

## Petrology and preliminary organic geochemistry of conodonts: implications for analyses of organic maturation

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### ABSTRACT

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The petrology and organic geochemistry of conodonts of various ages and conodont alteration index (CAI) have been investigated utilizing fluorescence microscopy, pyrolysis gas chromatography and gas chromatography–mass spectrometry (GC–MS) in an attempt to refine the use of conodonts as a maturation index. Based on large field collections, an exponential correlation ( $r^2 = 0.96$ ) between vitrinite reflectance and CAI has been established which places the top of the oil window at CAI 2.5. Comparison of samples collected from the field and those subjected to laboratory experiments involving exposing vitrinite and conodont elements to the same thermal conditions, suggest that the CAI values of the field samples correlated to lower levels of vitrinite reflectance than those subjected to a short period of heating. There is a progressive divergence of the CAI from the calibration of vitrinite reflectance from low to high levels of thermal maturity. Under blue and ultraviolet light excitation conodonts exhibit fluorescence. In blue light the fluorescent colour progressively shifts from yellow (CAI 1), to yellow-orange (CAI 2) and brown (3), but there is no measurable systematic shift in the wavelength of maximum intensity accompanying progressive increase in CAI (maturation). There is, however, a distinct and systematic decrease in overall fluorescence intensity as CAI increases from 1 to 4. In this CAI range, fluorescence intensity measurements have the potential of providing a sensitive measure of maturity.

The total pyrolysable organic matter content of the conodonts ranges from about 55 to 1250 ppm and generally decreases with increasing CAI. The pyrolysis products include aliphatic, aromatic and traces of polynuclear aromatic compounds. The n-alkane series are present in all samples with a general trend towards decreasing abundance and carbon number with increasing CAI. The carbon preference index (CPI) of the pyrolysate varies from 1.4 to 0.6 and there is a general trend to low CPI with increasing maturity. GC–MS analysis of pyrolysate from the sample with the lowest CAI and highest organic carbon content revealed the presence of branched alcohols such as 3,7,11-trimethyl-1-dodecanol, 3,7,11,15-tetramethyl-1-dodecanol, a branched  $C_{18}$  alcohol and acenaphthylene or biphenylene. Trace alkylated benzenes and trace polynuclear aromatics were investigated but occur in too low concentrations for positive identification. Several compounds similar to 1H-purin-6-amine

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were detected, suggesting the presence of derivatives of the amino acid purine. Our results suggest that, given a sufficient quantity of raw material, it should be possible to conduct more complete organic chemical analyses of the conodonts. Such studies will enable a better understanding of conodont alteration and potentially provide additional evidence for their taxonomic affinity.

## INTRODUCTION

Conodonts are hard parts of extinct animals of uncertain biological affinity (Aldridge, 1986; Aldridge and Briggs, 1986; Aldridge et al., 1986; Szaniawski, 1987) that occur in strata of late Precambrian to Triassic age (Clark, 1983; 1987) (Fig. 1). Conodonts have been considered to have affinities with plants, aschelminths, conulariids, gnathostomulids, molluscs, annelids, arthropods, tentaculates, chaetognaths and chordates (Aldridge, 1987). One of the most

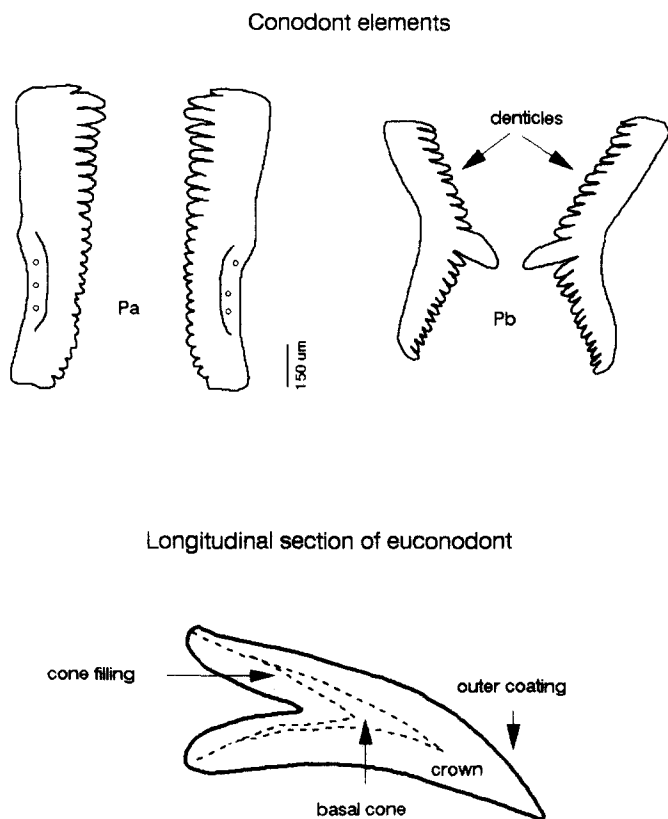


Fig. 1. General morphology of a typical conodont such those analyzed in this study. Most common conodont elements (*Pa*, *Pb*) and longitudinal section of a single element (after Norby, 1976; Szaniawski, 1987).

current of the hypotheses is that conodonts represent a separate group of jawless craniates (Aldridge, 1987).

Although composed mainly of apatite (Ellison, 1944; Hass and Lindberg, 1946; Rhodes and Wingard, 1957; Pietzner et al., 1968), conodonts also contain trace amounts of organic matter. It has been well established that with thermal maturation (metamorphism), conodonts undergo progressive, systematic and irreversible color changes as a result of alteration and/or loss of organic matter. The progressive color changes are now quantified routinely and referred to as the "conodont alteration index" (CAI), an index proposed and standardized by Epstein et al. (1977). The CAI has been demonstrated to be a valuable measure of organic maturation, particularly in rocks where other maturity indices such as vitrinite reflectance cannot be used. The CAI technique has been applied in many sedimentary basins to reconstruct their thermal history (e.g., Perry et al., 1979; Kovacs and Arkai, 1987; Legall et al., 1982; Nowlan and Barnes, 1987). However, CAI remains a semi-quantitative index and the correlation between CAI and vitrinite reflectance (the most common measure of organic maturation) and the organic chemistry of conodonts remains poorly documented.

Our studies were designed to develop both a more quantitative index of conodont alteration and a better correlation between CAI and vitrinite reflectance (and thus organic maturation). Further, in order to understand the changes in CAI or other measures of maturity based on conodonts, it is essential to comprehend the geochemistry of their organic matter. To this end we have undertaken preliminary organic geochemical studies of conodont specimens of various degrees of maturity (CAI). In this paper we: (1) describe the correlation between CAI and vitrinite reflectance based on large field collections as well as experimentally matured samples; (2) review the utility of conodont fluorescence as a quantitative index of the degree of organic maturation; and (3) present some preliminary analyses of the organic geochemistry of conodont suites of varying maturities.

## METHODS

### *General*

The conodonts used in this study were from strata that span the time interval from the Early Silurian to Late Triassic. Because it was desirable to work with conodonts from a broad range of CAI (<1.5 to over 6) samples were collected from a wide range of geographic localities.

The conodont elements were isolated using standard acetic acid/heavy liquid (tetrabromoethane) procedures, except for elements used in the organic geochemical studies. These elements required concentration by hand picking to avoid organic contamination where possible. Conodont elements

used for geochemical analyses were carefully soaked and rinsed in acetone to remove any residual tetrabromoethane, dust or extraneous rock material. All glassware used in concentrating the conodonts was carefully rinsed in acetone to avoid possible contamination. The conodont alteration index (CAI) was determined based on visual comparison with standards compiled from a broad spectrum of CAI values present in the 375 conodont collections from the Kunga Group in the Queen Charlotte Islands (Orchard and Forster, 1991). The standard collection comprises entirely gondolelloid taxa and has the advantage of being composed entirely of elements of similar age and morphology and which are biologically related.

A fibre optic light source and a magnification of between 40 and 50 times were used. The CAI of all collections were evaluated on a white card background. Wherever possible comparisons were made between specimens of the same size because larger species appear darker than small ones due to their greater thickness. Some specimens showed more intense color towards their core, possibly due to iron oxide impregnations. To compensate for such problems, the CAI was determined from the margin of the elements. Overall, moderate sized specimens gave the best resolution at CAI values of 1–3, whereas at CAI values around 5 smaller elements proved the greatest utility.

The Kunga Group standard utilized in this study has 12 divisions that, based on comparison with Paleozoic indices provided by A.G. Harris (personal communication, 1989), range from CAI 1 to 8. For fluorescence microscopy conodont elements were mounted in transoptic and polished using standard coal sample preparation techniques (Bustin et al., 1985). Relative fluorescence intensity was determined in blue and ultraviolet light excitation with a Leitz MPV II microscope using a uranyl glass as a standard.

The organic matter used for vitrinite reflectance was isolated from the light fraction obtained during conodont extraction. The reflectance of vitrinite was determined using a Leitz MPV II microscope, following routine procedures as summarized by Bustin et al. (1985). Wherever possible, at least 50 vitrinite reflectance measurements were made per sample.

### *Laboratory experiments*

In order to compare the affect of temperature on conodont coloration and vitrinite reflectance, samples of various conodont genera and CAI, together with vitrinite isolated from a high-volatile bituminous coal were heated in nitrogen-flushed ampules for 72 h at atmospheric pressure. Thermal conditions were kept as similar as possible.

### *Field comparison*

Samples used for comparison of vitrinite reflectance and CAI were obtained from either the Maude or Kunga Groups from the Queen Charlotte

Islands (Orchard and Forster, 1991) or the Triassic Pardonet Formation from northeastern British Columbia. The CAI and vitrinite reflectance were determined by separate operators without prior knowledge of stratigraphy, collection site or other data.

### *Geochemistry*

The problem of the organic geochemistry of conodonts is particularly intractable due to the very low concentrations of organic matter (in the parts per million range) retained in the elements. Due to the very low organic carbon content and small sample size, pyrolysis gas chromatography provided the only viable analytical technique. In addition, because the organic matter is embedded in a mineral matrix, it is not readily accessible to solvent extraction. In order to obtain as large and representative samples as possible, only particularly rich samples were selected for analysis. These had CAI values varying from 1 to 5 (Table 1).

For pyrolysis 6–10 mg of isolated conodont elements were weighed accurately and placed in a quartz tube. The conodont elements were then subjected to rapid pyrolysis under helium at 950°C, following the procedure outlined in Fig. 2. A constant flow of helium was passed over the samples during heating to 950 ± 20°C. A small plug of silanized glass wool was used to trap the volatiles produced during the rapid pyrolysis. The quartz tube was cooled

TABLE 1

Samples utilized in GC and GC–MS study: CAI, Total pyrolyzable organic matter and sample age and location.

Sample	CAI	Total pyrolyzable organic matter (ppm)	Age and sample location
PAN-9	1–2.0	1267	Pre-Welden shale, Pontotoc County, Oklahoma Tournaisian, Early Carboniferous
MISC-6	2.0–2.5	348	St. Clair Formation, Midwest Lime Quarry, near Batesville NE Arkansas, USA
CP2	3	54	Late Llandovery–early Wenlock, Early–Middle Silurian Exshaw Formation, Lewis River thrust sheet, highway 3 Crowsnest Pass, Alberta
HB-229	4	106	Tournaisian, Early Carboniferous, Star Peak Group, Favret Canyon, Augusta Mountains, northwest Nevada
HB-27	5	505	Middle Anisian, Middle Triassic, Star Peak Group, North Fork Strait Canyon, Humbolt Range, northwest Nevada Anisian, Middle Triassic

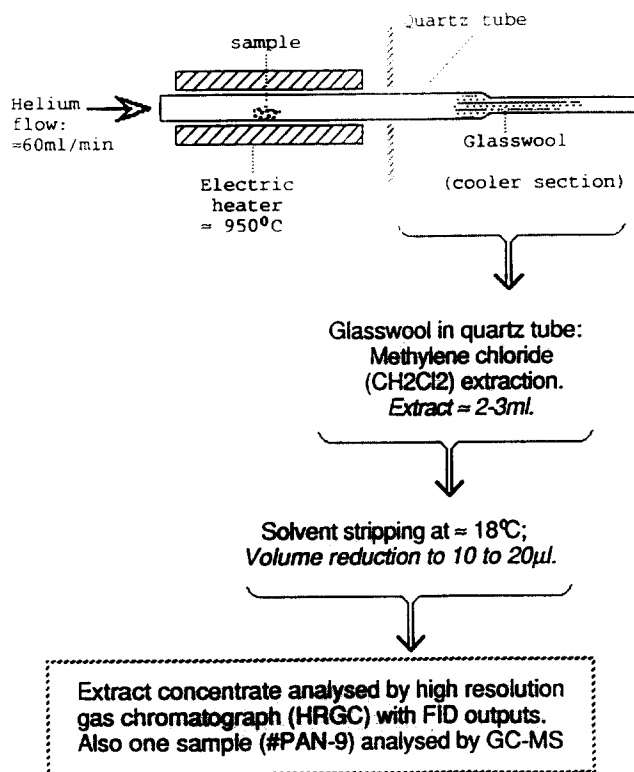


Fig. 2. Schematic flow sheet showing the pyrolysis procedures utilized in this study.

externally with methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) in order to enhance the trapping efficiency of the volatile pyrolysate. The trapped pyrolysate was subsequently extracted with 2–3 ml of methylene chloride. Solvent stripping was carried out at 18°C under reduced pressure to yield a concentrate. Ten to 20  $\mu\text{l}$  of spectroscopic grade benzene were added as a solvent to facilitate the transfer of the pyrolysate for gas chromatography (GC).

The GC analyses were carried out with a Varian 6400 equipped with a 30 m DB-5 chemically bonded capillary silica column (250  $\mu\text{m}$  sieve) and operated under the following conditions: helium flow of 30 ml/min; column temperature programming beginning at 80°C, ramping at 10°C/min to 200°C and holding at this temperature for 20 min. A flame ionization detector (FID) was used with a sensitivity range of  $10^{-12}$ . A n-alkane mixture in benzene was used as an external standard by serial dilution. The total FID response was calibration against the external standards to yield the total pyrolysable organic matter (TPOM) associated with each pyrolysate. This could then be expressed in parts per million (ppm) by weight of organics present in the original sample.

Gas chromatography-mass spectrometry (GC-MS) was carried out using a Carlo Erba GC and a Kratos (model MS-80) mass spectrometer. The same DB-5 column was used. Only sample PAN-9 yielded sufficient pyrolysate for reliable GC-MS analysis.

TABLE 2

Tentative assignments of some GC-MS peaks from the pyrolysate of PAN-9

GC-MS scan number	Mass ion m/e	Tentative assigned compound	
		Formula	Compound name
715	a	$C_{12}H_{10}FN_5$ <i>containing</i>	((2-Fluoro....)-1 H-purin-6-amine <i>related</i>
779		$C_{10}H_{16}O_2$	2-Butyl-1,3-cyclohexandione
835	223(?)	$C_{16}H_{22}O_4$	1,2-Benzenedicarboxylic acid <i>related</i>
839	152	$C_{12}H_8$	Acenaphthylene or biphenylene
839			
<i>also contains</i>	180	$C_{12}H_8O_2$	Benzo[c]cinnoline
847	a	$C_{12}H_{10}FN_5$ <i>containing</i>	((2-Fluoro....)-1 H-purin-6-amine <i>related</i>
850	154	$C_{11}H_7N$	1-Naphthalenecarbonitrile or 1-iso-cyanonaphthalene
850			
<i>also contains</i>	155	N.A.	Quinoline <i>related</i>
867	278	$C_{16}H_{22}O_4$	1,2-Benzenedicarboxylic acid <i>related</i>
890	228 or 288	$C_{15}H_{32}O$  $C_{20}H_{42}O$	3,7,11-Trimethyl-1-dodecanol  3,7,11,15-Tetramethyl-1-hepta-decanol
895	254 or 270	$C_{18}H_{38}$  $C_{18}H_{37}OH$	a branched $C_{18}$ alkane  a branched $C_{18}$ alcohol
901	a	$C_{12}H_{10}FN_5$ <i>containing</i>	((2-Fluoro....)-1 H-purin-6-amine <i>related</i>
951	a	$C_{12}H_{10}FN_5$ <i>containing</i>	((2-Fluoro....)-1 H-purin-6-amine <i>related</i>
981	224 or 252	$C_{16}H_{32}$  $C_{18}H_{36}$	(z)-7-Hexadecene or 1-Hexadecene  (E)-5-Octadecene or (Z)-7-Tetradecene
1037, 1077, 1133, 1150, 1193, 1246 and 1313	a	$C_{12}H_{10}FN_5$ <i>containing</i>	((2-Fluoro....)-1 H-purin-6-amine <i>related</i>
1487	280	$C_{20}H_{40}$	(E)-5-Eicosene
1687	252 or 304	$C_{18}H_{36}$  $C_{16}H_{32}O_3S$	(E)-9-Octadecene or (E)-5-Octadecene  6-Dodecyl-1,2-oxathiane

\*Cannot be determined due to weak parent peak or background peaks.

## RESULTS

*Correlation between CAI and vitrinite reflectance*

**Field correlation:** Over 200 samples were selected for conodont extraction and organic matter concentration (for vitrinite reflectance determination) from strata of varying organic maturity. Of these samples, some 172 yielded both sufficient numbers of conodonts and organic matter to permit comparison between vitrinite reflectance and CAI. The results of these analyses are shown in Fig. 3. The raw data yield a moderate linear correlation coefficient ( $r^2 = 0.72$ ) and only slightly better power or exponential regression coeffi-

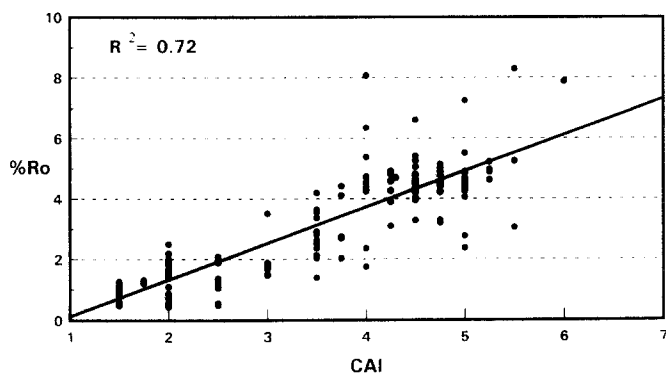


Fig. 3. Field data: correlation between CAI and mean random vitrinite reflectance.

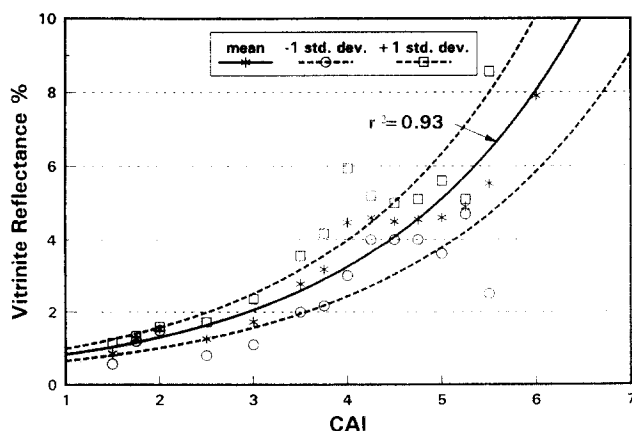


Fig. 4. Exponential regression curve ( $\pm 1$  standard deviation) of Huber's estimator for central tendency of field CAI and vitrinite reflectance data.



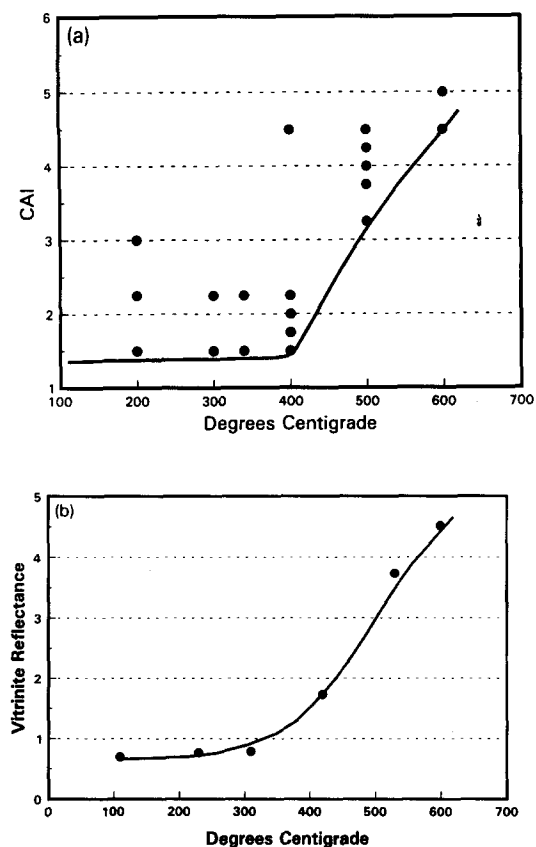


Fig. 5. Results of laboratory heating. (a) Heating of conodonts. Elements of varying CAI were exposed to temperatures ranging from 200 to 600°C. Thus at a given temperature the lowest CAI values preserved define the CAI against temperature curve. (b) Heating of vitrinite.

cients ( $r^2=0.74$  and  $r^2=0.76$ , respectively). Huber's estimator (a robust estimator; Huber, 1972) for calculation of the central tendency followed by regression, yields a linear correlation coefficient of  $r^2=0.72$  and an exponential correlation coefficient of  $r^2=0.93$ ). In Fig. 4, exponential least-squares regression of the field data ( $\pm 1$  standard deviation of the regression line), utilizing the Huber's estimator for the central tendency, have been plotted. This plot shows a greater scatter between CAI and  $R_o$  at higher levels of maturity and enables a quantitative appraisal of the expected variation in estimating maturity (vitrinite reflectance) from CAI data.

*Experimental correlations:* The results of laboratory heating of conodonts and vitrinite isolated from high volatile bituminous coal are summarized in Fig. 5. At temperatures below 400°C there is no evident change in CAI even for conodonts with an original CAI of 1 (Fig. 5a). By 500°C conodonts of

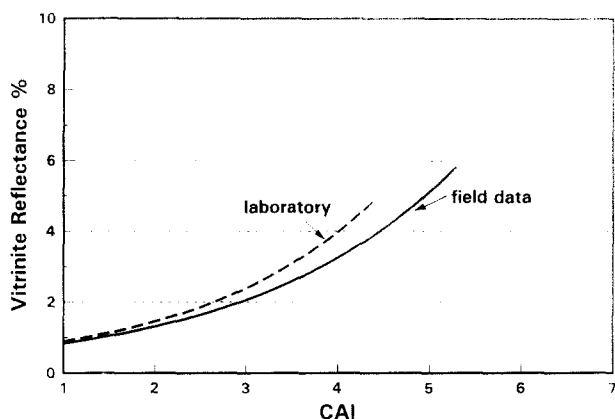


Fig. 6. Comparison of the correlation between CAI and mean vitrinite reflectance of laboratory treated samples and field collections.

CAI less than 3 have increased in CAI to 3 and at 600°C conodonts with CAI values of less than 4.5 have increased to this value. The change in vitrinite reflectance during the same heating conditions (Fig. 5b) is more dramatic. Starting at 220°C the vitrinite has responded to increasing temperature and shows an exponential increase in reflectance over the temperature range of the experiments.

Figure 6 compares the regression curves obtained from laboratory experiments and mean values (Huber's estimator) from field collections. This comparison indicated that the field CAI data correlate to lower vitrinite reflectance values than the laboratory analyses.

### *Fluorescence microscopy*

Under ultraviolet and blue light excitation, conodonts fluoresce within the CAI range 1–3 (Mastalerz et al., 1992). Samples with CAI 1 fluoresce relatively strongly, being almost entirely yellow in blue light excitation; only rarely do they show yellow-orange or orange color in the basal body or basal filling (Fig. 7a and b). Elements of CAI 1.5–2.5 are yellow orange and orange in the crown, while their basal filling is orange-brown, brown to dark brown (Fig. 7c–e). Conodonts with CAI 3 are uniformly brown and only their axial parts are brighter (yellow or orange), while those of CAI 4 do not fluoresce at all or show only weak fluorescence on their margins (Fig. 7f).

The emission spectra for conodont elements in CAI range 1–3 show a slight, but here considered insignificant, shift towards lower wavelength for both ultraviolet and blue light (Fig. 8) excitation. The variations in emission spectra within a given conodont element are of similar magnitude to those between

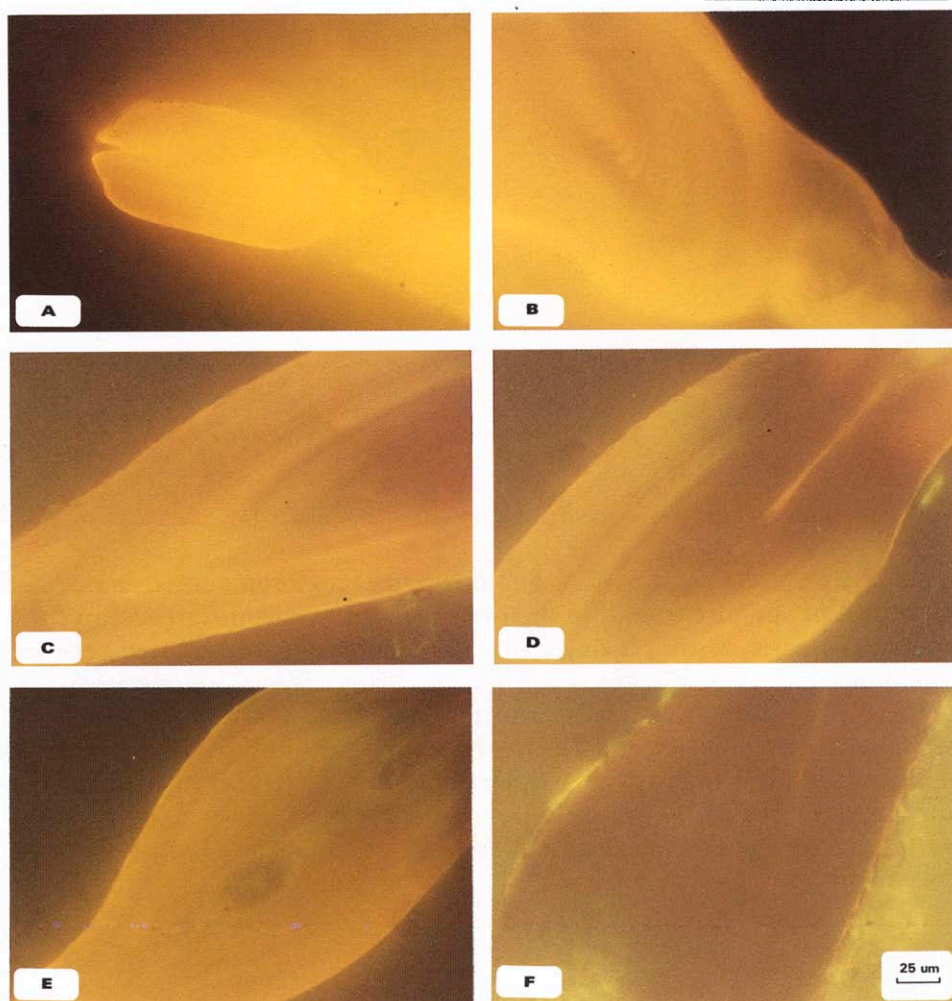


Fig. 7. Fluorescence of conodonts. All photomicrographs are taken with reflected blue light excitation. (a) and (b) CAI 1. (c) CAI 2. (d) CAI 2.5 and CAI 4.

conodonts of differing CAI. The wavelength of maximum fluorescence intensity ranges from 430 to 530 nm (Fig. 9) in ultraviolet light and from 530 to 620 nm in blue light (Fig. 10). There is a slight shift towards lower  $\lambda_{\max}$  for both ultraviolet and blue light excitation. Dispersion of maximum wavelength values for particular samples decreases with increasing CAI, however. There is a progressive decrease in relative fluorescence intensities of conodonts with increasing CAI from 1 to 3, both in blue (Fig. 11) and ultraviolet light (Fig. 12). Above a CAI of 3 the fluorescence intensity is very low and

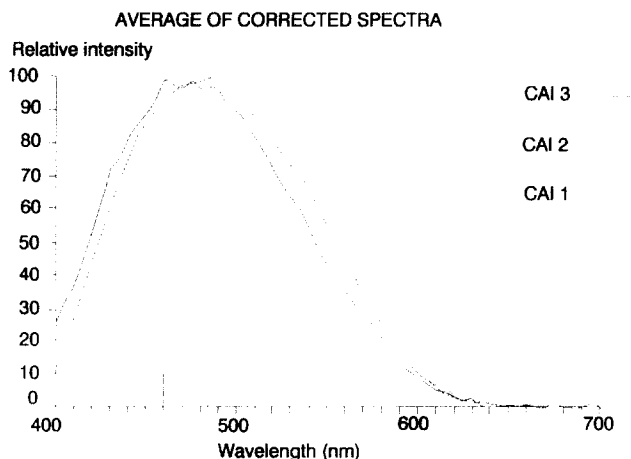


Fig. 8. Fluorescence emission spectra of conodonts of CAI 1, 2 and 3. UV excitation.

cannot be precisely measured. As all fluorescence measurements were made in the crown of conodonts, and in their brightest parts, the differences in fluorescence intensity within a single conodont are far less than those between conodonts.

The observed decrease in fluorescence intensity with CAI provides evidence for the organic origin of the fluorescence. The fluorescence of minerals would not be expected to decrease markedly over the temperature range that our samples have been exposed to. A second line of evidence is the observed continued fluorescence of the conodont residue following decalcification of the conodont.

### *Organic geochemistry*

The results of gas chromatography of the pyrolysate from five conodont samples are shown in Fig. 13. The total pyrolyzable organic matter (TPOM) ranges from 54 ppm (sample MISC-6) to 1267 ppm (PAN-9) (Table 1). There is no consistent trend in TPOM content with CAI although the sample with lowest CAI (PAN-9, CAI 1–2) has over twice the organic carbon content of the other samples. Such results must be considered preliminary inasmuch as the possible catalytic effects of mineral matrix and volatile loss during the sample preparation cannot be ruled out. The gas chromatography indicates the presence of n-alkanes as secondary constituents in the pyrolysis products of the organic matter and, in general, there is an overall decrease in n-alkanes and trend to those with lower carbon numbers with increasing CAI (Fig. 13).

Only samples PAN-9 yielded sufficient pyrolysate to warrant further study

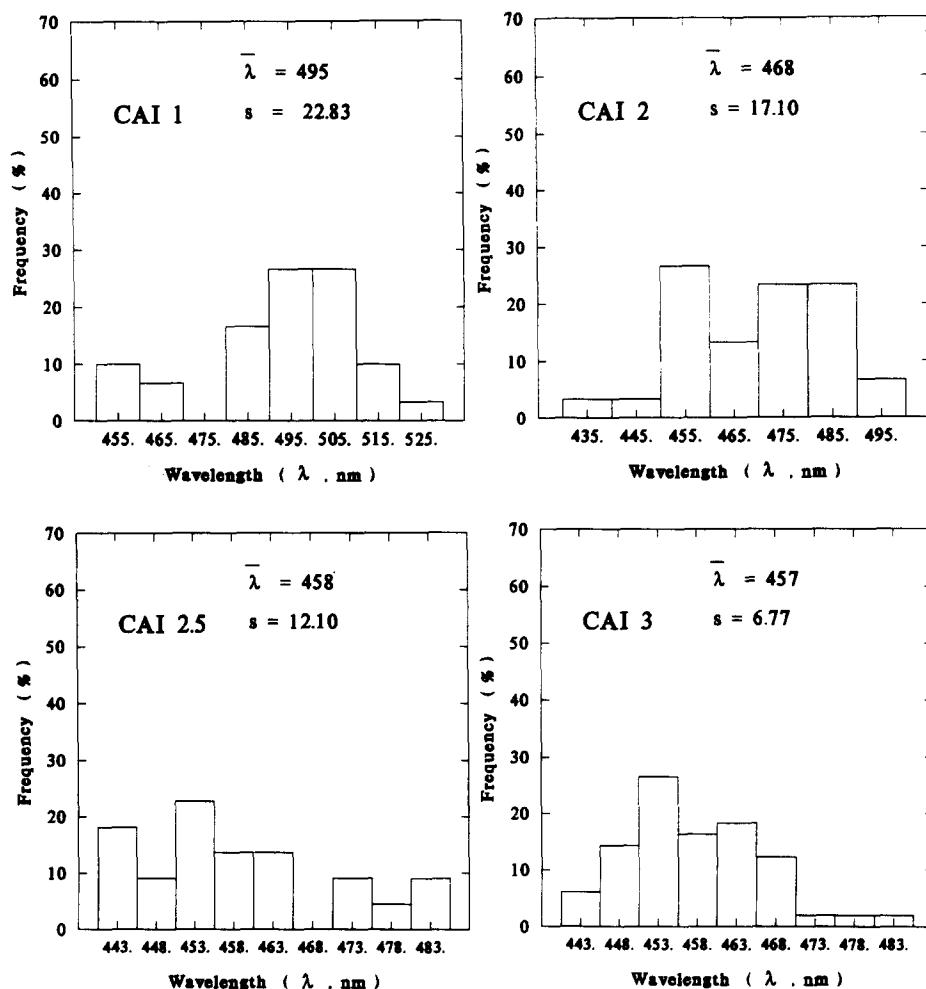


Fig. 9. Histograms of the wavelength of maximum fluorescence intensity for CAI 1–3. Ultraviolet light excitation (modified from Mastalerz et al., 1992).

by GC–MS and even this sample yielded results which are only marginal in quality. The results from the GC–MS are summarized in Table 2. In general, the pyrolysate comprises oxygen- and nitrogen-containing groups, aromatics, n-alkane series hydrocarbons, alcohols and some fatty acid-like compounds. The branched alcohols, such as 3,7,11-trimethyl-1-dodecanol, 3,7,11,15-tetramethyl-1-dodecanol, and a branched C18 alcohol, together with acenaphthylene or biphenylene, were identified in the sample. The presence of the n-alkane series was also confirmed by selective ion monitoring (SIM) mode. The occurrence of trace alkylated benzenes and trace polynuclear aro-

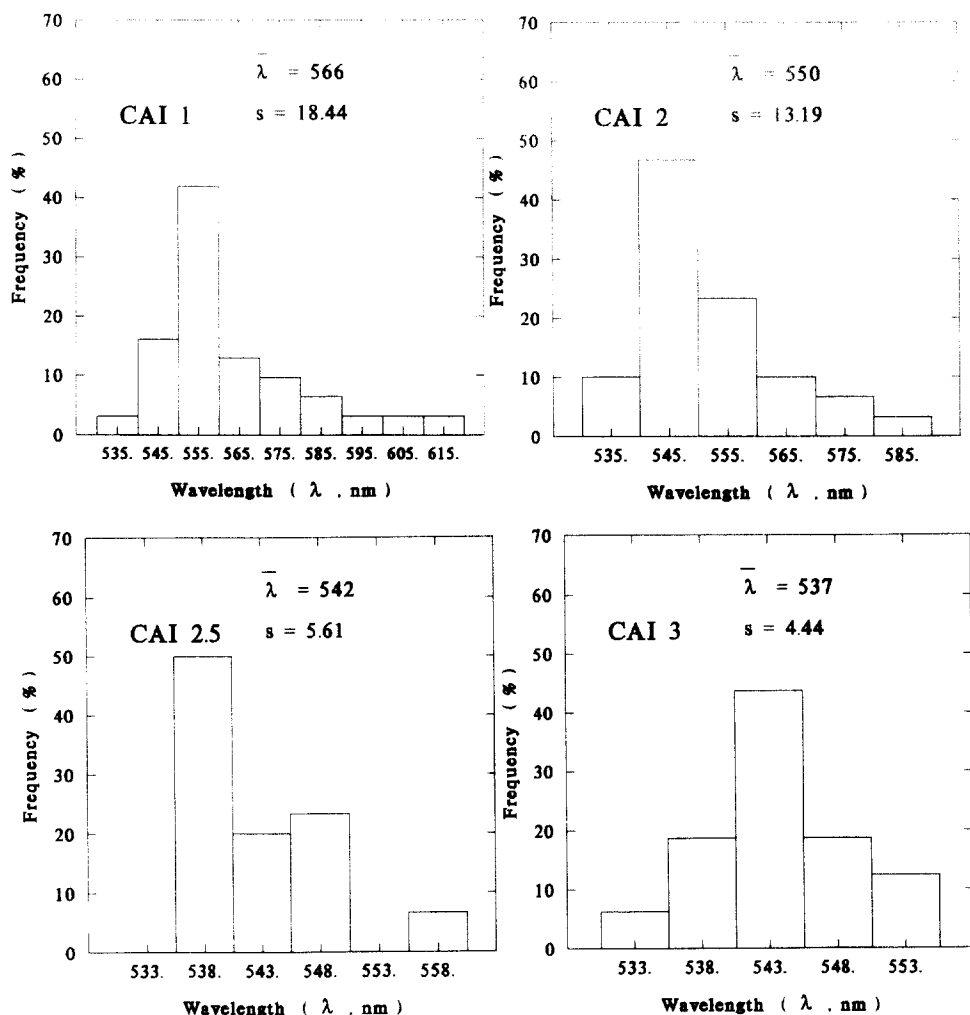


Fig. 10. Histograms of the wavelength of maximum fluorescence intensity for CAI 1–3, blue light excitation (modified from Mastalerz et al., 1992).

matics were also investigated by SIM mode. Positive identification of individual aromatic hydrocarbons was, however, not successful. Derivatives related to 1H-purin-6-amine were scattered along the retention time scale on the chromatograms. The oxygenated compounds listed above are unlikely to be major constituents of the pyrolysis products of ancient organic matter and thus are probably contaminants.

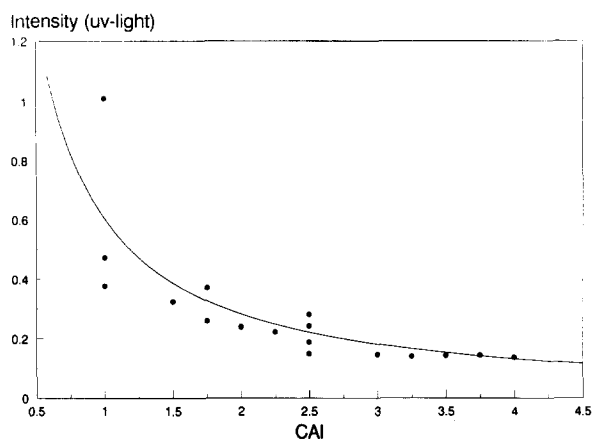


Fig. 11. Relationship between fluorescence intensity and CAI (blue light excitation). Intensity scale is relative. An intensity of 10 was arbitrarily assigned to conodonts with a CAI of 1 and which displayed the maximum measured fluorescence intensity.

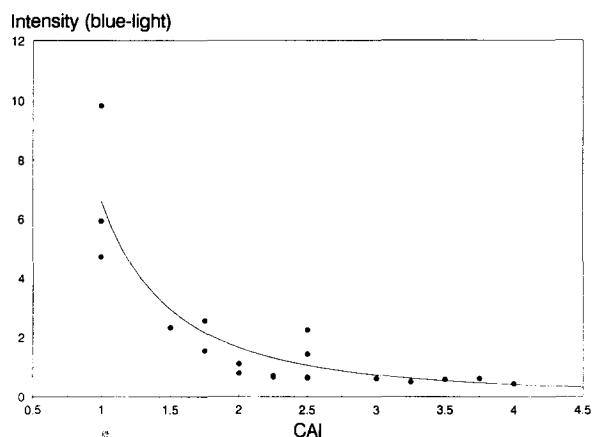


Fig. 12. Relationship between fluorescence intensity and CAI (ultraviolet light excitation). Intensity scale as in Fig. 11 (modified from Mastalerz et al., 1991).

## DISCUSSION

### *General*

It is well established that discrete organic matter or organic matter dispersed in fossil skeletal material undergoes progressive alteration in response to thermal exposure. The alteration of the organic matter is manifested by chemical and physical transformations as well as petrographical changes (see

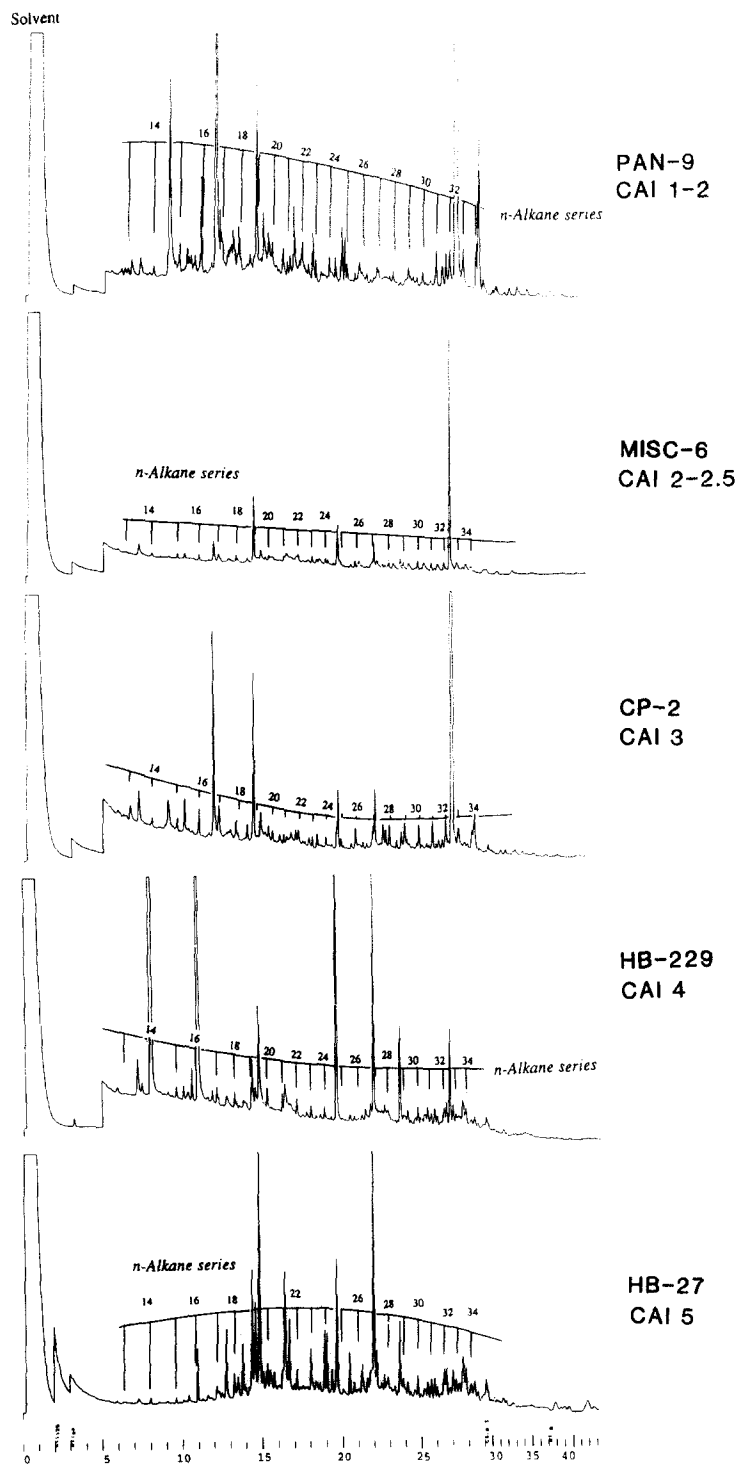


Fig. 13. Gas chromatograms of conodont pyrolysates.



summary by Bustin et al., 1985). The color alteration of conodonts has been known for over 100 years: Harley (1891) proposed that iron compounds were responsible for conodont color. Subsequent studies, however, have demonstrated that variation in inorganic composition of conodonts is not responsible for color alteration (e.g. Burnett, 1988; Mastalerz et al., 1992). It is now widely accepted that trace amounts of organic matter in the conodont elements are responsible for their color and that the color alteration reflects evolution of organic matter in response to thermal exposure (time plus temperature).

In detail, however, little is known about the nature of the organic matter, the alteration of organic matter at different levels of CAI nor how this alteration leads to variation in color. From CAI 1 to 5, it has been argued that color changes reflect progressive carbonization of the organic matter whereas above CAI 5 the change in color reflects a "burning off" of residual fixed carbon, followed at higher levels of alteration by a recrystallization which makes the conodont translucent (Epstein et al., 1977; Rejebian et al., 1987; Burnett, 1988). Burnett (1988) has further suggested that the size of the conodont elements is important: up to a CAI of 5 color change is a result of carbon fixing process. This means that small specimens may reach CAI levels more slowly than large ones that contain relatively more organic matter. Above a CAI of 5, where Burnett (1988) considered color change to be the result of oxidation and volatilization of oxides, smaller specimens precede larger ones in reaching higher CAI values (due to lesser amount of organic matter to be volatilized and a higher surface area to volume ratio). Thus, in samples of high CAI, where less robust forms are less likely to be recovered, CAI values will be too low (Burnett, 1988).

Rejebian et al. (1987) reported the opposite results based on pyrolysis: larger platform conodonts reached high CAI values faster than small forms in the same sample. It has also been argued that there is a difference in the process leading to the alteration of conodonts under contact and laboratory experiments and regional metamorphism. Conodonts heated in the laboratory and in contact metamorphism characteristically have a cloudy hue, which is sometimes described as a grey patina (Rejebian et al., 1987; Burnett, 1988) which Rejebian and co-workers attributed to the near-surface loss of organic matter. Our results, based on laboratory and field studies, indicate that, everything else being equal, laboratory heated samples of a given CAI reflect a higher temperature of exposure than field samples of the same CAI.

Such results support the kinetic studies of Epstein et al. (1977), who found that, on the laboratory time scale, higher temperatures are required to obtain the same CAI as field collections. The importance of time (kinetics) on the maturation of other types of organic matter are well documented (e.g., Bustin et al., 1990). In our laboratory experiments, the grey patina described by Rejebian et al. (1987) and attributed to heating of short durations, was not ev-

ident. It is possible that a fluid phase is required to produce the patina. Further, in our sample suite there was no clear relationship between the size of elements and color for either the field collection or laboratory experiments.

Considering the heating duration of even short laboratory experiments it is impossible that the volume, surface area or size of conodont elements could have any effect on their relative thermal exposure as suggested in the literature. In our study we found it necessary to work with specimens of about the same size because larger species generally appear darker than small ones (due to greater thickness); this does not suggest different responses to thermal maturation. An alternative possible explanation for the lower CAI of small elements in our study and those reported in the literature is the affect of oxidation. Studies of coal and organic matter dispersed in source rocks have demonstrated the dramatic effects of oxidation by atmospheric oxygen or oxygenated ground waters on the chemical and physical properties of the organic material (e.g., Bustin et al., 1990). Since oxidation acts centripetally, small particles, which have larger surface areas relative to particle size, oxidize much more readily. Thus, it is not uncommon in rocks to find kerogen of various particle sizes exhibiting different chemical and petrological characteristics in response to differential oxidation.

### *Geochemistry*

Our geochemical studies, although preliminary, suggest that, over the CAI range studied, the organic matter of conodonts is of generally the same character. Although no general decrease in TPOM of the samples with increasing CAI was found, the sample with the lowest CAI has over twice the TPOM content of the other samples. This points to a rapid decline in organic matter content between CAI 1 and 2. Such results are consistent with the marked decline in fluorescence intensity observed with increasing CAI between 1 and 2. In general, the decrease in heavier n-alkane series with increasing CAI follows well-documented trends for kerogen of progressively high thermal maturities and is interpreted as reflecting the progressive cracking of longer chain molecules.

The gas chromatography and gas chromatography-mass spectrometry of our samples provide some insight into the nature of the organic matter. Of particular importance is the occurrence of 1H-purin-6-amine, one of the key derivatives of the amino acid purine which is a building block of polypeptides and biological enzymes occurring widely in plants and animals. Amino acids have previously been isolated from conodonts (Armstrong and Harlstead Tarlo, 1966; Savage et al., 1990) using extraction techniques. Savage et al. (1990) used an acid digestion hydrolysis method to retrieve amino acids associated with the polypeptides of well preserved Ordovician conodonts. Their results indicated an amino acid content of 0.04–0.05% by weight (400–500

ppm). The results of this study suggest a total organic carbon content (as n-alkane equivalent) of 54–1267 ppm, which is of a comparable order to the results of Savage et al. (1990). The presence of the amino acid derivatives led Savage et al. (1990) to suggest that collagen figured prominently in the organic structure of conodonts. Collagen is a glycoprotein and comprises an important constituent of connective tissues and bone, teeth and skin of chordates (Leninger, 1975, p. 135). Although our data supports such an interpretation, the additional presence of branched alcohols, alkylated benzene and traces of nuclear aromatic hydrocarbons in our MS scans indicates that the organic matter is not a simple collagen structure or not only collagen. Further geochemical analyses are clearly required prior to drawing any substantive conclusions.

#### *Application in organic maturation analysis*

The results of our field study provide, for the first time, a large data set suitable for directly correlating CAI with vitrinite reflectance (which is generally considered the best and most precise measure of maturity). The overall scatter in the cross-plot of raw vitrinite reflectance and CAI values (Fig. 3) obtained in this study provides a measure of the precision of CAI as a maturation index. The scatter in the cross-plot reflects the subjectivity of CAI measurements and categorical nature of CAI measurements (CAI assignments are made in 0.5 increments and the scale is thus not continuous). In addition, some of the variation in the cross-plot can undoubtedly be attributed to problems associated with recognition of vitrinite. Particularly in carbonate rocks and following acid digestion, the origin of the organic matter may not be obvious and, thus, differentiating vitrinite from bitumen or liptinite macerals can be difficult.

The correlation between CAI and vitrinite reflectance for CAI values of less than or equal to 2 found in this study compares favorably with the published accounts of Epstein et al. (1977) and those reported in numerous publications. Above CAI values of 2, the CAI data obtained from this study correlate to higher vitrinite reflectance values than in previously published accounts. Based on our correlation between CAI and vitrinite reflectance, the upper limit of the oil window is defined as occurring at a CAI of about 2.5 (with a standard deviation of 0.5 CAI). Using our correlations the base of the oil window is between CAI of 1 and 1.5. However, in practice, the base of the oil window is not defined by CAI alone because values less than 1 are not reported.

The marked fluorescence of conodonts at low levels of maturity as reported here and previously (Mastalerz et al., 1992) suggests that measurement of fluorescence intensity may provide a non-subjective technique for using conodonts as a maturation index. Although the fluorescence emission spectra show only slight shift with varying CAI, fluorescence intensity is strong enough at

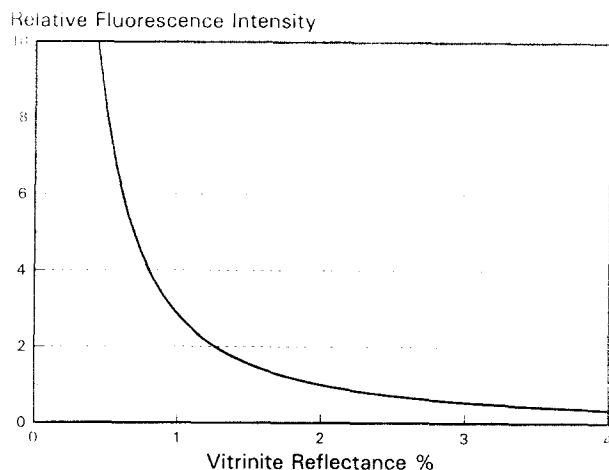


Fig. 14. Correlation between fluorescence intensity of conodont elements and vitrinite reflectance. This graph was constructed based a power regression of the data presented in Figs. 4 and 11. The relationship between fluorescence intensity and reflectance shown must thus be considered preliminary because the variance in the correlations shown in Figs. 4 and 11 and because the fluorescence intensity scale is arbitrary.

low levels of CAI to be a good indicator of maturation: relative intensity changes distinctly between individual samples and is strongly CAI-dependent. By measuring this intensity only in the brightest parts of each conodont element, intensity differences within a single element can be neglected. Differences between conodonts in a single sample are still significant and may be related to the type of element, species and possibly host rock lithology. These differences, however, are less than those between samples at different CAI levels, which makes it possible to determine precisely and objectively the degree of organic maturation within a given sequence of conodont specimens.

Conodont fluorescence intensity thus provides a useful measure of maturation, particularly for levels of maturation encompassing the oil window where CAI is a poor indicator of maturation (because CAI ranges only from 1 to 2.5 within the zone of oil generation). Thus, fluorescence intensity measurement of a conodont sample makes it possible to determine the degree of maturation with much greater precision and higher resolution than is possible using the CAI alone. In particular, conodont fluorescence measurement may enable definition of the top of the oil window. However, in order to make conodont fluorescence intensity a useful maturation parameter, the correlation between absolute fluorescence intensity and maturation parameters such as vitrinite reflectance must be established. Figure 14 shows the preliminary correlation between vitrinite reflectance and fluorescence intensity. However, it must be noted that calibrating fluorescence intensity with CAI and vitrinite reflectance with CAI (as was carried out to generate Fig. 14) cannot yield a corre-

lation between fluorescence intensity and vitrinite reflectance which is more precise than the current CAI scale. Establishing a scale of fluorescence against maturation (vitrinite reflectance) will require systematic sampling of a thick continuous succession of conodont- and vitrinite-bearing strata of low maturity and/or detailed laboratory experiments.

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