# Preliminary results on the fluorescence properties of organic cement in Recent and fossil agglutinated foraminifera

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## ABSTRACT

Fluorescence microspectrometry analysis of organic cements within Recent and fossil agglutinated foraminifera has been conducted using incident light microscopy for three thermally immature samples. Lambda max (455 to 650 nm) and Q (0.14 to 1.6) values for the organic cements record a progressive red shift in the fluorescence to longer wavelengths with increasing thermal maturity between Foraminiferal Colouration Index (FCI) of FCI-0 (0.15 to 0.20 vitrinite %Ro) to FCI-7 (0.56 vitrinite %Ro). The rate of fluorescence red shift for the foraminiferal cement is more rapid over this maturity range compared with the rate of red shift for hydrogen-rich, sporopollenin- and algaenan-based dispersed organic matter (DOM; e.g., spores and algae). Variation in the rate of change of fluorescence properties between the foraminiferal cements, and algae and spores with increasing maturity is attributed to substantial differences in the chemical composition.

## INTRODUCTION

The Foraminiferal Colouration Index (FCI) monitors progressive, thermally-induced changes in the colour of organic cements within agglutinated and calcareous benthic foraminifers (McNeil *et al.*, 1989). The FCI is an average of numerous visual colour evaluations of the foraminiferal organic matrix made at relatively low magnification (x250) using reflected light (*ibid.*). The FCI ranges from 0 (Recent organic matrix; 0.15-0.20 %Ro vitrinite) to 10 (colour of thermally overmature matrix; > 3.5 %Ro vitrinite). Recently this technique has proven to be a reliable and sensitive indicator of thermal maturity levels in the Mesozoic and Cenozoic sections of the Beaufort-Mackenzie Basin, Arctic Canada (McNeil *et al.*, 1996). In this paper, we present preliminary results of the fluorescence microspectrometry of the organic cement within a small set of foraminifera and evaluate the data in relation to FCI values and the flourescence properties of other types of dispersed organic matter.

The flourescence properties of hydrogen-rich, sporopollenin– and algaenan–based dispersed organic matter (DOM; e.g., algae, spores, and cuticles) have been widely used for evaluating the thermal maturity of coals and potential hydrocarbon source rocks (Teichmüller & Ottenjann, 1977; Ottenjann, 1980; Teichmüller & Durand, 1983; Thompson-Rizer & Woods, 1987; Michelson & Khavari-Khorasani, 1990; Mukhopadhyay, 1992; Stasiuk, 1994). The fluorescence from DOM is primarily a function of energy interactions within conjugated bond systems of unsaturated organic molecules such as aromatics, substituted aromatics, isoprenoids, carotenoids, and polyenes (Lin *et al.*, 1987; Lin & Davis, 1988). The chemical composition of the organic linings, organic cements, and secretion products of foraminifera is dominated by unbranched, sulphated polymeric polysaccharides (Langer, 1992). This type of organic material typically does not autofluoresce (the effect of sulphation is not known), suggesting that undetectable fluorophores or early diagenetic processes may have resulted in molecular chemical changes in the organic linings resulting in fluorescence.

In general, immature organic matter (%Ro vitrinite <0.50) DOM exhibits blue fluorescence. With increasing thermal maturity the fluorescence of DOM exhibits a progressive red shift to longer and longer wavelengths (Ottenjann, 1980; Mukhopadhyay, 1992). Visible light region fluorescence of most DOM is lost, or of very low intensity by the late oil to gas generation stage of thermal maturity, although some algae and acritarchs exhibit low intensity, long wavelength, red region fluorescence well into the dry gas generation zone (*e.g.*, Van Gijzel, 1981).

## MATERIAL AND METHODS

Three collections of well preserved specimens of agglutinated foraminifera were examined from three different geographic, geological, and thermal settings. From the Recent sedimentary environment, specimens of *Rhabdammina* sp. (FCI-0) were chosen from deep-sea ooze in the Baltimore Canyon in the North Atlantic. Specimens of *Ammotium* sp. Cushman (FCI-2) from Albian shales in central Saskatchewan were chosen to represent low levels of thermal maturity and shallow burial. Finally, specimens of *Labrospira turbida* Schröder-Adams & McNeil (FCI-7) were collected from Oligocene sedi-

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ments buried to a present depth of 4 km in the Beaufort Sea of Arctic Canada.

Resin pellets (2.5 cm in diameter x 2 cm high) were prepared in molds and allowed to harden. Shallow small diameter holes (0.4 cm) were then drilled into the pellets. The foraminiferal specimens representing FCI-0, FCI-2, and FCI-7 were placed into the hole and covered with resin. The samples were then carefully ground to the level of the foraminifera in the pellet and polished with 0.3 μm polishing alumina in water slurry. Fluorescence intensity measurements were made between 400 and 700 nm using a Zeiss MPM II Universal incident light microscope (HBO 100 ultraviolet source), 03 photomultiplier, a continuous filter monochromator b (1/2 band width of 14 nm at 540 nm) and Zeiss UMSP controller pc-based computer system. An epiplan-neofluor water immersion 40x objective was used for the analysis (total magnification x640). An ultraviolet G 365 nm excitation filter (395 nm beam splitter; 420 nm barrier filter) was used for sample illumination; Zeiss Lambda Scan software was used to record the spectra. Background fluorescence (black body radiation) was subtracted from the spectra of the organic matrix. The spectra were normalised to the wavelength of maximum energy emission. The number of spectra averaged for each of the FCI levels ranged from 2 to 5. Lambda max in nm (Lmax = wavelength of maximum fluorescence intensity) and red/green quotient (Q = Intensity@650nm/Intensity@500 nm) were calculated for each sample.

Some areas within the organic matrix of the FCI-0 specimens have been impregnated with epoxy. Possible oxidation of the FCI-0 specimens is also indicated by the presence of iron oxides, although some morphotypes are known to contain a ferruginous component within the organic matrix (Langer, 1992). Bitumen and sulphides were noted in the FCI-2 specimens. In order to minimise the effect of these 'contaminants' in the fluorescence spectra of these samples, unaffected regions within the organic matter were selected for analysis.

## RESULTS AND DISCUSSION

An example of the foraminiferal organic cement/matrix on which the fluorescence microspectrometry analysis was conducted is shown in Figure 1. The data are summarised in Table 1. The visual fluorescence colours of the three sets of foraminifera examined are as follows:

(i) the matrix in the FCI-0 specimens has an intense blue-green fluorescence;

(ii) the FCI-2 matrix is dominated by an intermediate intensity, orange yellow fluorescence;

(iii) the FCI-7 specimens are dominated by a low intensity brown yellow to yellow brown to orange brown fluorescence.

Fluorescence spectra of FCI-0, FCI-2 and FCI-7 foraminifera are presented in Figure 2. The FCI-0 sample has the shortest wavelength ("bluest") and most intense autofluorescence (Table 1). Lambda max values for the FCI-0 specimens range from 455 to 480 nm, with Q values ranging from 0.14 to 0.21. The FCI-2 sample has intermediate Lmax values ranging from 520 to 550 nm, Q varies from 0.65 to 0.76. The organic matrix within the FCI-7 specimens exhibit the longest wavelength ("reddest") fluorescence with Lmax values ranging from 630 to 650 nm and Q ranging from 1.3-1.6.

The chemical composition of the organic linings, organic cements, and secretion products of foraminifera is dominated by unbranched, sulphated polymeric polysaccharides (Langer, 1992). This organic material typically does not autofluoresce (the effect of sulphation is not known), suggesting that undetectable fluorophores or early diagenetic processes may have resulted in molecular chemical changes in the organic linings resulting in fluorescence. The thermal maturity level of the foraminiferal specimens examined in this study represent a narrow range of thermally immature samples. In terms of vitrinite reflectance, the thermal maturity level for the suite of samples ranges from approximately 0.15-0.20 %Ro for FCI-0, to 0.30-0.35 %Ro for FCI-2, to 0.56 %Ro for FCI-7 (Table 1). The fluorescence data from this study demonstrate that there is a corresponding progressive red shift to longer wavelength fluorescence with increasing thermal maturity (FCI and vitrinite/huminite %Ro) in the three samples studied. Algae and spores also exhibit a red shift in fluorescence over a similar maturity range (Ottenjann, 1980; Thompson-Rizer & Woods, 1987; Mukhopadhyay, 1992; Stasiuk 1994); however, the overall fluorescence red shift shown by Lmax and Q values for the foraminifera organic matrix is much greater over this maturity range compared with sporopollenin- and algaenan-based DOM. The preliminary data from this study appear to indicate that the fluorescence properties of foraminiferal organic material are more sensitive to increases in thermal maturity within immature strata compared with the fluorescence properties of algae and spores. The marked red shift in fluorescence corroborates the sensitivity of the FCI for evaluating thermal maturity within this range of thermal maturity as previously noted by McNeil *et al.* (1996).

A thermally-induced red shift in fluorescence of organic matter typically results from removal of saturated structures and alkyl substituents within aromatic nuclei, as well as condensation and cross-linking polymerization (Lin & Davis, 1988; Khavari-Khorasani, 1987). Considering the above discussion, this process is clearly accelerated in the organic cements of foraminifera relative to the spores and alginites. Preliminary data suggest that the rate of fluorescence red shift in foraminifera is more comparable to the rate of red shift noted in

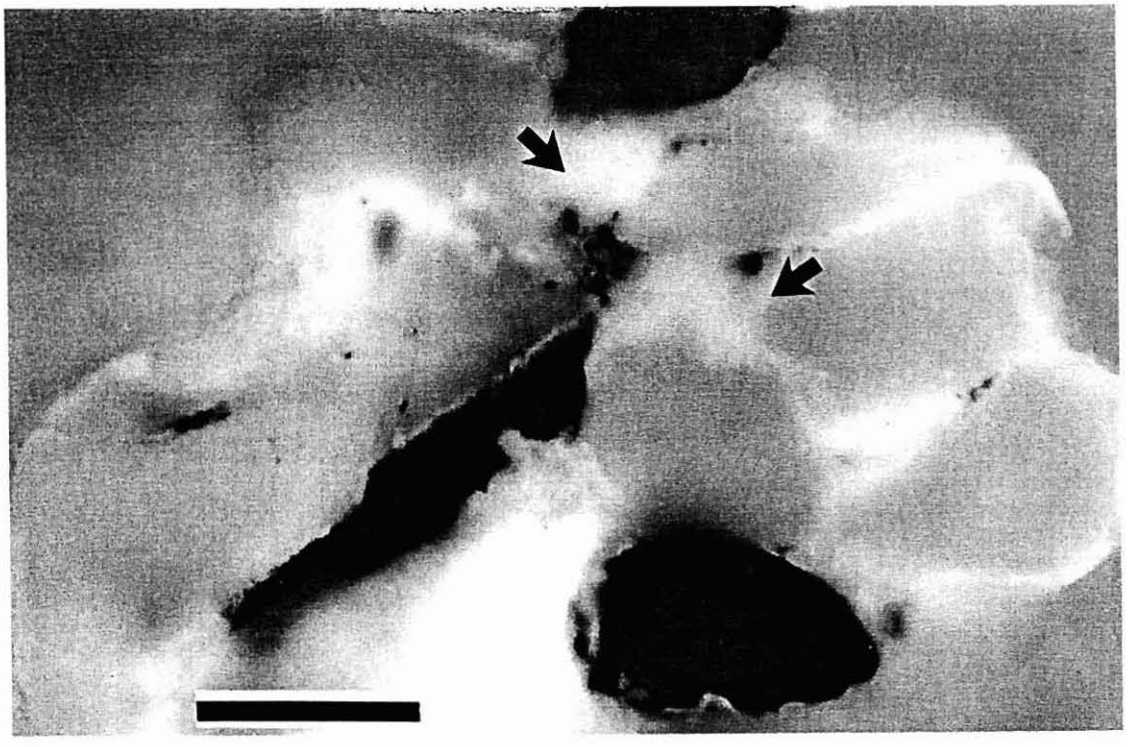

**Figure 1.** Photomicrograph of organic cement (arrows) associated with quartz grains in FCI-7 specimen (*Labrospira turbida*); water immersion objective, fluorescent light (365 nm excitation); scale bar = 50 μm.

vitrinite/huminite at low levels of thermal maturity (Lin *et al.*, 1987). The chemical composition ofthe organic linings, organic cements, and secretion products of modern foraminiferal tests largely consists of various types of unbranched polymeric polysaccharides although there is some variation in chemistry (e.g., sulphated polymers) related to foraminiferal morphotypes (Langer, 1992). Considering that the rapid red shift in foraminiferal organic fluorescence is comparable to the degree of red shift in huminite fluorescence between peat and sub-bituminous levels of coalification, the chemistry of the organic matter within foraminferal tests may be grossly similar to that of thermally immature ligno-cellulosic cellular material within huminite macerals of peats and brown coals. The Lmax fluorescence properties of cell wall material from recent and peatified hardwoods and softwoods (Lmax = 455 nm; Stout & Spackman; 1989) are similar to the Lmax values recorded for the FCI-0 foraminifera specimens (Lmax = 455 to 480 nm). The Q values of the FCI-0 foraminifera (Q = 0.13-0.21) are higher than the Q values of the cell walls of the recent hardwoods and softwood (Q = 0.01 to 0.02) reported by Stout & Spackman (1989), perhaps suggesting a greater contribution of higher aromaticity or NSO-compounds (Lin & Davis, 1988) within the foraminiferal organic cement.

Further studies are needed to investigate the fluorescence properties of foraminiferal organic matter beyond FCI-7 and to evaluate the fundamental chemical changes that are controlling the changes in the fluorescence properties of the organic matter with increasing FCI and thermal maturity.

## CONCLUSIONS

Preliminary fluorescence microspectrometric analysis of organic cements within Recent and fossil agglutinated foraminifera has noted a progressive red shift to longer wavelengths with increasing thermal maturity. Between Foraminiferal Colouration Index (FCI) of FCI-0 (0.15 to 0.20 huminite %Ro) and FCI-7 (0.56 vitrinite %Ro), there is a corresponding increase in the wavelength of maximum emission from 455 nm to 650 nm. This red shift in organic cement fluorescence reflects the sensitivity of the FCI (McNeil *et al.*, 1996) for evaluating the thermal maturity levels of host strata. The rate of red shift for the foraminiferal cements over this maturity range is greater than that for sporopollenin- and algaenan-based dispersed organic matter such as algae and spores.

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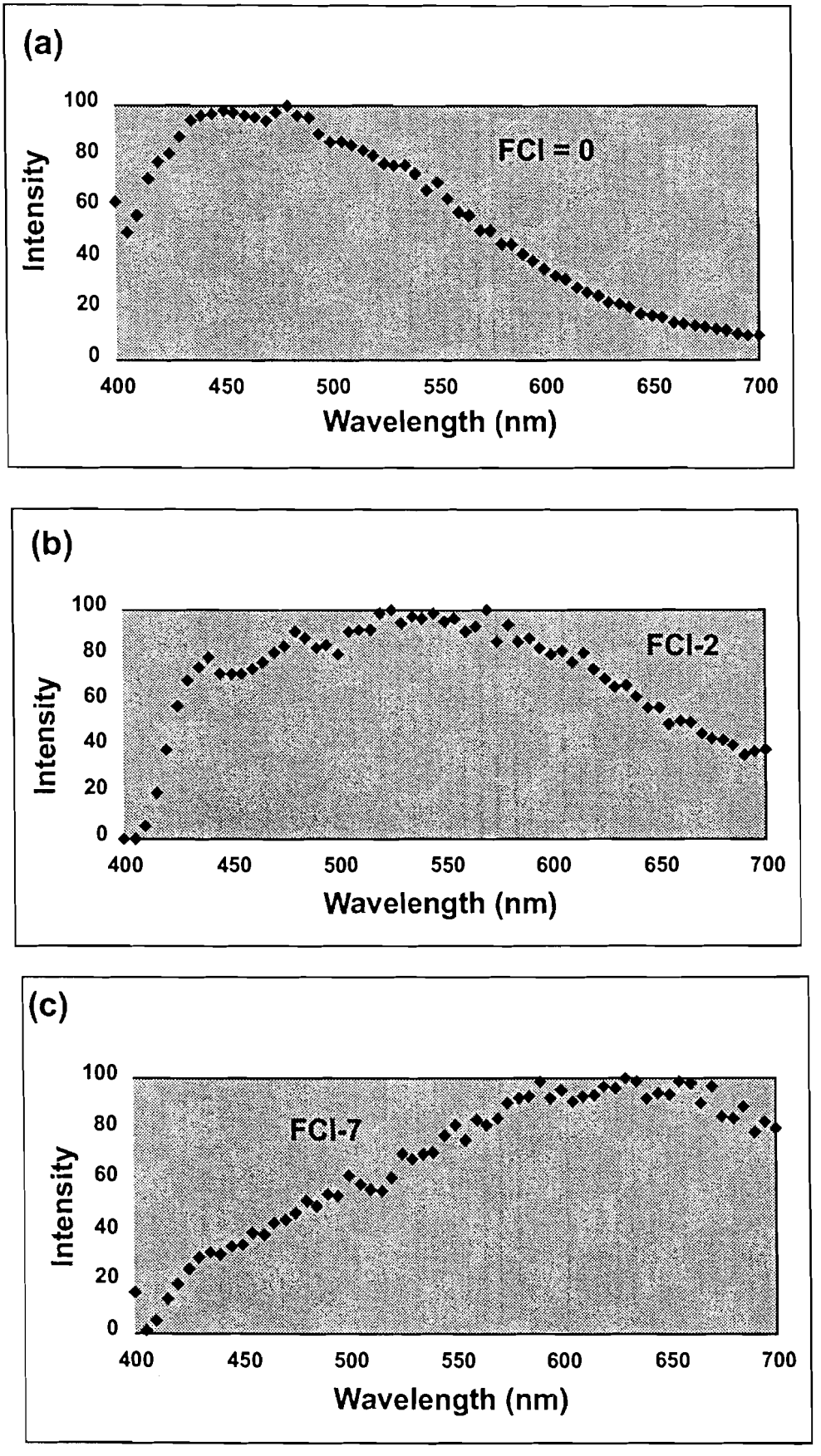


**Figure 2.** Plot of normalised fluorescence against wavelength (nm) for fluorescing organic matrix within FCI-0 (a), FCI -2 (b) and FCI-7 (c) specimens. The wavelength of maximum intensity (Lmax) displays a progressive red shift to longer and longer wavelengths with increasing FCI.

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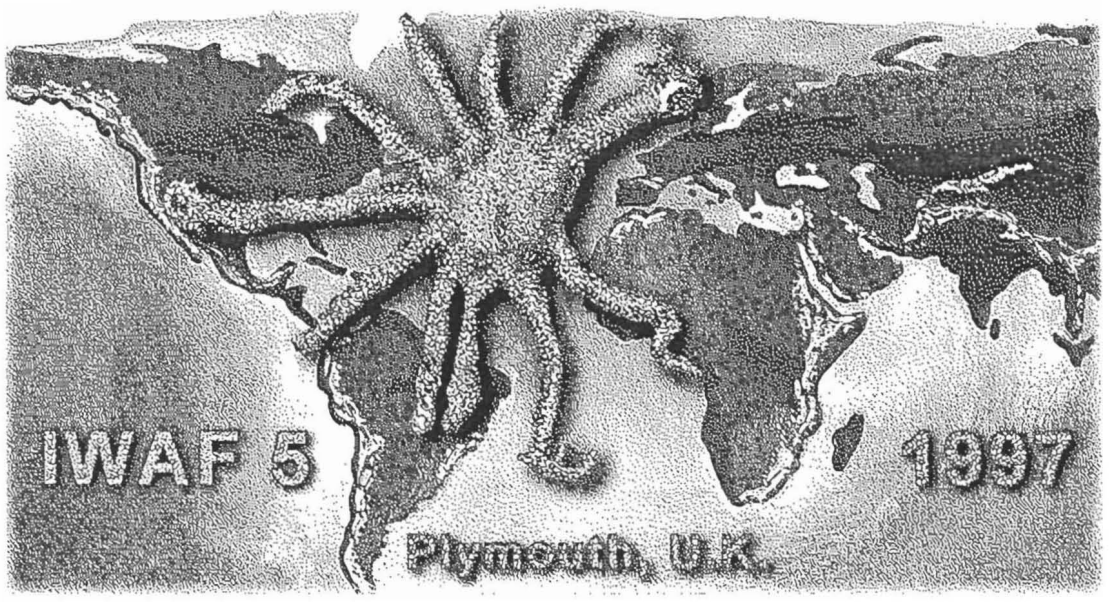
**Table 1.** FCI, huminite/vitrinite reflectance (%Ro measured within same samples for which FCI was determined), fluorescence microspectrometric data (Lmax and Q) and fluorescence colours for the three samples examined in this study.

| Sample | %Ro | Lmax (nm) | Q | Fl. Colour |
|---|---|---|---|---|
| FCI-0 (pellet #392/97) | 0.15-0.20 | 455-480 | 0.14-0.21 | blue-green |
| FCI-2 (pellet #393/97) | 0.30-0.35 | 520-550 | 0.65-0.76 | orange-yellow |
| FCI-7 (pellet #395/97) | 0.56 | 630-650 | 1.30-1.60 | brown-yellow to orange-brown |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