

The Role of Aliphatic and Aromatic Coal Structures and Macerals in Low Temperature Oxidation Processes

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INTRODUCTION

Low temperature ($\leq 100^\circ\text{C}$) coal oxidation processes are known to have a pronounced effect on important coal properties such as coking and caking behavior (1,2,3), heat of combustion (3), floatability (2) slurry pH (2), tar yield and extractability (3). However, the mechanisms and kinetics of the chemical reactions underlying such "weathering" processes in coals are far from well understood. Among the most promising analytical methods for elucidating the structural and compositional changes during coal weathering are Fourier Transform infrared (FTIR) spectroscopy (4,5) and pyrolysis mass spectrometry (Py-MS) (6,7). FTIR studies performed by Painter et al. (8) show a strong increase in carbonyl as well as ester moieties. Recent Py-MS experiments by Jakab et al. (9) have demonstrated a pronounced decrease in the pyrolysis yields of phenolic and naphthalenic components accompanied by increased production of highly polar (carboxylic and carbonylic) short chain aliphatic moieties. Py-MS techniques based on the combination of Curie-point pyrolysis, low voltage mass spectrometry and computerized multivariate data analysis methods were found to be sensitive enough to detect changes in bituminous and lower rank coals after exposure to air at 80°C for only 1 or 2 days (9). Moreover, time-resolved Py-MS techniques capable of recording up to 10 spectra per second at heating rates of approx. 100°K/s were shown to provide valuable information about the mechanisms and kinetics of vacuum pyrolysis processes in fresh and weathered coal (9). Meuzelaar et al. (3) interpreted the pronounced decrease in extractable alkylnaphthalene moieties in high volatile B bituminous Hiawatha coal as a loss of "mobile phase" components by attachment to the "network phase". Under the conditions employed in those experiments, such "grafting" processes appear to be more prevalent than the often hypothesized crosslinking reactions between macromolecular components. These interpretations find support in recent studies by Larsen et al. (10) on the influence of weathering processes on coal swelling properties in solvents.

In the present article new Py-MS data on low temperature oxidation effects in several U.S. coals of different rank and origin will be discussed with special emphasis on the role of different coal macerals.

EXPERIMENTAL

Three separate experiments were performed: (a) oxidation under dynamic reactor flow conditions; (b) oxidation under static conditions; and (c) pyridine extraction of fresh and oxidized coal.

Under dynamic conditions, 20-24 g aliquots (-60 mesh) of four coals (Wyodak, Adaville #6, Hiawatha, Upper Freeport) were exposed to an air flow of 5.10 ml/min in a 100 ml glass reactor, at 100°C for 170-212 hours (11). Under static conditions, four maceral concentrates were oxidized with air, viz. vitrinite and semi-fusinite fractions prepared by density gradient centrifugation of Dakota seam coal (New Mexico, PSOC 858), sporinite prepared by density gradient centrifugation, from Brazil block seam, Indiana Eastern (PSOC 107) and a hand-picked resinite sample from the Wattis seam (Utah). Twenty five mg aliquots of these macerals were exposed to air at 100°C for 100 hours in sealed 2 l flasks.

Pyridine extraction was performed on Hiawatha coal in a regular Soxhlet extractor for 24 hours at room temperature. A weathered coal sample for pyridine

extraction was prepared by exposing a 15 g aliquot (-60 mesh) to air at 100°C for 212 hours (12) under dynamic flow conditions.

All whole coal samples as well as insoluble extraction residue were hand ground under nitrogen atmosphere into a fine, uniform suspension in Spectrograde methanol (5 mg of sample per ml of methanol). The pyridine-extracted fraction was dissolved in a mixture of benzene and methanol (3:1, v/v) at a concentration of 2 mg/ml. Five microliter drops of the above suspensions and the solution were coated on the ferromagnetic filaments used in Curie-point pyrolysis and air-dried under continuous rotation, resulting in approximately 20 µg of dry sample on the filament.

Pyrolysis MS runs were performed under the same conditions for all samples, i.e., electron energy 12 eV, mass range 20-260 m/z, scanning rate 1000 amu/s, temperature rise time about 6 s, equilibrium temperature 610°C, total heating time 10 s (13,14). In order to evaluate weathering-induced differences, computerized multivariate analysis techniques such as factor analysis and discriminant analysis were applied to the MS data (14,15).

RESULTS AND DISCUSSION

Low voltage pyrolysis mass spectra of fresh and weathered coals are shown in Figures 1-4. Comparison of the spectra of the four fresh coal samples in Figures 1a-4a shows the obvious effects of rank differences between the two subbituminous coals (Adaville #6 and Wyodak) and the two high volatile bituminous coals (Upper Freeport and Hiawatha). Whereas the spectra of the former (figs. 1a and 2a) are dominated by dihydroxybenzenes and phenols of various degrees of alkylsubstitution, the spectra of the latter (figs 3a and 4a) show a dramatic decrease in dihydroxybenzene signals coupled with a markedly higher abundance of aromatic hydrocarbon series such as naphthalenes and benzenes. This trend appears to be most pronounced in the Upper Freeport sample, perhaps due to its slightly higher rank (borderline hvAb/mvb) than the Hiawatha coal (hvBb/hvAb). However, the major differences in age and origin between the two samples (Upper Freeport - Carboniferous, Interior Province; Hiawatha - Cretaceous, Rocky Mountain Province) should also be kept in mind. As noted by Given et al. (16) Western coals tend to have lower hydroxyl content than Interior and Eastern Province coals of comparable rank. For a detailed discussion of rank effects on the low voltage pyrolysis mass spectra of 102 Western U.S. coals the interested reader is referred to previous publications (6,7).

The differences between the spectra of the two subbituminous coals (figs. 1a and 2a) are far less pronounced. Again a small rank effect may be present. On the basis of equilibrium moisture content some Wyodak coal samples could be classified as lignites (17) whereas the rank of the Adaville #6 coal is subbituminous B. Although the pyrolysis mass spectra of Western lignites and subbituminous coals do not show marked differences (7), the slightly higher relative abundance of the naphthalene series in the Adaville coal (Figure 2a) is rather typical as is the somewhat different distribution of phenols.

It should be pointed out here that chemical identification of the different peak series in the low voltage pyrolysis mass spectra of coals is tentative only and is based largely on supporting data obtained by GC/MS (18,19), MS/MS (20) and NMR (21) studies of similar coal pyrolyzates. Moreover, since every mass peak is likely to contain contributions from more than one chemical compound, the use of chemical labels is only meant to identify those components thought to contribute most strongly to the respective peak series.

The effects of low temperature oxidation on the four coals can be examined by "subtracting" the spectra of the weathered coal samples in Figures 1b-4b from those of the corresponding fresh samples using a discriminant analysis procedure (9) (Figures 1a-4a). This results in the discriminant spectra shown in Figures 1c-4c. Comparison of the latter reveals an intriguing, generalized trend. The aromatic components of the four coal pyrolyzates have decreased markedly, whereas the strong aliphatic signals (e.g., corresponding to C_nH_{2n+1} , C_nH_{2n} , C_nH_{2n-1} and C_nH_{2n-2} ; $n \leq 10$) in each spectrum appear to have remained constant. This apparently reflects a difference in susceptibility to weathering effects between those structural moieties

producing the abovementioned aliphatic peak series and those moieties giving rise to the aromatic hydrocarbon and hydroxyaromatic peak series.

A second, intriguing observation from Figures 1c-4c is the qualitative similarity between the low molecular weight ion signals found to increase upon weathering. In all four coals these peak series appear to represent highly polar short chain aliphatic compounds such as CO^+ (m/z 28), CO_2^+ (m/z 44), and CH_3COOH^+ (m/z 60). Furthermore, it is interesting to note the high intensity of m/z 32, thought to represent increased retention of the methanol solvent (used to prepare coal suspensions for Py-MS analysis) in the more polar, weathered coals.

First, let us concentrate on the differential loss of aromatic vs. aliphatic pyrolyzate components. It is tempting to try to explain this on the basis of possible differences in the susceptibility of the different coal maceral components. As evident from the averaged pyrolysis mass spectra of maceral concentrates in Figure 5, marked differences exist between the relative aliphaticity and aromaticity of pyrolyzates from fusinites (highly aromatic), vitrinites and sporinites (primarily aliphatic). Other liptinitic macerals such as alginite and cutinite provide even stronger aliphatic Py-MS patterns than sporinite (22), whereas resinites from Western U.S. coals are characterized by alicyclic and hydroaromatic series (23). Thus, in principle it would be possible that low temperature oxidation could effect primarily the more highly aromatic vitrinitic and/or fusinitic macerals while leaving the more aliphatic macerals relatively unaffected.

This brings up the interesting question which of the various liptinites are primarily responsible for the remarkably similar aliphatic patterns observed in all four coals in Figures 1-4. Although sporinite is likely to contribute to the Py-MS pattern of the Carboniferous Upper Freeport coal, Cretaceous (Adaville, Hiawatha) and Tertiary (Wyodak) Western coals generally contain only minor amounts of sporinite. Many Western coals, however, are known to contain marked amounts (e.g., 5-10%) of resinite (23). Nevertheless, typical Py-MS patterns of resinites are quite different from the prominent aliphatic hydrocarbon patterns in Figures 1-4. Consequently, the authors believe that two ubiquitous liptinitic macerals, namely alginite (or detrital forms such as bituminite) and cutinite are primarily responsible for the observed aliphatic Py-MS patterns and may well be present in much larger quantities than estimated by micropetrographic techniques. Evidence supporting the potentially important contributions of algal coal components has been presented (though not completely interpreted) in previous Py-MS studies of over 130 U.S. coals (7,17), whereas the grossly underestimated role of cutinitic macerals has recently been highlighted in several studies by De Leeuw and co-workers (24).

Pyridine extraction of Hiawatha coal before and after low temperature oxidation (Figure 6) not only shows a dramatic decrease in extraction yield (22% 4%) but also reveals a nearly complete separation between aromatic peak series (dominant in the extract) and aliphatic peak series (retained in the residue). Although it should be pointed out that the residue is likely to contain more or less highly condensed aromatic components as well (which may well have remained "invisible" to the Py-MS procedure), the apparent insolubility of the aliphatic hydrocarbon components is in line with the previous contention that alginite and/or cutinite derived macerals are likely to be responsible for the bulk of the observed aliphatic hydrocarbon signals in Py-MS patterns of whole coal. Both types of macerals are notoriously difficult to dissolve (cutinites and algal kerogens can be purified by means of strong acids!).

Careful examination of Figure 6 also provides an important clue with regard to the possible fate of the disappearing aromatic moieties during low temperature weathering. Py-MS analysis of the pyridine residue of the weathered coal sample reveals a clear series of alkylnaphthalenes, apparently liberated by the vacuum pyrolysis conditions. It is tempting to speculate that these aromatic moieties became linked ("grafted") to the macromolecular network during the weathering process. However, the possibility of physical entrapment (clathration) cannot be ruled out either. Present indications are that the grafted (or trapped) aromatic molecules alone cannot fully explain the marked loss of aromatic and hydroxyaromatic moieties but that some aromatic rings are destroyed by the oxidation process (in spite of the relatively low temperatures used), resulting in the formation of the

short chain aliphatic acids and ketones seen in Figures 1c-4c. Further support for this explanation is found in the results of low temperature oxidation studies on selected maceral concentrates of similar rank shown in Figures 7 and 8.

The factor score plot in Figure 7 reveals that the resinite and semifusinite concentrates underwent more severe oxidative changes, which resulted in the formation of oxygen containing aliphatic moieties, than the vitrinite concentrate. The sporinite concentrate showed the least severe weathering-induced degradation. This suggests that the abundant hydroaromatic and aromatic moieties in the resinite and semifusinite samples respectively, provide the most likely source for the short chain, carboxyl- and carbonyl-containing, aliphatic compounds observed in the Py-MS patterns of weathered coal.

In conclusion, aliphatic, hydrocarbon-rich coal structures thought to be derived from cutinitic or algal sources show little or no chemical changes under low temperature oxidation conditions whereas vitrinite and sporinite show a moderate oxidation tendency. Further oxidation experiments with coals and maceral concentrates from different sources will have to be carried out in order to determine the general validity of the observed phenomena for coals of different rank and depositional history.

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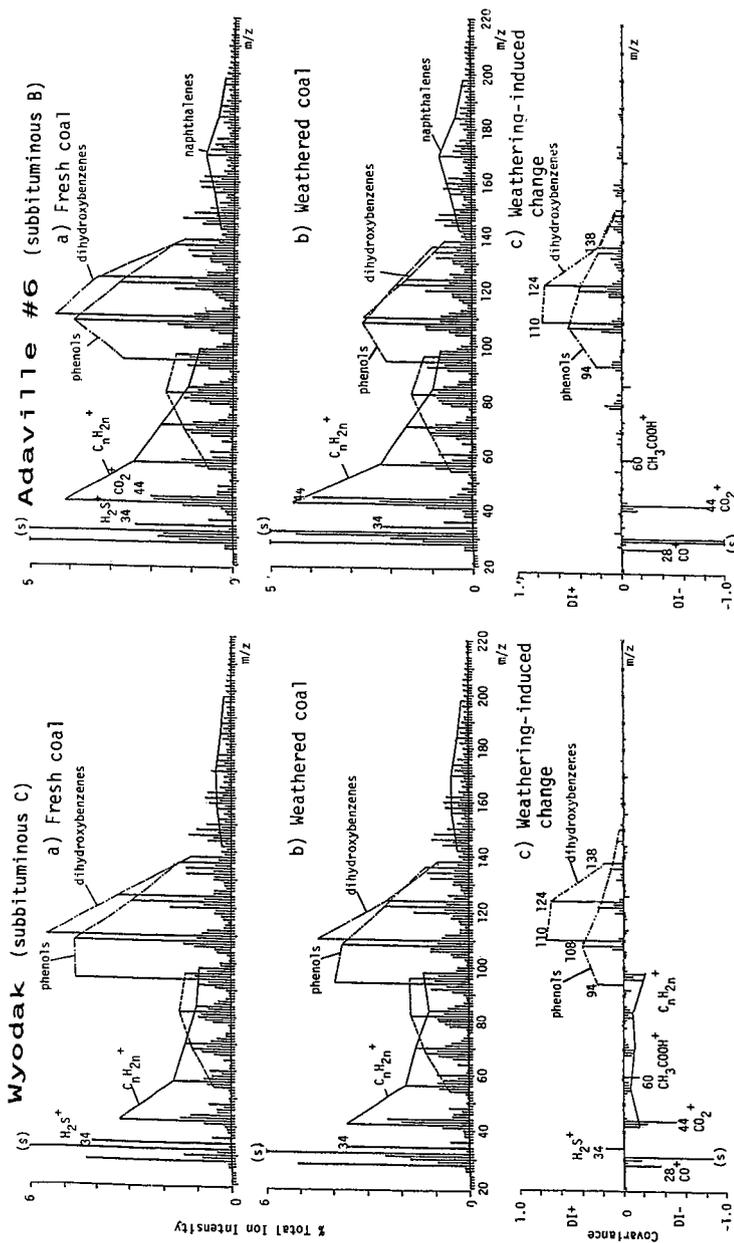


Figure 1. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Wyodak coal, and (c) discriminant spectra. Positive components (DI⁺) represent mass peaks decreased in weathered sample and negative components (DI⁻) represent compounds increased in weathered sample. (s) denotes peak originating from solvent.

Figure 2. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Adaville #6 coal, and (c) discriminant spectra. Positive components (DI⁺) represent mass peaks decreased in weathered sample and negative components (DI⁻) represent compounds increased in weathered sample. (s) denotes peak originating from solvent.

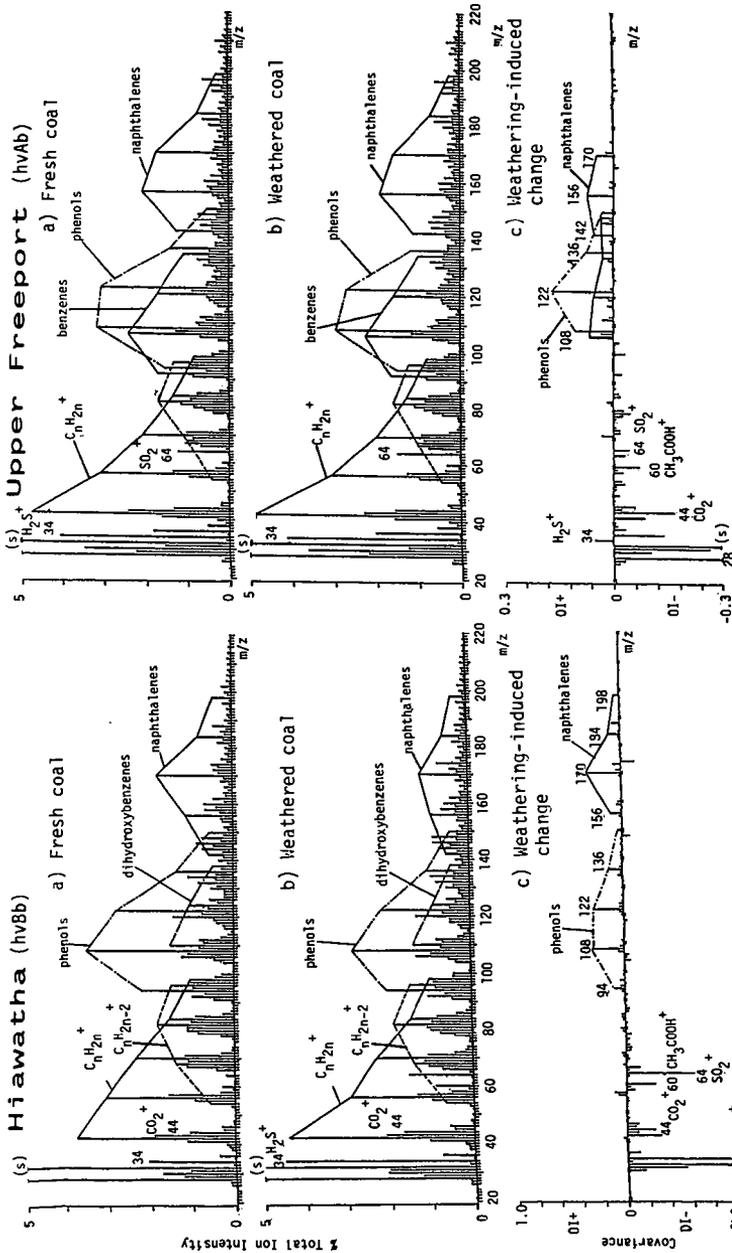


Figure 3. Curie-point pyrolysis mass spectra of (a) fresh, (b) weathered Hiawatha coal, and (c) discriminant spectra. Positive components (DI⁺) represent mass peaks decreased in weathered sample and negative components (DI⁻) represent compounds increased in weathered sample. (s) denotes peak originating from solvent.

Figure 4. Curie-point pyrolysis mass spectra of (a) fresh (b) weathered Upper Freeport coal, and (c) discriminant spectra. Positive components (DI⁺) represent mass peaks decreased in weathered sample and negative components (DI⁻) represent compounds increased in weathered sample. (s) denotes peak originating from solvent.

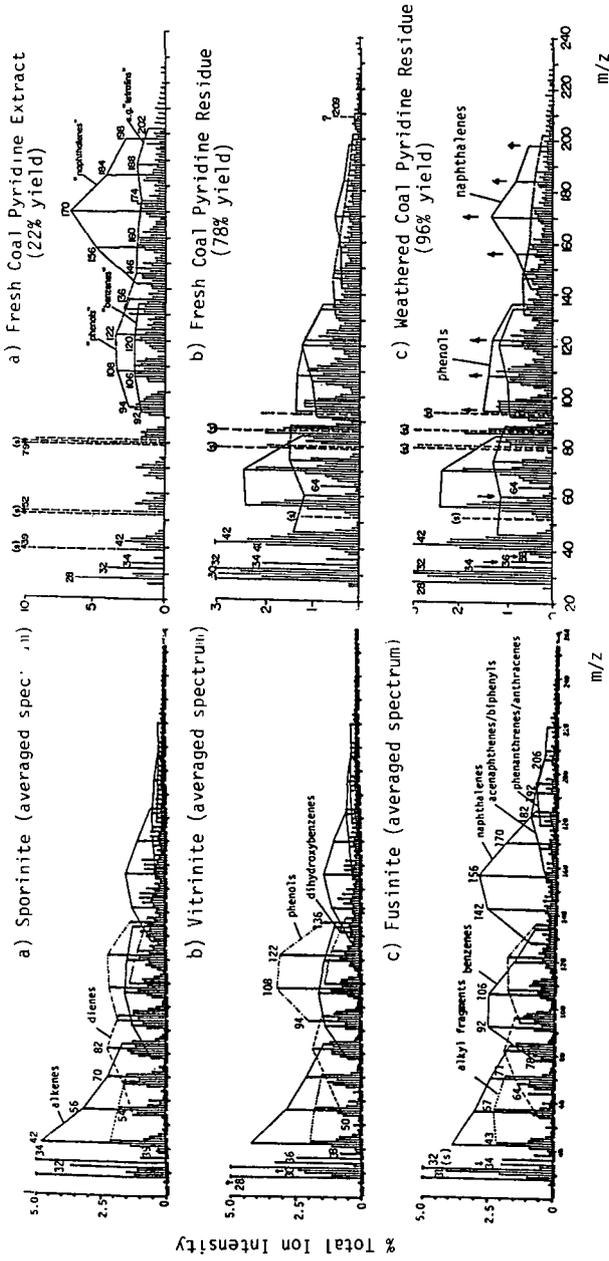


Figure 5. Typical pyrolysis mass spectra of three different maceral types obtained by averaging spectra of several different maceral concentrate samples, as obtained in an earlier study (25).

Figure 6. Low voltage desorption/pyrolysis mass spectra of pyridine extract and residues from Hiawatha coal. (s) denotes solvent peaks (pyridine solvent signals are indicated by dashed lines).

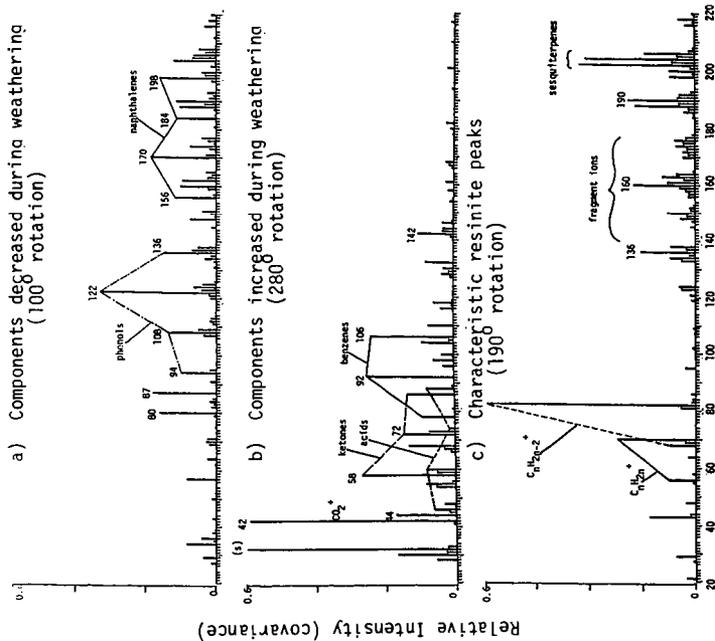


Figure 8. Discriminant spectra of macerals. 100° rotation is weathering direction and 280° rotation is resinite direction when compared with Figure 7.

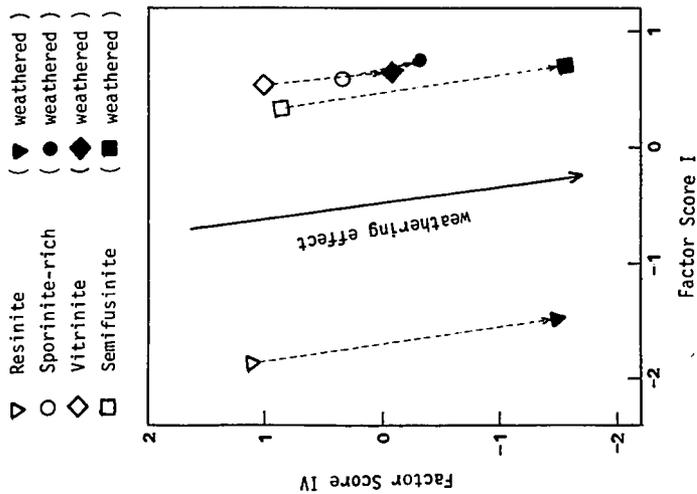


Figure 7. Factor score plot from Py-MS data sets on fresh and weathered macerals. 100° rotation clearly shows the weathering effect.