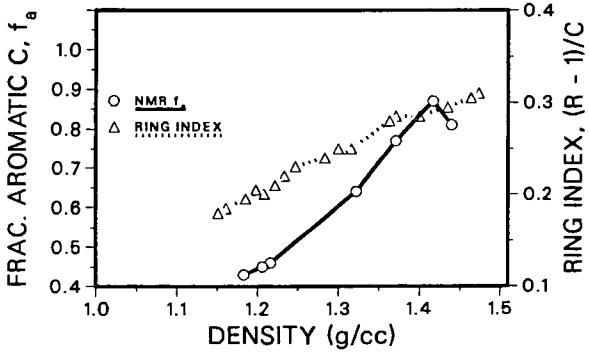

Figure 3. Variation of f_a and ring index with density in PSOC-106.

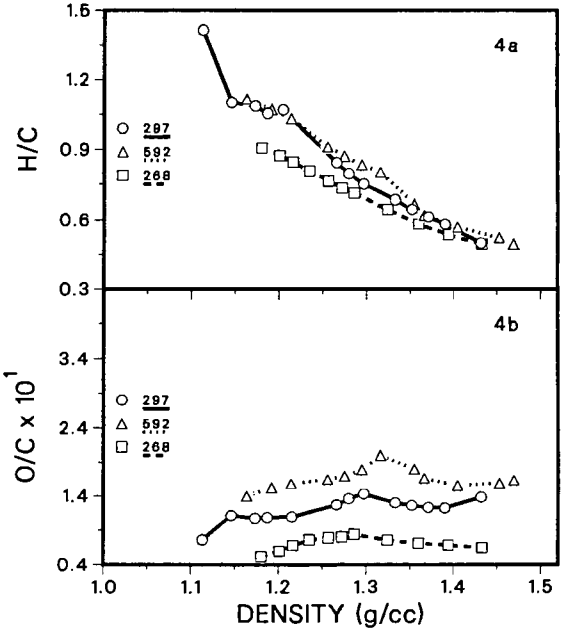

Figure 4a. Variation of H/C ratio with density.
4b. Variation of O/C ratio with density.