Part I: A Fluorogeochemical Model of Coal Macerals

Fluorogeochemistry embraces studies of the chemical theory and applications of the fluorescence phenomena of macerals, kerogen and other geopolymers. At this time our understanding of the subject is very limited because of difficulties related to the nature of the materials we attempt to study. First, we are dealing with undefined geopolymorphic macromolecules of great size and complexity. In contrast, chemists and physicists, from whom the basic knowledge of fluorescence is derived, are concerned with simple chemical systems like atoms or molecules; therefore they are able to treat fluorescence as a quantitatively exact science. Second, we are dealing with mixtures of molecules and macromolecules of greatly varying size, combined as very complex heterogeneous solids. The intramolecular and intermolecular interactions, energy transfer and photochemical reactions which can occur are unpredictable. What can be done in this situation? Just like the biochemists, who are dealing with the fluorescence of biopolymeric macromolecules, we will have to extend theory derived from simpler chemical systems in order to explain organic geochemical phenomena of fluorescence. The following model has been developed using molecular orbital theory to explain the observed fluorescence phenomena of coal macerals.

It has been observed that: the spectral fluorescences of coal macerals display a continuous red shift and an overall decrease in intensity with increasing peatification and coalification; inertinite macerals display visible fluorescence with an excitation source energy of longer wavelengths; vitrinite gives higher fluorescence yields by blue-light excitation than by UV excitation. All of these phenomena can be explained as the result of π-electron delocalization associated with the increased crosslinking and condensation that occurs during peatification and coalification. Limited by frontiers of modern quantum chemistry, the exact quantitative calculation of molecular orbitals of coal macromolecules are impossible because of their large size and undefined complexity (Fig. 1). For this reason, a semiquantitative model based on certain mathematical and geochemical approximations has been used. We employed the Hückel approximation of molecular orbital theory. Crosslinking and condensation reactions during peatification and coalification were statistically oversimplified as a linear increase in the length of conjugated polyene for liptinite macerals and of aromatic chains for vitrinite and inertinite macerals. Then, energy differences (ΔE) (Fig. 2) between the highest filled and lowest empty orbitals were calculated from:

For liptinite macerals:  \( \Delta E = 4B \sin \left( \frac{\pi}{2(A + 1)} \right) \)

where \( B \) is a constant and \( A \) is the number of carbon atoms per mean structural unit or molecule, and \( A = 1, 2, 3, \ldots, n \).