PYROLYSIS MECHANISMS AND WEATHERING PHENOMENA IN ROCKY MOUNTAIN COALS

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INTRODUCTION

During the past decade coal scientists and technologists have become increasingly aware of the potentially dramatic effects of oxidation ("weathering") on the structure and reactivity of coals. Presently known effects range from autoignition in mines [1] and piles [2], changes in electrostatic charge, slurry pH and flotability [3] or loss of caking properties [4-7] and calorific value [3,4] to decreased tar [8,9] and volatile matter yields, increased char yields [9,10] and altered char properties [3,5,6]. An excellent overview of coal weathering effects can be found in a recent paper by Cox and Nelson [11].

Because of a lack of generally accepted and standardized procedures for determining the degree of weathering (the "weathering index") of a given coal sample, most data on structure and reactivity reported in the literature thus far were obtained on coal samples of uncertain weathering status and should therefore be interpreted with great caution.

Unfortunately, this situation is compounded by the difficulty of obtaining "non-weathered" coal samples for structure and reactivity tests since even reference samples available from coal sample banks have sometimes been found to exhibit signs of weathering. In the near future a new collection of standard coal samples, the Premium Coal Sample Program currently underway at Argonne National Laboratory under the most stringent anaerobic collection, preparation and storage conditions [12], may help solve the availability problem. In the coal weathering experiments reported here high volatile B bituminous coal samples obtained directly from freshly exposed seam facies in the Wasatch Plateau field (Hiawatha and Blind Canyon seams, Emery County, Utah) were used.

The present study was prompted by the discovery of FSI values as high as 4.0 in coals obtained directly from fresh mine cuts in the Hiawatha and Blind Canyon seams [4]. Until then, coals from these seams were generally considered to be noncaking. Since FSI values $\geq$ 2.0 could interfere with pyrolytic conversion schemes under consideration by Utah Power and Light Company [13], a systematic study of the influence of weathering on the reactivity and structure of selected Wasatch Plateau coals was undertaken.

EXPERIMENTAL

Several hundred pounds of samples were obtained from the top, middle and bottom of freshly exposed cross sections of the Hiawatha and Blind Canyon seams and immersed in water until being crushed and milled to < 60 mesh in a nitrogen atmosphere. All sample storage took place under nitrogen in hermetically closed glass bottles at -20°C in the dark. In the laboratory weathering experiments, 10-15 g aliquots of < 60 mesh coal were exposed to different temperatures and atmospheric conditions (N_2 or air; dry or H_2O saturated) for periods up to several weeks or months using a specially constructed bench scale weathering system [4].

FSI determinations were performed according to ASTM Standard D-720-67, whereas standard ASTM proximate analysis, calorific value and total sulfur determinations were carried out by Standard Laboratories (Huntington, Utah). TG/DTG analyses were performed with a Mettler I thermal analyzer under the following conditions: (initial pyrolysis run) sample weight approx. 10 mg, nitrogen flow 100 ml/min, heating rate 15°C/min, end temperature 790°C, (subsequent char combustion run; after cooling down) air flow 100 ml/min, heating rate 15°C/min, end temperature 990°C.

Curie-point pyrolysis mass spectrometry was performed with an Extranuclear 5000-1 instrument under the following conditions: sample weight 20 μg (deposited from a fine suspension in MeOH), heating rate approx. 100°C/s, end temperature 610°C, total heating time 10 s, electron energy 12 eV, mass range scanned m/z 20-260, total number of spectra summed 150, total scanning time 30 s. Computerized data analysis involved normalization of signal intensities by means of the NORMA program [14] followed by factor analysis, discriminant analysis and canonical variate analysis using the SPSS program package [15].

RESULTS AND DISCUSSION

The FSI was found to be a highly sensitive indicator of the weathering status of these coals with a slight, but measurable drop in FSI value occurring overnight upon exposure of fresh coals to air at room temperature. Typical FSI weathering profiles are shown in Figure 1. Since coal weathering is often accompanied by complex weight changes due to the interplay of fluctuations in moisture content and oxidative phenomena, a series of weathering experiments was carried out while carefully monitoring changes in sample weight, as shown in Figure 2. Weight corrected weathering trends of several conventional parameters are illustrated in Figure 3a and Table I showing how misleading results are obtained if the original weight of the non-weathered sample is unknown (as is usually the case). Note that the weight corrected change in calorific value is -1.1% after 96 hours at 80°C in air and -2.1% at 100°C in air.

Much more informative about changes in reactivity and structure are the Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) data in Figures 4 and 5 and, in particular, the Pyrolysis Mass Spectrometry (Py-MS) data in Figures 6, 7, 8 and 9. The TG/DTG pyrolysis data in Figures 4a and 5a would seem to support a weathering mechanism dominated by the formation of crosslinks between coal molecules, thereby causing a widening of the temperature range of the pyrolysis process and a decrease in the maximum pyrolysis rate accompanied by increased char yields while having little or no influence the maximum rate temperature (~450°C). The results of the char combustion runs in Figures 4b and 5b indicate a similar kinetic trend (decreased reaction rate and increased temperature range) but are less definitive due to a lower level of reproducibility than in the pyrolysis runs.

Inspection of the pyrolysis mass spectra in Figure 6 shows the structural effects of weathering to be dominated by a decreased yield of phenolic and naphthalenic moieties and a relative increase in the yield of aliphatic carboxylic and carbonylic moieties, as further illustrated by the scatter plots of selected peak intensities in Figure 7. These findings are in excellent agreement with current views on chemical effects of coal weathering, according to which the process is characterized by the formation of ether bridges between aromatic nuclei with concurrent reduction in free phenolic hydroxyl groups [16], and by the oxidation of aliphatic moieties to carbonylic and carboxylic functional groups [17]. A more detailed picture of the complex changes in the pyrolysis mass spectra can be obtained by means of multivariate analysis techniques such as discriminant analysis, as illustrated in Figure 8. The application of these techniques to the evaluation of pyrolysis mass spectra of coal has been described elsewhere [14,18,19]. The discriminant analysis results in Figure 8 show that: (a) the first discriminant function exhibits no detectable changes in the coal spectra upon "weathering" at 80°C in a nitrogen atmosphere, (b)

weathering effects at 80°C and 100°C in air show strong quantitative differences, (c) several other series of aromatic, hydroaromatic and hydroxyaromatic compounds appear to decrease besides phenols and naphthalenes, and (d) the changes in aliphatic moieties are much more complex than the simple formation of carbonylic and carboxylic groups. Examination of the second discriminant function (not shown) confirmed the absence of detectable changes at 80°C in N_2 but revealed the presence of slight but significant qualitative differences between the 80°C and 100°C weathering trends, apparently reflecting transient chemical phenomena (peroxide formation?) during the weathering process.

Although, at first sight, the "classical" coal weathering concept of crosslinking through ether bridge formation between macromolecular chains appears to fit our observations quite well, modern views of vitrinite as a binary system consisting of a "mobile" phase and a macromolecular "network" phase necessitate a rethinking of the crosslinking concept. The binary phase model, recently summarized by Given [20], assumes that up to 50% or so of the bulk of the coal sample consists of relatively small, mobile molecules trapped in cages formed by a macromolecular network which makes up the remainder of the bulk. Direct evidence for the presence of a trapped mobile phase can be obtained by Time-resolved Py-MS, as shown in Figure 9. Approximately 50% of the C_2-alkylnaphthalene signal in Figure 9 is recorded well below typical pyrolysis temperatures for covalent bonds but far above the expected vacuum distillation point for these compounds. A crude attempt to visualize the proposed binary phase system is presented in Figure 10, demonstrating that, in principle, three possibilities for intermolecular bond formation exist in such a system: (1) "crosslinking" between network chains, (2) "condensation" between mobile phase constituents, and (3) "grafting" of mobile phase constituents onto the network chains.

To obtain a better insight into the behavior of the two phases, fresh and artificially weathered (212 hrs at 100°C in air) Hiawatha coal samples were submitted to vacuum distillation (30 hrs at 180°C and 10^{-3} Torr), pyridine extraction (24 hrs in Soxhlet extractor), short contact time (SCT) pyrolysis in a tubing bomb reactor (2.5 g coal in 5.0 g benzene, heating rate 20°C/s, end temperature 420°C, total heating time 40 s, H_2 pressure 1,000 psi initial to 1,700 psi final) and direct Curie-point Py-MS (1.5×10^{-5} g coal in vacuo, heating rate 100°C/s, end temperature 610°C, total heating time 10 s). Subsequently, the distillates, extracts or pyrolyzates, as well as the residues were analyzed by Py-MS. Preliminary results are shown in Table II and illustrate the dramatic effect of weathering on vacuum distillation yields, pyridine extraction yields and SCT tubing bomb reactor (TBR) pyrolysis yields. The yield of the small vacuum distillate fraction (4%, dominated by alkylnaphthalenes; see Figure 11a), shows a fourfold decrease upon weathering. The much larger pyridine-extractable fraction (22%, also dominated by alkylnaphthalenes but containing significant contributions from other aromatic moieties; see Figure 11b) decreases by a factor of five to six after weathering.

Hydroxyaromatics (e.g., phenols, dihydroxybenzenes), which are among the most abundant homologous ion series in pyrolysis mass spectra of fresh whole coals (see Figure 11d) are nearly absent in the vacuum distillate (Figure 11a) and relatively low in the pyridine extract (Figure 11b) but make a more prominent appearance among the SCT-TBR products shown in Figure 11c. Probably these hydroxyaromatics are partially produced through pyrolytic bond scissions and thus may represent the network phase. Additional support for this contention is provided by the much smaller reduction factor (2X) for the SCT-TBR yields from weathered coal.

A speculative interpretation of these findings might envisage a mobile phase representing 20-30% of the bulk of the fresh Hiawatha coal and undergoing a 4-6 fold reduction under the above weathering conditions. Presumably, this reduction is due to the formation of strong (diarylether?) bonds with hydroxyaromatic moieties in the network phase ("grafting"; see Figure 10). On this view, SCT pyrolysis results in

partial degradation of the network into hydroxyaromatic compounds and other small, mobile molecules. However, the pyrolysis conditions used appear to leave most of the new bonds formed in the weathering process intact, thus resulting in a marked decrease in overall pyrolysis yields from weathered coals.

Visual comparison of the four MS patterns in Figure 11 reveals an obvious trend towards increasing complexity from the vacuum distillate (Figure 11a) to the Curie-point pyrolyzate (Figure 11d). For the first three fractions this trend corresponds directly with increasing yields (from 4% for the vacuum distillate to 38% for the TBR pyrolyzate) and, if extrapolated, would indicate a yield of between 40-50% for the Curie-point pyrolyzate, which is in good agreement with previous estimates for hvb Utah coals [18].

At the same time, these observations highlight the fact that under SCT pyrolysis conditions some 50% of the (m.a.f.) coal forms a char. This char, which is difficult to analyze by most techniques currently available, might incorporate as much as 2/3 of the network phase. This leads to the question whether the pyrolysis products obtained from the network phase are representative for the overall chemical structure of the network. In his comprehensive discussion of the binary phase nature of coal, Given [20] concludes that in spite of all available data from sophisticated analytical methods, including FTIR and 13C NMR, the chemical nature of the network phase remains pretty much a mystery.

If the binary phase concept is valid indeed, much effort will have to be devoted to the elucidation of key structural features of the macromolecular network if a more comprehensive picture of the effects of weathering on the structure and reactivity of coals is to be obtained within the foreseeable future.

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CREDIT

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TABLE I

EFFECT OF WEATHERING ON CALORIFIC VALUE

Calorific Value (BTU)	Fresh	80°C in N_2 120 hours	Δ* (%)	80°C in air 96 hours	Δ* (%)	100°C in air 96 hours	Δ* (%)
- as received	12028	12556	+4.4	12299	+2.3	12063	+0.3
- dry	12457	12575	+0.9	12318	-1.1	12078	-3.0
- weight corrected	12028	12003	-0.2	11893	-1.1	11773	-2.1

* difference with corresponding "fresh" value.

TABLE II

WEATHERING EFFECTS ON HIAWATHA COAL PROCESS YIELDS

Process	% Yield	
	Fresh Coal	Weathered Coal
Vacuum Distillation	4	1*
Pyridine Extraction	22	4
SCT-TBR Pyrolysis	38	17

* Value from a single experiment; all other values averaged from two or more experiments.

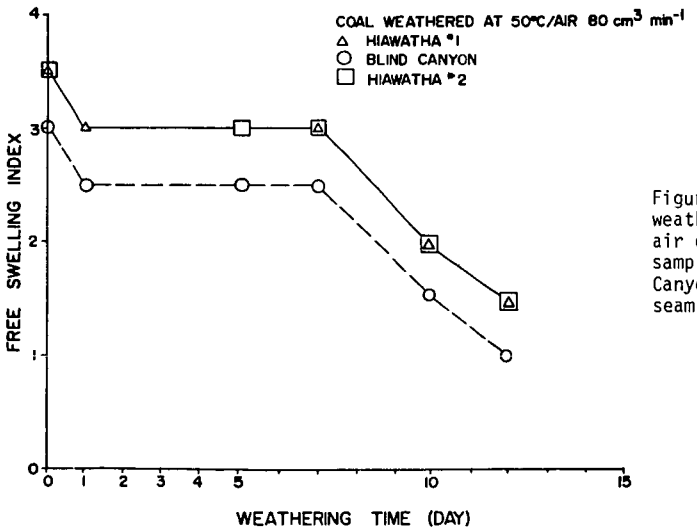

Figure 1. Effect of weathering at 50°C in air on FSI of coal samples from one Blind Canyon and two Hiawatha seam mines.

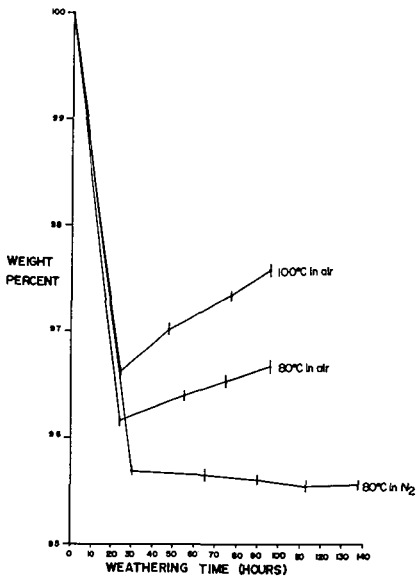

Figure 2. Effect of weathering on weight of Hiawatha seam coal. Note usefulness of control samples in N_2 for distinguishing effects of moisture loss (~4.4%) from effects of oxidative weight gain. Error bars represent range of values for three independently weathered aliquots.

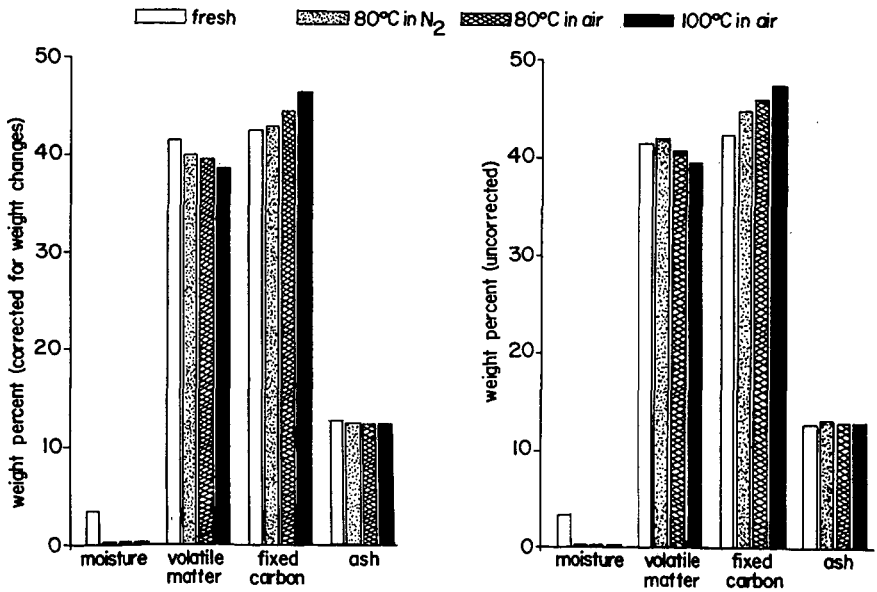

Figure 3. Effect of weathering on proximate analysis of Hiawatha coal.

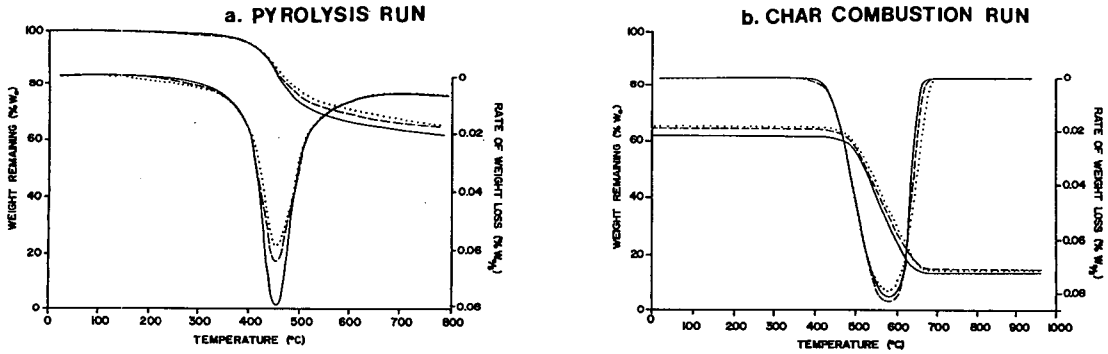

Figure 4a and b. Effects of weathering on TG/DTG profiles of Hiawatha coal. Each curve averaged from three replicate runs. W_0=original sample weight. —— fresh coal; ---- weathered at 80°C in air (96 hours); .... weathered at 100°C in air (96 hours).

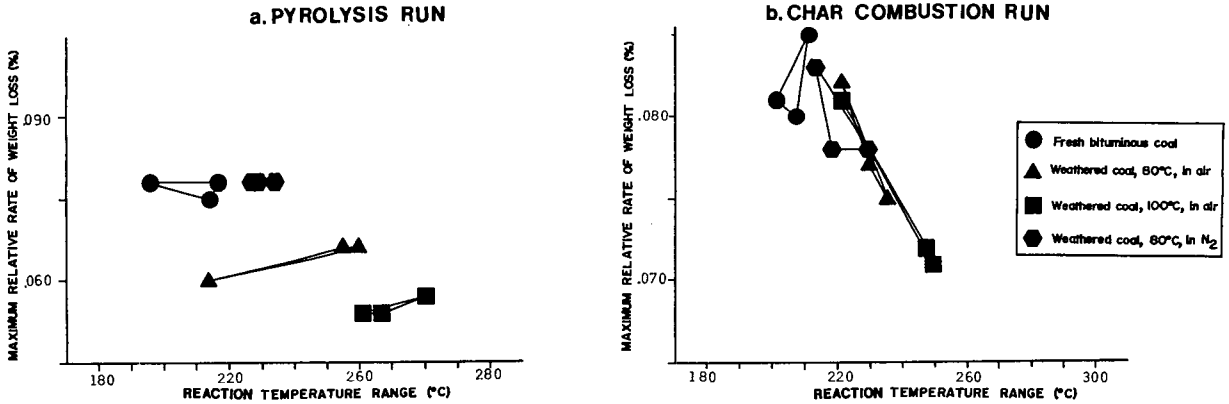

Figure 5a and b. Effects of weathering on selected TG/DTG parameters. The "Reaction Temperature Range" is defined as the temperature range over which the (pyrolysis or combustion) reaction rate is ≥3% of the maximum rate (compare with Figure 4). Data points on replicate weathering experiments connected by solid lines.

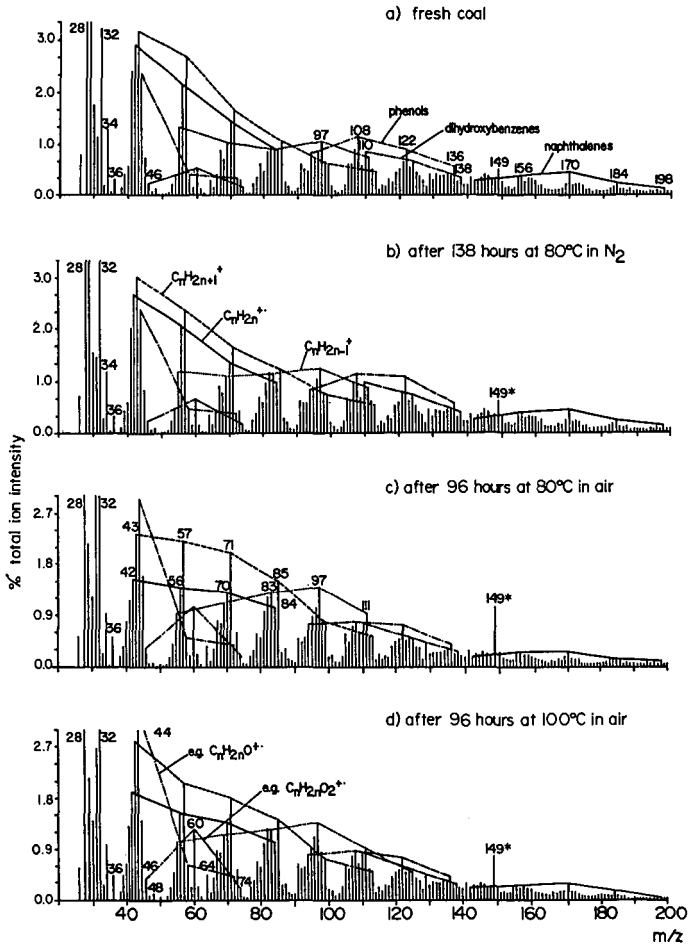

Figure 6. Curie-point pyrolysis mass spectra of fresh and weathered Hiawatha coal samples. Note high degree of similarity between spectra a) (fresh coal) and b) (80°C in N_2) and obvious changes in spectra c) (80°C in air) and d)(100°C in air). Overall weathering effects appear to be: decreased aromatic series; increased carbonylic ($C_nH_{2n}O$) and carboxylic ($C_nH_{2n}O_2$) series; decreased H_2S peak (m/z 34); increased CO_2 (m/z 44) and SO_2 (m/z 64) peaks; increased MeOH solvent retention (m/z 23); altered distribution of aliphatic hydrocarbon series. The phthalate fragment ion peak at m/z 149 may be due to contamination.

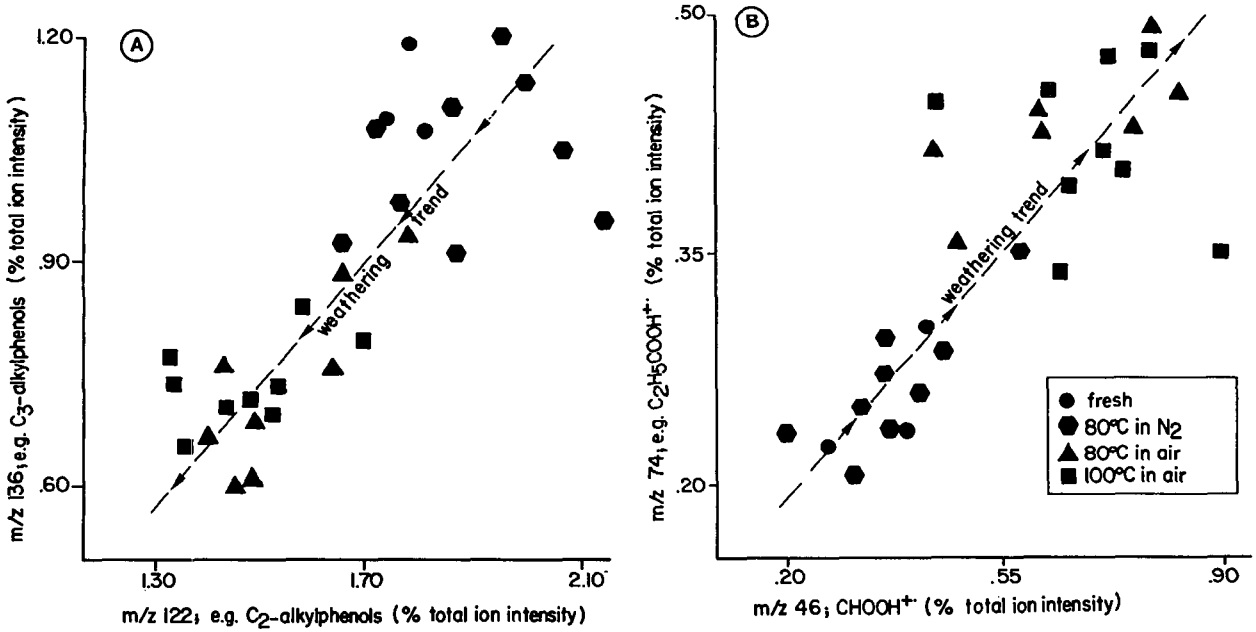

Figure 7 a and b. Scatter plots of selected ion intensities from the pyrolysis MS data set (compare with Figure 6) showing the effects of weathering on alkylphenol signals (strong decrease; see Figure 7a) and on short chain carboxylic acid signals (marked increase, see Figure 7b).

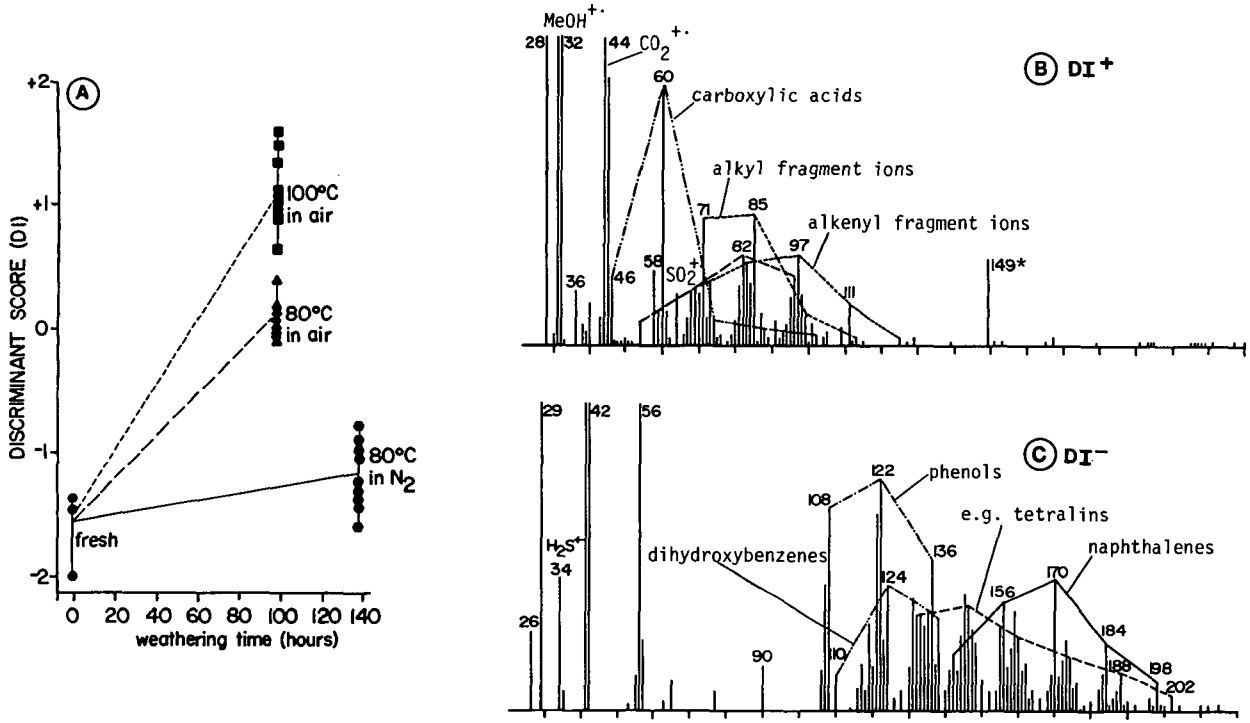

Figure 8. Discriminant score plot and associated "discriminant spectra" obtained on pyrolysis mass spectra of fresh and weathered Hiawatha coal samples (see Figure 6). Air and N_2 exposures were carried out with three different aliquots analyzed in triplicate, resulting in 27 spectra representing 3 categories (80°C in N_2, 80°C in air, 100°C in air). The triplicate spectra of the fresh coal sample were treated as "unknowns" in the discriminant analysis procedure. The two spectra correspond to the positive (DI^+) and negative (DI^-) components of the discriminant function.

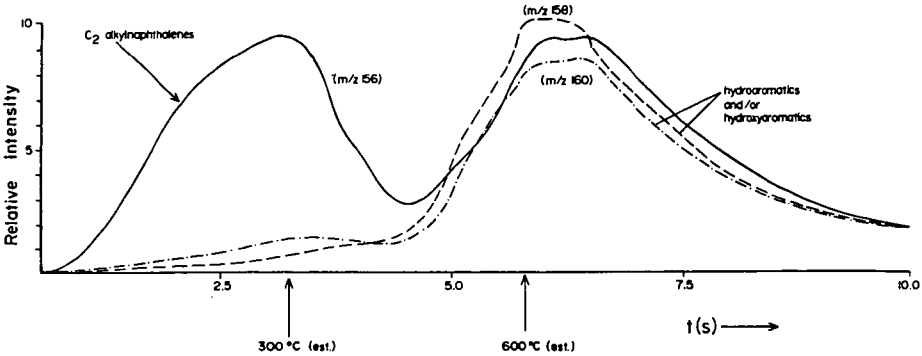

Figure 9. Time-resolved recording of the mass peaks at m/z 156 (mainly C_2-alkylnaphthalenes), m/z 158 (e.g., methylnapthol and/or C_2-alkyl dihydronaphthalenes) and m/z 160 (e.g., C_2-alkyl tetralins) during Curie-point pyrolysis of a 20 μg sample from a hvb Wasatch Plateau coal. Note bimodal character of the signal at m/z 156.

Figure 10. Highly schematized representation of all three possible types of weathering-induced bridge formations in a binary phase (mobile phase/network phase) coal model.

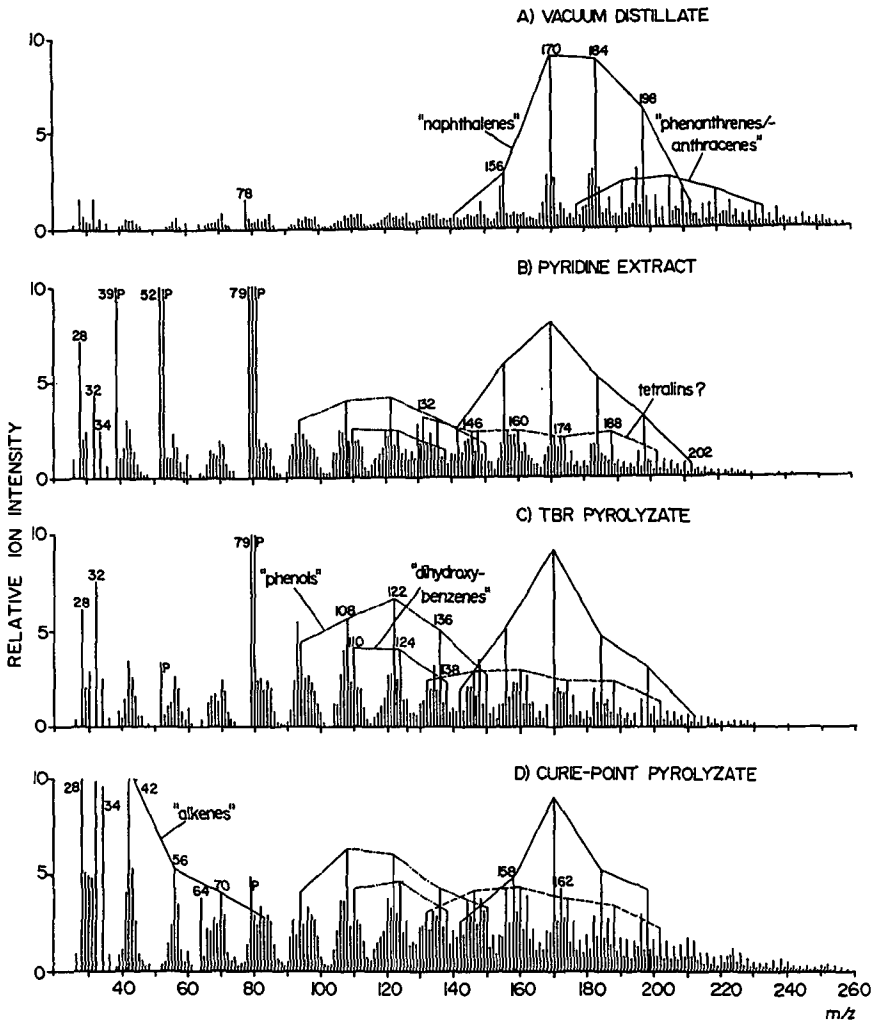

Figure 11. Curie-point desorption/pyrolysis mass spectra of tar fractions from a nonweathered ("fresh") Hiawatha coal obtained by different techniques. Compare with Table I. Note increasing complexity from a to d (exaggerated in d by the presence of gaseous, low molecular weight products, e.g., alkenes, lost during collection of a-c). Peaks labeled "P" represent pyridine residues and/or background signals.