DEVELOPMENT OF GRAPTOLITE REFLECTANCE AS AN INDICATOR OF PALEOTEMPERATURE AND THERMAL MATURATION

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CHAPTER I

INTRODUCTION

Petroleum hydrocarbons are generated from certain types of organic matter found in some sedimentary rocks. The generation of oil and gas from organic matter occours during the process of thermal maturation. Thermal maturation is caused by increasing temperature during and after the burial of sediments in a sedimentary basin. Thermal maturity with respect to the generation of liquid hydrocarbons is obtained when the sediments and associated organic material are heated to temperatures of 60-170°C (Staplin et al., 1969). If the temperature does not exceed 60°C, the rock is thermally immature and would not yield oil, but it will still yield biogenic methane. If it exceeds 170°C, the rock is termed post-mature and the liquid hydrocarbons generated are then destroyed. Heating during burial also produces changes in the physical and chemical properties of organic matter. The changes thus produced are irreversible and can be detected by several existing techniques.

During the past decade the determination of thermal maturity has emerged as a rapidly developing discipline in the exploration of petroleum hydrocarbons. Researchers have developed a variety of techniques for determining thermal maturity. These are based on detecting and measuring chemical and physical changes produced in organic matter by increasing temperature. Properties measured include reflectance, luminescence, fluorescence, color, and transparency.

Among the several techniques now employed to determine thermal maturity are geochemical analysis, palynomorph and kerogen translucency, conodont-color alteration, and vitrinite reflectance. Vitrinite reflectance is, if not the most, certainly one of the most used techniques. The changes in the reflectance of vitrinite (woody organic material) with increasing coal rank have been attributed to increasing temperatures during burial (Castano and Spark, 1974; Teichmuller, 1974; Ammosov, 1961; Dow and O'Connor, 1982). Vitrinite reflectance increases exponentially with a linear increase in temperature (Hunt, 1979; Dow and O'Connor, 1982). Another useful tool in the study of source rock maturation is conodont-color alteration. Conodonts are the microscopic hard parts of an unknown group of organism (Cambrian - Triassic) with a calcium phosphatic composition (Lindstrom, 1964). They are known to change color in response to increasing temperature. Epstein et al. (1977) developed the Conodont Alteration Index (C.A.I.) by artificially heating conodonts in the laboratory and correlating the color change with percent fixed carbon and vitrinite reflectance.

Although the techniques of vitrinite reflectance and conodont-color alteration are widely used, some inherent difficulties limit their application. The problems with vitrinite reflectance have been discussed in detail in many previous works (Price and Barker, 1985; Heroux et.al., 1979; Ting, 1978). The major limitations of vitrinite reflectance are that vitrinite is absent from pre-Devonian rocks and rarely preserved in clean marine carbonates. Conodont-color alteration, on the other hand, has different limitations. Owing to processing difficulties, conodonts are rarely extracted from clastic rocks. An individual color-alteration index may represent a wide temperature range (e.g. 80°C). Above all, conodont-color alteration is a subjective tool depending heavily on the observer's perception of gradual color changes.

Graptolite reflectance is a relatively new technique. It is a yet to be developed analytic tool that can overcome some of the problems with vitrinite reflectance and conodont-color alteration. Graptolites are common fossils in Ordovician to lower Devonian rocks, although some orders of class Graptolithina may extend from Cambrian to Pennsylvanian. Graptolites can occur in a range of marine facies, from shallow water carbonates to deep marine clastics. They possess an organic skeleton or periderm. The periderm is composed of callogenous polysacchride (Towe and Urbanek, 1972). Previous studies have noted that the graptolite periderm, when affected by high temperatures during burial, changes in reflectance. Based on studies of coal and other organic matter, the change in the reflectivity of the periderm can be attributed to the arrangement of carbon molecules and expulsion of the volatiles with increasing temperatures. As the carbon chains lengthen, the periderm reflects more light. This change in reflectance is irreversible and can be calibrated to measure paleo-temperatures. Graptolite reflectance, if developed, can be used in pre-Devonian strata where vitrinite is lacking and in clastics, especially from deep-water environments, where conodonts are rarely found. In rocks where graptolites co-occur with vitrinite or conodonts, graptolite reflectance can serve as an additional and possibly more precise technique for analyzing maturation.

Recently, several German and Australian scientists have reported on graptolite reflectance (Teichmuller, 1978; Teichmuller & Teichmuller, 1982; Stach et al., 1982; Clausen & Teichmuller, 1982; Kurylowicz et al., 1976; Gorter, 1984; and Jackson et al., 1984;). None of them, however, attempted to calibrate a maturation scale for graptolite reflectance. Most recently Goodarzi (1984) and Goodarzi and Norford (1985) tried to calibrate a scale. However, their data is limited, and the resulting index is not very precise. Thus, there is still a need to calibrate a scale for graptolite reflectance, if it is to be used for determining maturation of source rocks.

Purpose Of Study

The purpose of this study is to calibrate a scale of graptolite reflectance which could be used to determine paleo-temperatures and thermal maturity of hydrocarbon source rocks. Several steps are involved in calibrating a scale. The first step is to show that graptolite reflectance does vary irreversibly and consistently with paleo temperatures to which the graptolite-bearing strata have been subjected. The second step, which will require more data, is to calibrate a scale. Both steps require that graptolite reflectance for each sample be compared to some other measure of paleo-temperature. Among the various techniques available, conodont-color alteration is probably the most suitable for this work. Conodonts and graptolites often occur together in Ordovician to Devonian strata, and samples are available from a variety of lithologies and depositional and tectonic settings representing a wide range of paleo-temperatures. Graptolite reflectance might be dependent on the lithology of the host rock. For this reason, graptolite reflectance of samples from different lithologies but similar paleo-temperature are compared.

CHAPTER II

PREVIOUS STUDIES

Several techniques are available to assess thermal maturation of sedimentary organic matter and its subsequent transformation to oil and/or gas. Those involving petrography include palynomorph color, spore translucency, vitrinite reflectance, fluorescence microscopy, and conodont-color alteration. These techniques involve examination of particulate debris derived from terrestrial or marine sources. Terrestrial organic matter consists of woody particles, pollens, spores, plant cuticles, resins, and freshwater algal matter. Marine organic matter includes phytoplanktons and zooplanktons (Haseldonckx, 1979). Techniques that use these materials have been discussed at length (Alpern, 1972; Bostick, 1979; Burgess, 1974; Castano and Sparks, 1974; McCartney and Teichmuller, 1972; Ottenjann et al., 1974; Powell et al., 1982; Stach et al., 1982; Staplin, 1977; Price, 1985; Teichmuller and Teichmuller, 1978; Van Gizal, 1973). A summary of these techniques and their correlation is given by Heroux et al. (1979). Optical methods for determination of thermal maturity use both transmitted and reflected light microscopy originally developed for coal and coal-rank determination. These techniques are now used for determination of thermal maturity of petroleum source rock. A brief review of some of the optical techniques follows.

Palynomorph Color and Spore Translucency

Several publications have described changes in palynomorph color and spore color and translucency with increasing maturity of their host rock. Gutjahr (1966) documented progressive and irreversible color changes in palynomorphs, from pale yellow through brown to black. The color change can be observed visually through microscopic comparison with a set of standard color slides. Staplin (1969, 1977) established a Thermal Alteration Index (T.A.I) based on color changes in spores due to depth of burial. Another scale, similar to T.A.I., known as State of Preservation (E.C.), was proposed by Correia (1967, 1971) and Correia and Peniguel(1975). Both T.A.I. and E.C. scales are based on color changes and are most useful in the mature to post-mature range. However, they are not precise in the immature to mature range. A ten-point Spore Coloration Index (S.C.I.) was developed by Barnard et al. (1976) to overcome these problems by calibrating color changes at all levels of maturity. A correlation of these indicies is given in Figure 1. Photometric observations of spores (Gutjahr, 1966; Burgess, 1977) show a progressive absorption of red light over S.C.I. range of 1-7, and progressive increase of blue light absorption over the range

LEVEL OF MATURATION	S.C.I Barnard	 Batten 1976	T.A.I Staplin 1974	E.C Correia 1975	TRANSLUCENCY % Grayson 1975	VITRINITE REFLECTANCE OIL Dow 1982
IMMATURE	1	1	1	1		·22
						·4
	2					
			2			
TRANSITION	3	2			±50	·5
	4	3		±2		
MATURE			2.5		±40	·7
	5					·8
	6					·98
		4				
	7					1·19
				±3		
TRANSITION	8	5	3			1·35
					±5	
POST-MATURE	9	6	3·5	4		1·50
	10	7	4	5		1·90

Figure 1. Correlation of spore coloration and palynomorph translucency indicies with vitrinite reflection and stages of maturation (modified after Haseldonckx 1979).

of 7-10. The absorption or translucency of individual specimens records the level of thermal maturity.

There are problems with the use of palynomorphs and spores because their properties of translucency and color vary with different types of spores and pollen. The methods employed are slow, and it is difficult to find the same type of spores in rocks of different ages. Palynomorph and spore coloration and spore translucency provide only a qualitative assessment of carbonization trend or degree of maturation (Burgess, 1977), and the accuracy of the results depends heavily on the experience of the observer.

Fluorescence Microscopy

Fluorometry is employed to determine the degree of maturity of certain macerals which fluoresce in response to ultraviolet excitation. Qualitative assessment of spectral colors as well as quantitative fluorescence studies are helpful in determining the degree of organic maturity. Fluorescence intensity and color are directly related to the amount, type, and maturation of the organic matter present in the host rock. Fluorescence intensity decreases with increasing maturity of the organic matter (Ottenjann et al., 1979). Fluoresence intensity has been correlated with the vitrinite reflectance scale for the determination of maturity of source rocks. Only certain maceral types of typeI and II kerogen,which in coal petrological term are inertinite and liptinite group, fluoresce. The absence of most of these macerals makes it impossible to apply this technique to pre-Devonian rocks.

Vitrinite Reflectance

Hoffmann and Jenkner (1932) first noted reflectance changes in vitrinite with increasing maturity. Teichmuller (1950) was the first to relate vitrinite reflectance to the generation of petroleum hydrocarbons. A score of papers has since been published on this subject (Teichmuller and Teichmuller, 1982a; Hacquebard and Donaldson, 1970; McCartney & Teichmuller, 1972; Hood et al., 1975; Stach et al. 1982; Price, 1983), and all have mentioned the significance of vitrinite reflectance for determination of organic maturation. Changes in the reflectance of vitrinite are attributed to increasing temperatures during burial (Castano and Sparks, 1974; Teichmuller, 1974; Ammosov, 1961; Dow and O'Conner, 1982). The change in reflectance is caused by the change in molecular structure of vitrinite due to heating. Vitrinite reflectance increases exponentially with the linear increase in temperature (Ting, 1975). When plotted on a semilog graph, vitrinite reflectance will follow a straight line and the slope of the line is a function of the geothermal gradient and the age of the rock (Ting, 1975); (Figure 2).

In spite of its wide use, there are several problems with the vitrinite reflectance technique (Heroux et al., 1979). Vitrinite is absent from pre-Devonian rocks.

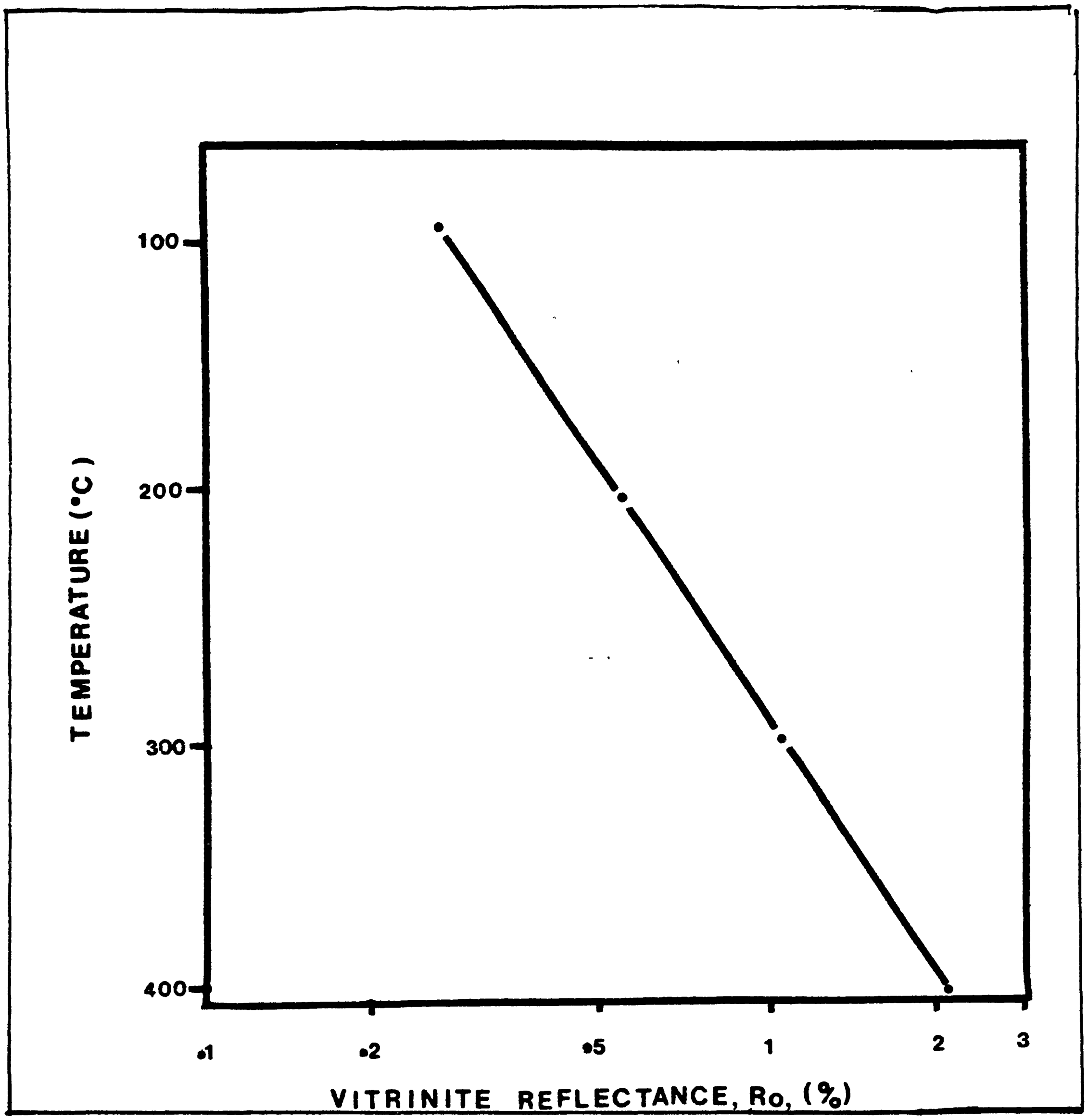
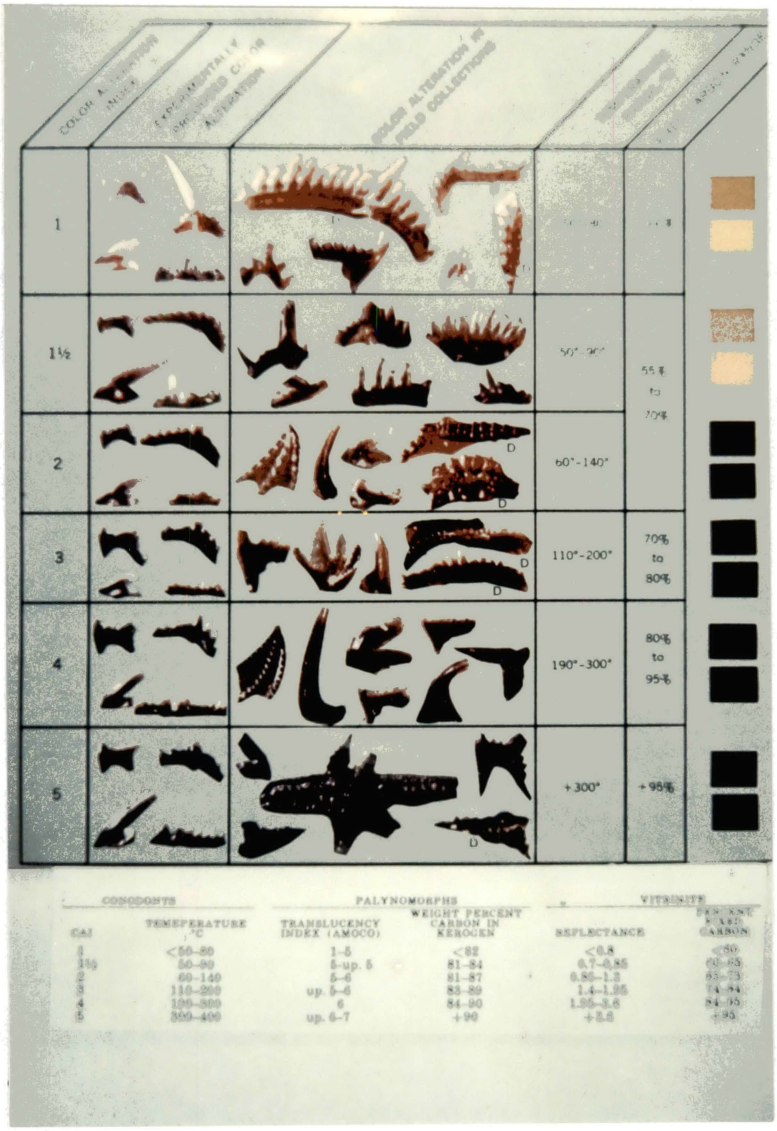


Figure 2. Plot of vitrinite reflectance versus temperature, on a semilogrithmic scale. (Note: These laboratory produced temperatures are much higher than the natural situation) (Ting, 1975).

Vitrinite is difficult to distinguish from other macerals of similar character, but for which reflectance properties are poorly known. Lithology can influence the degree of reflectance. Oxidation can reduce the reflectance of vitrinite. Price and Barker (1985) observed that vitrinite reflection is suppressed in the presence of significant amounts of resinite, a maceral of the exinite group, and that there are problems with the accuracy of reflectance values of 0.6 to 1.35, which represent the so-called oil window.

Conodont-Color Alteration

Epstein et al. (1977) established an index of organic metamorphism based on color changes in conodonts. Conodonts are phosphatic skeletal elements of an extinct animal group. These elements change color with heating. Epstein et al. (1977) produced a complete range of color changes by artificially heating conodonts in the laboratory. The color changes were related to an increase in percent fixed carbon and in nature can be produced by increased heating as the host rock is buried. The color change is from pale yellow to black. A scale of conodont-color alteration, the conodont alteration index (C.A.I.), is shown in Figure 3. Each C.A.I is correlated with percent fixed carbon and vitrinite reflection. This scale is a relatively fast and inexpensive method for determination of thermal maturity. Conodont-color alteration can be used in rocks heated up to



CONODONTS		PALYNOMORPHS		VITRINITE	
CAI	TEMPERATURE °C	TRANSLUCENCY INDEX (AMOCO)	WEIGHT PERCENT CARBON IN KEROGEN	REFLECTANCE	PERCENT FIXED CARBON
1	<50-80	1-5	<82	<0.8	<60
1½	50-90	5-up. 5	81-84	0.7-0.85	60-65
2	60-140	5-6	81-87	0.85-1.3	65-73
3	110-200	up. 5-6	83-89	1.4-1.95	74-84
4	190-300	6	84-90	1.95-3.6	84-95
5	300-400	up. 6-7	+90	+3.6	+95

Figure 3. Conodont Alteration Index, correlated to other other indicies for measuring paleotemperatures (Epstein, et al., 1977).

a temperature of 500^{o}C. This scale is particularly suitable for marine carbonates of pre-Devonian age, which lack vitrinite.

Although a very useful tool, conodont-color alteration does have its limitations, most of which are mentioned above. Unfortunately the conodont color-alteration index is a subjective tool heavily reliant on the observer's judgement, and its precision is no greater than 80^{o}C.

Graptolite Reflectance

Reflectance of graptolite periderm has been used for the evaluation of thermal maturation of sediments. It was observed that the graptolites show a wide range of reflectance (0.36-12.0 %) and that this reflectance is a function of the maturity of the host rock (Kurylowicz et al., 1976; Clausen and Teichmuller, 1982; Goodarzi, 1984; Goodarzi and Norford, 1985). Kurylowicz et al. (1976) in their study of the Amedeus Basin, Australia, considered the optical properties of graptolite to be comparable to those of vitrinite. Clausen and Teichmuller (1982) described the structure of some graptolites under reflected light in detail, distinguished and described the ultrastructure of the periderm, and noted increased reflectance of some samples from greater depth and thus greater paleo-temperature. Goodarzi (1984) also concluded that reflectance of the graptolite periderm increases with increasing temperature and can be used as a maturity indicator for the host sediments. Goodarzi et al. (1985) compared a few graptolite-reflectance values to rock-eval. More recently, Goodarzi and Norford (1985) examined several samples from Canada and compared the reflectance values to conodont CAI's from the same rocks. In this way, they tried to relate graptolite reflectance to the paleo-temperatures of the host rock. They also noted that graptolite reflectance was dependent on the lithology of the host rock. Graptolites preserved in carbonates show lower bireflectance than those preserved in shale at the same paleo-temperatures.

CHAPTER III

SAMPLING AND ANALYTICAL METHODS

General Statement

Standard techniques for sample preparation and reflectance measurements used in coal petrology are employed for determining reflectance of graptolite periderm. Graptolite bearing rocks of various lithologies were obtained from the collections of Dr. S. C. Finney. The samples were collected from several localities in United States and Europe (Table 1). They represent a variety of ages, lithologies, tectonic settings and paleotemperature values. In addition conodont alteration indicies are readily available for most of these samples.

Graptolite samples were embedded in pellets and polished. Graptolite reflectances were measured using standard procedures described in ASTM Standards (1982), Bostick and Alpern (1976), Davis (1978), Dow and O'Conner (1982), Hunt (1979), and Stach et al. (1982).

The conodont alteration index (C.A.I) is determined by dissolving the conodonts from the rock sample in acid (Epstein et al., 1977). Conodonts are picked and examined under the binocular microscope for the color. The C. A. I. value of the rock sample is then determined by comparing

TABLE I

LIST OF SAMPLES

SAMPLE NO.	LOCALITY, FORMATION, AGE, AND LITHOLOGY
A	Lowest Bigfork Chert Formation, Stringtown quarry, T.1S., R.12E., Atoka county, Oklahoma. Limestone. Middle Ordovician.
B	Lower Viola Springs Formation, E 1/2, SW 1/4 sec. 22, T.2S., R.1W, near Mountain Lake, Carter county, Oklahoma. Limestone. Middle Ordovician.
C	Basal Viola Springs Formation, SW 1/4, sec24, at Interstate 35, South flank of Arbuckle anticline, Carter county,Oklahoma. Limestone Middle Ordovician.
D	Same as A.
E	Lowest Viola Springs Formation, at Interstate 35, south flank of the Arbuckle anticline, SW 1/4, sec 25, T.2S., R.1E., Carter county, Oklahoma. Limestone. Middle Ordovician.
F	Viola Springs Formation, near Fittstown, NW 1/4, NE 1/4, sec. 12, T.2S., R.6E, Pontotoc County, Oklahoma. Limestone. Middle Ordovician.

TABLE I (Continued)

G	Maysville Stage, Cincinnatti region, Kentucky. Limestone. Upper Ordovician.
H	Viola Spring Formation, section Q, Rayford quarry, NW 1/4, NE 1/4, sec 28, T.1S., R.2E. Oklahoma. Limestone. Middle Ordovician.
I	Viola Springs Formation, Rock Crossing, sec 35, T.5S. R.1E. Carter county, Criner Hills, Oklahoma. Limestone. Middle Ordovician.
J	Athens Shale, Pratts Ferry, Alabama. Shale Middle Ordovician.
K	Athens Shale, Pratts Syncline, Bibb County, Alabama. Shale. Middle Ordovician.
L	Athens Shale, Pratts Syncline, Bibb County, Alabama. Shale. Middle Ordovician.
M	Viola Spring Formation, . Core from Kaiser Francis 8-20 Dillard well, Sec 20, T. 4S, R. 5W., Jefferson County. Limestone. Oklahoma. Middle Ordovician.
N	Viola Spring Formation, . Core from Kaiser Francis 8-20 Dillard well, Sec 20, T. 4S, R. 5W., Jefferson County,.Oklahoma. Limestone. Middle Ordovician.

TABLE I (Continued)

O	Upper Table Head Formation, Poit-aux Port Penninsula Western Newfoundland. Shale. Middle Ordovician.
P	Ottosee Formation, Midway Roadcut, East Tennesse. Limestone. Middle Ordovician.
Q	Nicolet River Formation. Ontario, Canada. Limestone. Upper Ordovician.
R	Woods Hollow Shale, Marathon region Texas. Shale. Middle Ordovician.
S	Blockhouse Formation, East Tennesse. Shale. Middle Ordovician.
T	Athens Shale, Calera, Shelby County, Alabama. Shale. Middle Ordovician.
U	Martinsburg Formation, Newport, Virginia. Limestone. Middle Ordovician.
V	Block House Formation, Water Gap, East Tennesse. Directly beneath Smoky Mountain thrust. Shale. Middle Ordovician.
W	Anderson Shale. Jamtland, Sweden. Shale. Middle Ordovician.
X	Oran Shale. Oran River, Jamtland, Sweden. Shale. Upper Ordovician.
Y	Oran Shale. Ostersund, Jamtland, Sweden. Shale. Upper Ordivician.

the color of the conodont to laboratory produced standards. The C.A.I. values for the samples in this study were available in the published literature (Epstein et al., 1977; Bergstrom, 1980) or were determined by conodont specialists (Bergstrom and Sweet, personal communication).

Sample Preparation

Several methods of preparation of the graptolite specimens were employed. Specimens isolated from matrix were mounted in pellets and slides, and whole rock samples enclosing graptolite specimens were mounted as pellets or thin sections.

Specimens were isolated by dissolving the rock in dilute hydrochloric acid to free the graptolites from the matrix. The residue was then sieved and the graptolite fragments were hand picked from the residue. These samples were then cleaned and dried to get rid of any moisture. The isolated specimens were then made into pellets. The technique employed is that used for macerated vitrinite (Cardott, personal communication). Polished thin sections of isolated graptolites were also prepared, but the delicate, brittle carbonized periderm of the graptolite could not withstand the harsh grinding and polishing steps. A problem with imbedding isolated graptolites in pellets was obtaining the proper orientation of the specimen for the maximum reflectance measurements. Polished thin sections of graptolite in rock matrix were also prepared. In this case obtaining the proper orientation of the specimen for true maximum reflectance measurements was difficult. Best results are obtained by the preparation of whole rock samples in pellets. The rock was cut parallel to the bedding plane to get the true maximum reflectance of the graptolite periderm (Davis, 1978). The rock pieces with graptolite were then embedded in synthetic resin to make the pellets. Pellets were allowed to dry over a period of 24 hours before grinding and polishing steps. For grinding the pellets 320, 400, and 600 grit silicon carbide papers were used. The best polished surface was obtained by polishing with alumina based slurry of 0.3 and 0.05 um.

The graptolite material may be very soft in shales to very hard and brittle in limestones. Very gentle treatment is needed during grinding and polishing. Weathered or highly oxidized outcrop samples are very difficult to polish. Fresh outcrop samples and core samples give the best results during the polishing stage. Freezing is recommended before polishing very soft material (Goodarzi and Norford, 1985). After polishing, the samples are kept in a desiccator to get rid of moisture content which could alter the reflectance (Harrison, 1965, Harrison and Thomas, 1966).

Reflectivity Measurements

Reflectance measurements were taken on a Nikon Optiphot polarizing microscope adapted for reflected white (halogen) light microscopy (Figure 4). Oil immersion objectives of 20x, 40x and 50x magnification were used with a 10x ocular. A stablized light source is required for accuracy in reflectivity measurements. A Lambda model LP-5300-FM power supply was employed for this purpose. Photometric oculars adapted with a fiber-optic probe were used for measuring reflectivity of the sample. The probe was connected to a Gamma Scientific D-47A photomultiplier equipped with 546 nm filter and a digital radiometer. All of the reflectance readings were in oil immersion, using Cargille type B oil (n_e= 1.5180). Crossed or plain polarized light was used to examine the samples.

The procedure for measuring reflectivity is the same as that employed in organic petrography and coal petrology (A.S.T.M. Standards, 1982; Bostick and Alpern, 1976; Davis, 1978; Stach et al., 1982). The microscope and the measuring equipment must be standardized. Standards that have been used in reflected light microscopy include glasses, minerals, and synthetic minerals of known reflectivity and refractive index (Table 2). The standards used in this study are glass standards of known reflectivity and refractive index (Table 3). The glass standards are embedded in dark plastic with the lower face of the glass cut at an angle of 30^o to eliminate internal reflectance of the glass (Davis, 1978). During standardization the reflectance values should not vary more than ± 0.01% of the given value.

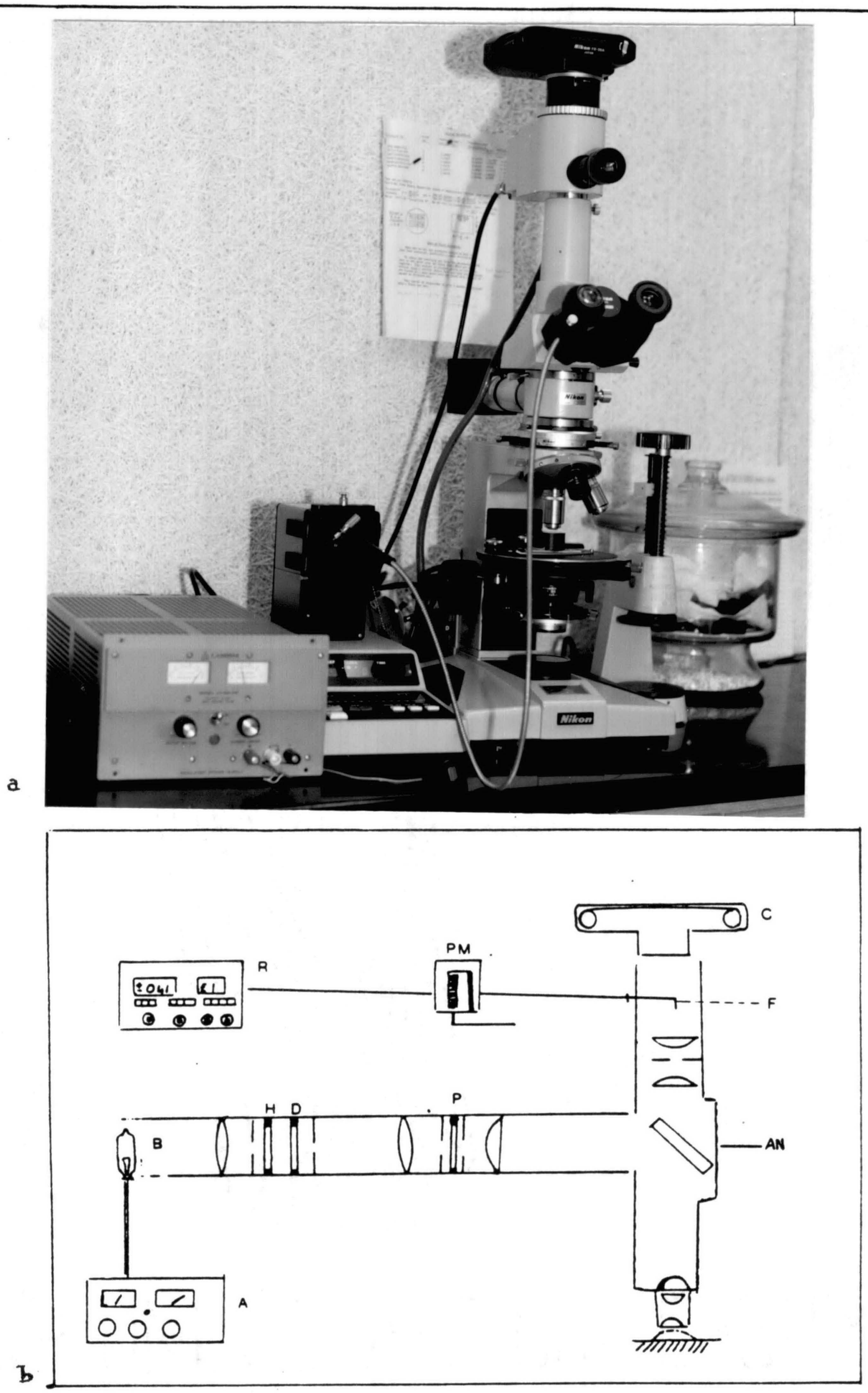


Figure 4. Photograph (a), and schematic diagram (b), of the microscope setup for measuring reflectance. A = Stablized power source, An = Analyzer, B = Halogen lamp, C= camera, D= Diffuser filter, P= Polorizer PM= Photomutiplier, R= Radiometer.

TABLE II.

REFRACTIVE INDEX AND REFLECTANCE OF STANDARDS USED IN COAL PETROGRAPHY

STANDARD	REFRACTIVE INDEX	REFLECTANCE
Leuco-sapphire	1.772	0.598
B. L. 689309	1.6945	0.303
B. L. 751278	1.7572	0.535
B. L. 850324	1.8564	1.008
B. L. 915213	1.9255	1.403
B. L. 980222	1.9908	1.819
Diamond	--	5.305
Carborundum	--	7-7.3

(After Stach et al., 1982)

TABLE III

REFRACTIVE INDEX AND REFLECTANCE OF STANDARDS USED IN THIS STUDY

STANDARD	REFRACTIVE INDEX	REFLECTANCE
SF8-689-312	1.6945	0.3026
SF13-714-276	1.7477	0.4958
LaF12-836-423	1.8400	0.9207
LaSF9-850-322	1.8567	1.0085
LaSF18-913-325	1.9273	1.4130
LaSF6-961-349	1.9670	1.6618

The pellets are pressed into clay on a metal or glass slide to assure that the pellet surface is perfectly parallel to the microscope stage. Graptolite reflectance is measured in oil. Maximum and minimum reflectances are measured by rotating the stage through 360°. The statistical mean of anywhere between 20 - 60 individual readings of maximum and minimum reflectance are reported for each sample. These values are then entered into a general statistics program for computation. Histograms were generated which aided in the interpretation of the reflectance measurements. Bireflectance (maximum reflectance minus minimum reflectance) was calculated for each sample to determine if it varies with paleotemperature. These data allow calibration of reflectance with conodont color-alteration. The reflectance data were plotted against C.A.I. values for the samples in order to: 1) determine if there is a progressive irreversible change in reflectance with the increased paleotemperatures and 2) calibrate a scale of graptolite reflectance against paleotemperature.

CHAPTER IV

GRAPTOLITE: MORPHOLOGY AND OPTICAL PROPERTIES

Morphology

Graptolites are an extinct group of colonial, planktonic, marine organism. They are the most important index fossils for lower Ordovician to lower Devonian strata worldwide. Graptolites are found most commonly in dark colored shales, to a lesser extent in limestones, and rarely in sandstones. Their skeletal material , periderm, is often very well preserved in three dimensions in limestones. In shales , the periderm is almost always flattened. Sometimes it is still well preserved, but often it is reduced to a carbon film.

The skeleton of the graptolite colony or rhabdosome consists of thecae, which were the living chambers of the zooids. The rhabdosome starts as an initial shell or sicula that housed the founding zooid of the colony. The rhabdosome grows by the distal addition (asexual budding) of thecae arranged in single or double rows forming a variable number of branches or stipes. Each theca consists of two parts, the proximal protheca, and the distal metatheca (Figure 5) (Bulman, 1970). The opening or aperture of theca

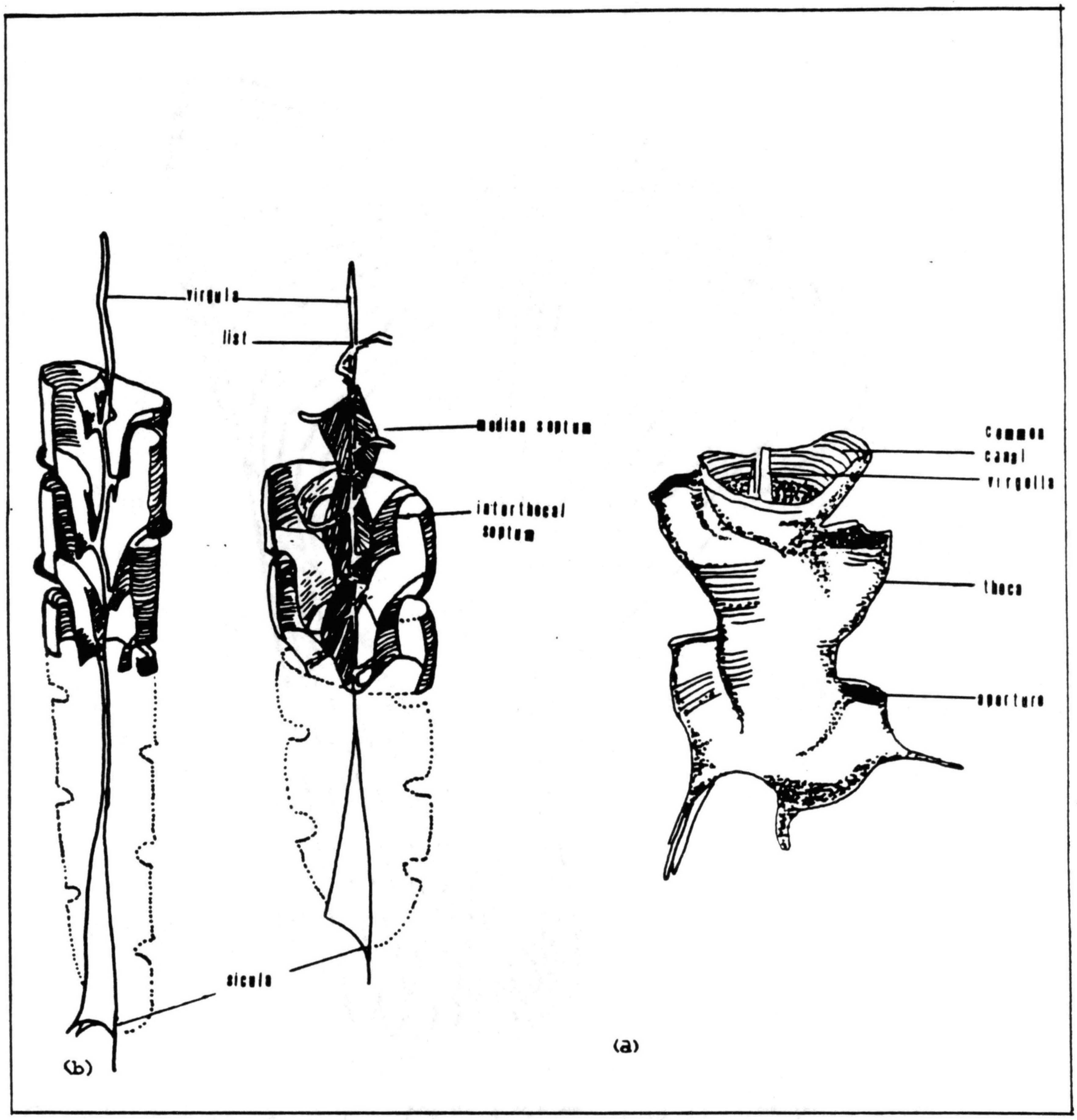


Figure 5. (a) Simplified morphology of graptolite (after, Jackson et al., 1973); (b) cross section across a rhabdosome showing the internal structure, the box represents the area shown in Figure 6.

is located on the distal end of the metatheca. Two types of septa (walls) are present within the graptolite rhabdosome: the interthececal septum, which is both the dorsal wall of one theca and the ventral wall of the succeeding theca, and the median septum, which is composed of segments of dorsal walls of succeeding protheca in biserial graptolites. These major internal and external morphological features are visible in many of the samples prepared for reflectance measurements (Figure 6).

The graptolite periderm is composed of two layers, a thicker inner fusellar layer, and a thinner outer cortical layer (Bulman, 1970) (Figure 7). Both are readily recognizable under reflected light.

Structure And Composition Of The Periderm.

The structure and composition of the graptolite periderm have been extensively studied by the use of electron microscopy (Towe and Urbanek, 1972; Urbanek and Towe, 1974, 1975; Crowther and Rickard 1977; and Crowther 1981). Under the transmission electron microscope the cortical and the fusellar tissues appear as highly organized and differentiated structures (Urbanek and Towe, 1974, 1975). The cortical and fusellar tissues differ in their mode of origin, growth and fabric.

The fusellar tissue is the primary component and forms the thick inner layer of the periderm. The fusellar layer is composed of tissue in semicircular half-rings, and

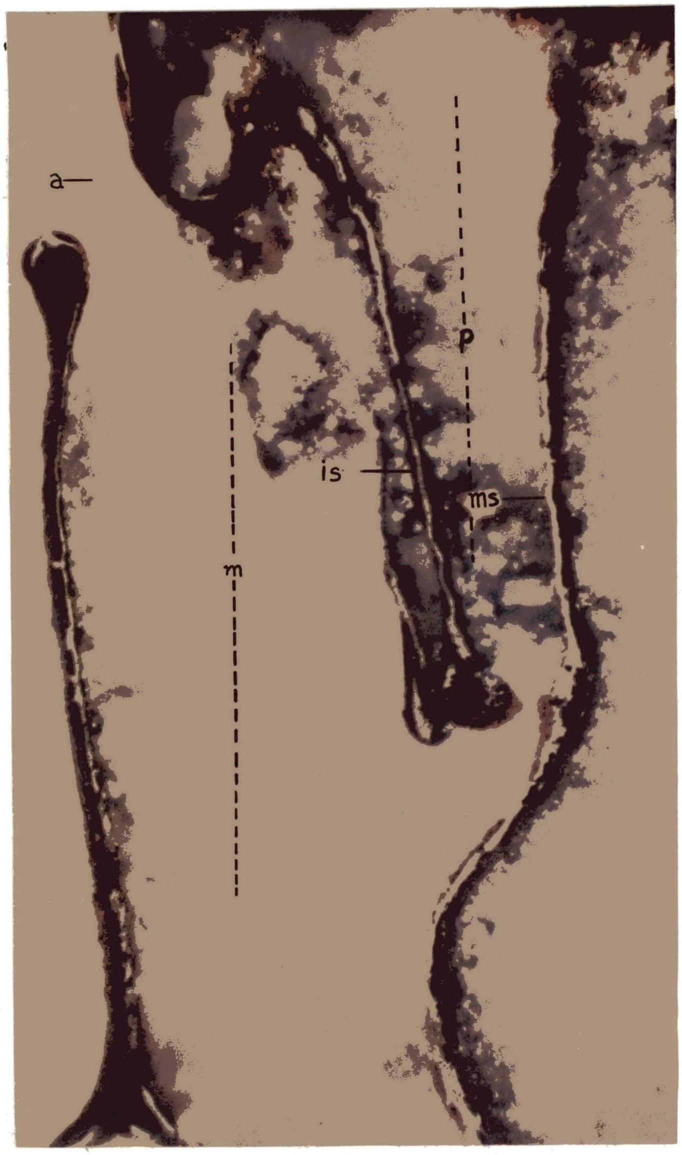


Figure 6. Internal structure of a graptolite rhabdosome, as seen under reflected light (100x oil). a= aperture, is= interthecal septum, ms= median septum, p= protheca, m= metatheca.

succeeding half-rings overlap one another (Crowther, 1981) (Figure 7a). The fabric of the fuselli is built up of loosely packed, anastomosing fibrils without any ground mass. This layer is therefore translucent , porous and spongy. The fusellar layers are usually sandwiched between dense layers (endocortex and ectocortex) of the periderm.

The cortical layer is the secondarily secreted layer covering the primary fusellar layer. It is deposited longitudinally over the fusellar layer (Figure 7a). The cortex is composed of several layers of varying orientation. These layers, called bandages, can be straight or sinuous. The tissue composing the cortical bandages is composed of closely packed, parallel unbranched fibrills and is enveloped by bounding sheet fabric (Crowther and Rickard, 1977; Rickard and Dumican, 1984). These delicate layers of the graptolite periderm are easily recognized in polished specimens under reflected light microscopy (Figure 8 and 9). Graptolite periderm is scleroprotiec in nature (Bulman, 1970). The two type of fabrics the cortical and the fusellar fibrils (Towe and Urbanek, 1974,1975) recognized under transmission electron microscope represent the callogen group of fiberous proteins or polysacchrides. Recent microprobe studies on the periderm demonstrate its pure organic nature. Carbon, sulpher, chlorine and sodium are the characteristic elements of the graptolite skeleton (Clausen and Teichmuller, 1982). The presence of sodium and chlorine is attributed to the inclusion of sea water in the

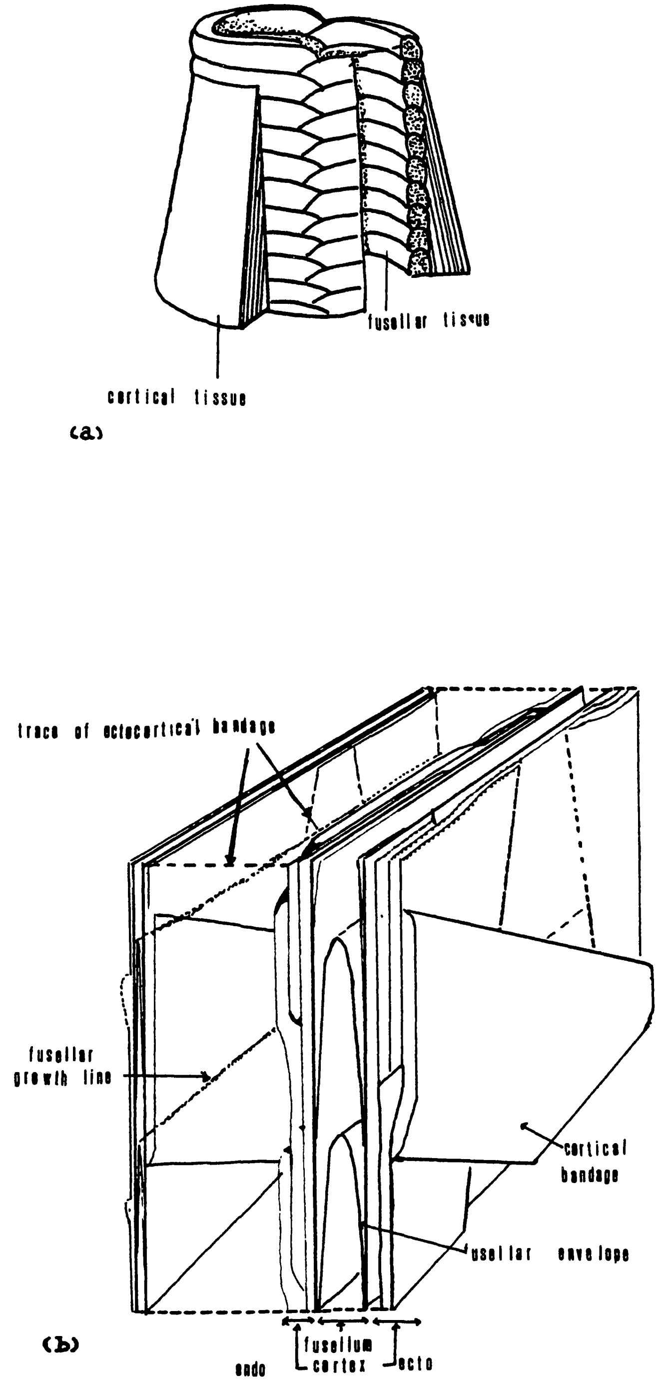


Figure 7. Structure of graptolite periderm; (A) development of cortical and fusellar tissues (after, Bulman, 1970). (B) Simplified block diagram of periderm wall, (after, Crowther, 1981).

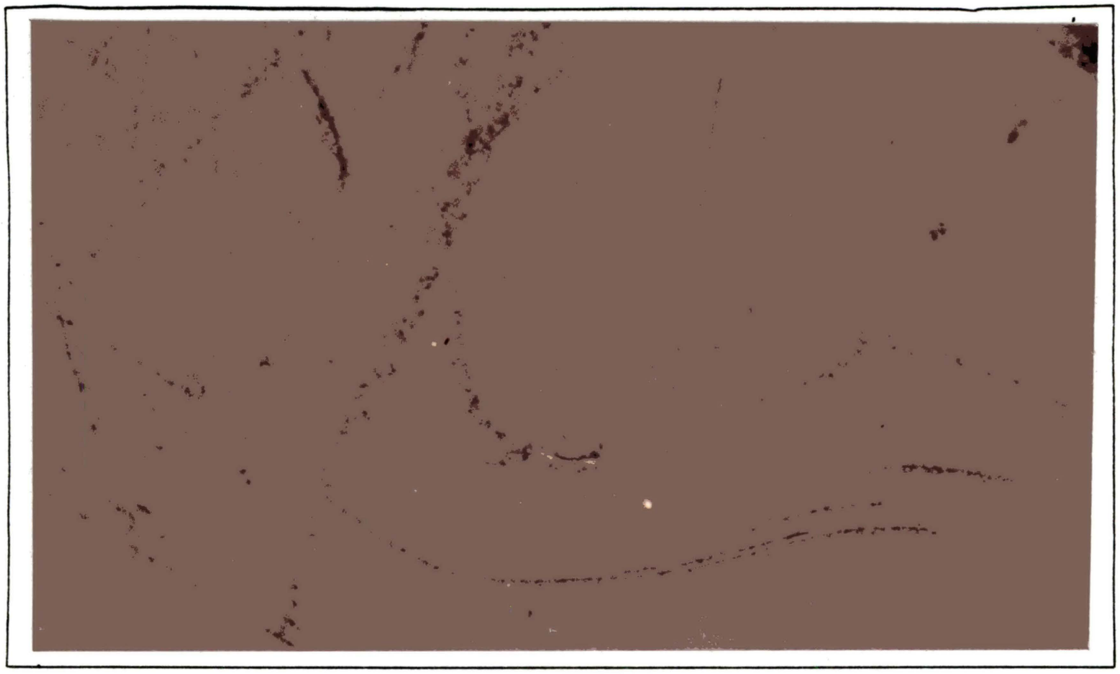


Figure 8. Bright and dark lamellae of the graptolite periderm under reflected light. (200x, oil).

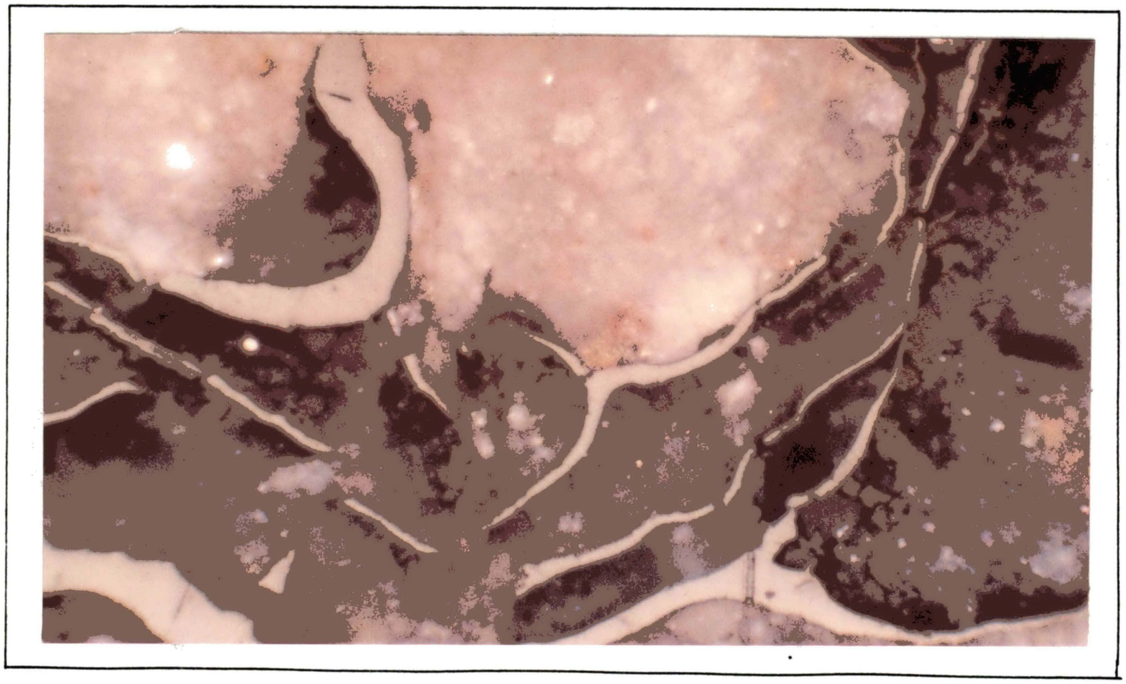


Figure 9. Complex internal structure of the graptolite rhabdosome. Carbonate matrix. (100x, oil).

submicroscopic pores of the periderm after death of the organism and during deposition and burial of the skeleton.

Preservation Of The Periderm

Graptolites exhibit a range of preservation conditions, ranging from three dimensional undistorted specimens in full relief to completely compressed carbonized films. Some degree of flattening is observed in most specimens. With flattening, the periderm is buckled to some degree. Most of the graptolites are very brittle and fragile, and during polishing the periderm often breaks giving it a fragmentary appearance.

In most of the specimens examined it was noted that the cortical wall of the periderm is well preserved. The ultrastructural fabric of the fusellar layer is often not present in graptolite samples due to its delicate nature (Crowther, 1981). Most of the samples examined tend to preserve the fibrillar nature of both cortical and fusellar layers. The internal structure (interthecal and median septa) of the graptolites are often well preserved especially in specimens in full relief (Figure 5).

Specimens preserved in a carbonate matrix exhibit impressions of calcite rhombs on their surface. Calcite also fills in the internal cavities of the rhabdosome. Syngenetic pyrite nodules also commonly fill in the cavities of the rhabdosome. These pyrite nodules are capable of preserving the layering of the cortical fibers, and

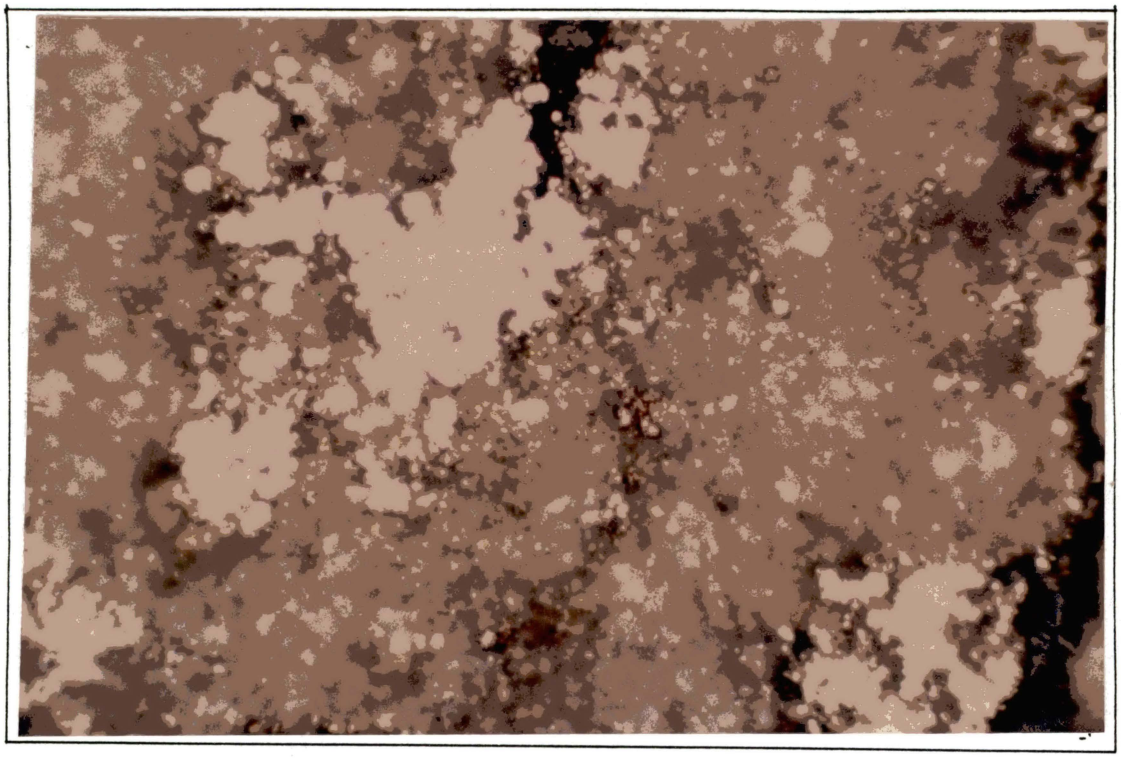


Figure 10. Pyrite nodules in the graptolite rhabdosome. (100x, oil).

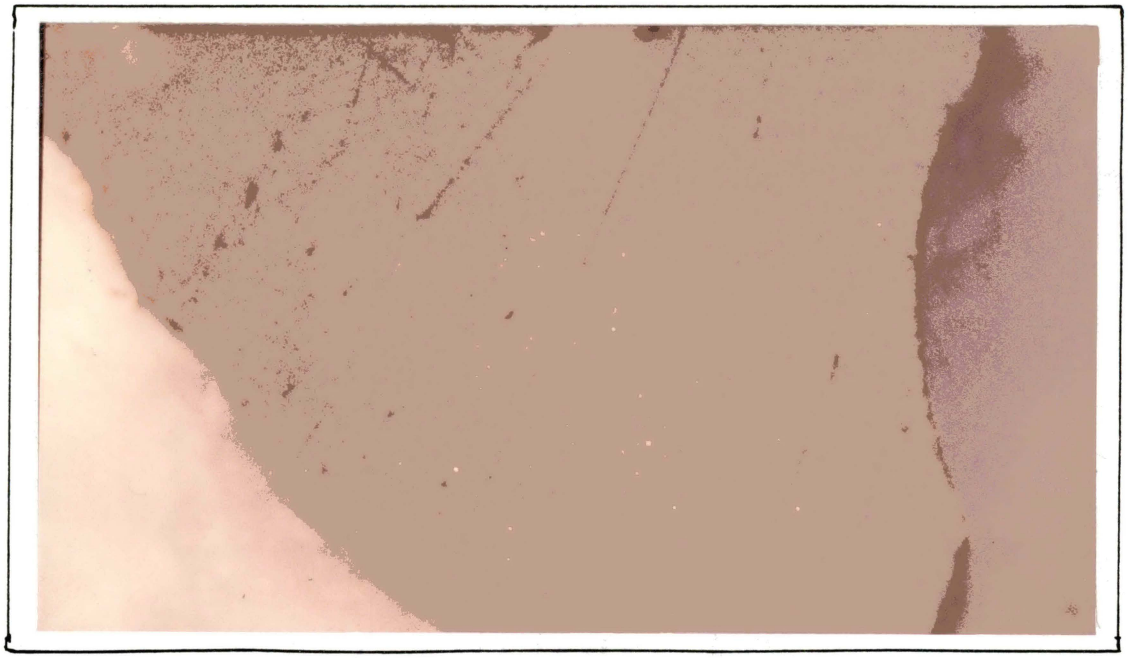


Figure 11. Fine parallel bandings of the periderm (200x, oil).

pyritized specimen are often undistorted (Crowther, 1981). Pyrite can form complete internal molds and can also occur in the form of isolated spheres within the rhabdosome. Pyrite when present increases the reflection of the surrounding periderm; therefore such regions should be avoided when measuring reflectance. Graptolites from the Nicolet River Formation are an excellent example of such pyritization (Figure 10).

Optical Properties Of The Graptolite

The sectioned and polished graptolite specimens examined under the microscope ranged from 10 um to a few centimeters in size. Under reflected light they appear as thin elongated bodies and are easily recognized by the characteristic internal layering of the periderm. They exhibit a color range of medium to light grey, although some specimens are yellowish brown to yellowish grey. Goodarzi and Norford (1985) reported a color range of N6-N8 on the Munsill color chart for specimens preserved in a carbonate matrix and a range of N5-N9 for specimens in shales. Most graptolites, under cross or plane polarized reflected light, exhibit anisotropy with bireflectance values ranging from .036 to 5.66%, (Kurylowicz, 1976; Goodarzi and Norford, 1985; this study).

Under reflected light, polished graptolite fragments differ from other dispersed sedimentary organic matter by:

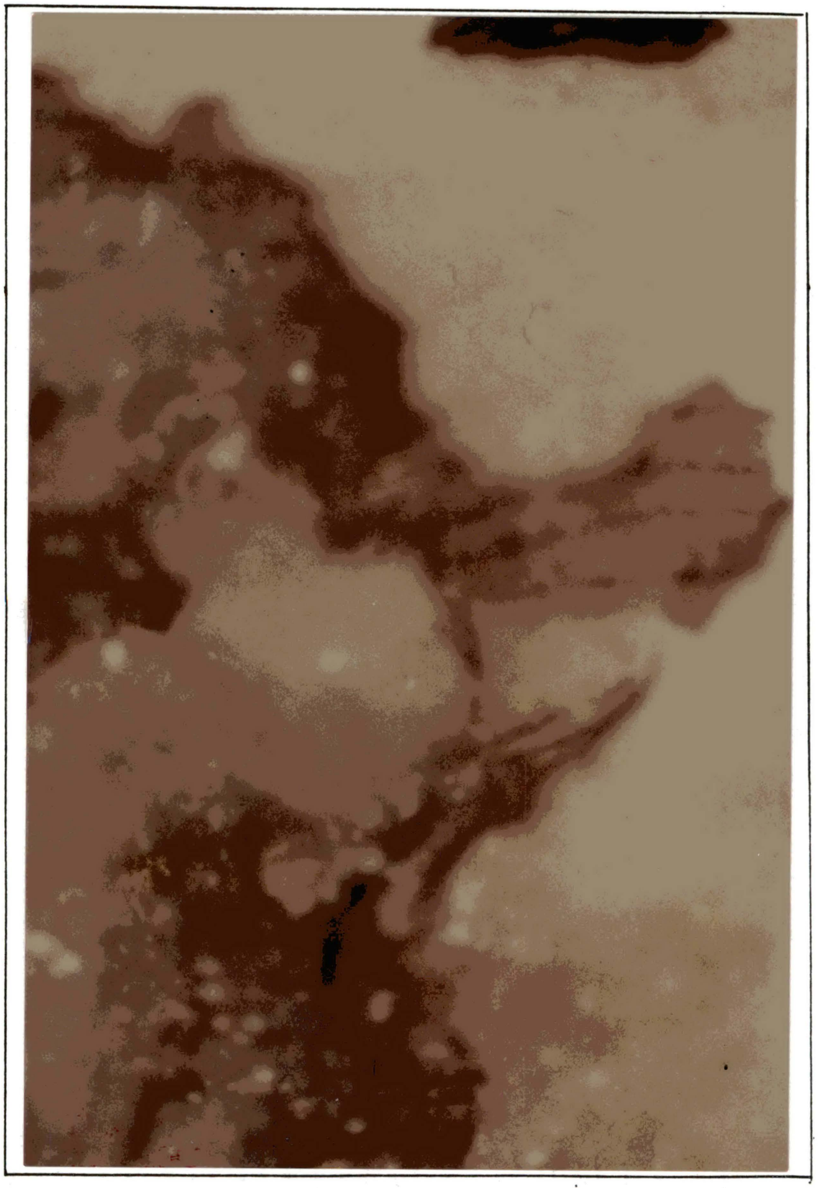


Figure 12. Bandings of the fusellar tissue, exhibiting growth pattern of a graptolite rhabdosome, (100x, oil).

1) its thin elongated shape,

2) its lobate morphological structure,

3) its characterstic fine internal layering,

4) its sharp boundries with the enclosing rock matrix,

5) its granular and nongranular texture.

These features allow graptolite fragments to be readily distinguished from other sedimentary organic matter, such as vitrinite or bitumen.

Graptolite fragments often possess lobate shapes, which represent the curved walls of the rhabdosome. These fragments have sharp boundaries with the enclosing rock matrix.

Graptolite fragments high magnification show characteristic, fine parallel banding (Figure 11 and 12). Two types of lamellar bands are usually observed, a thick brighter lamellae and thin darker lamellae, and they are arranged parallel to each other. The weaker reflecting lamellae are 1-2 um wide and the thick darker lamellae are 2-4 um wide. The brighter lamellae exhibit distinct pleochroism. They are generally wider in curved zones of the periderm; this is observed in particular in the samples where the spine is readily visible (Figure 13).

The texture of the graptolite periderm also differs depending on the enclosing rock matrix. Goodarzi and Norford (1985) reported two type of textures, non-granular and granular, which were also observed in the present study. Graptolites preserved in shale matrix have a nongranular smooth texture (Figure 14). Those preserved in a carbonate matrix have a granular texture (Figure 15). Graptolites with a granular texture are soft and weakly reflecting; those with a non-granular texture are brittle and highly reflective . The reflectance of graptolite fragments is optically similar to pyrobitumen. However both granular and nongranular fragments exhibit defined morphology, whereas pyrobitumin is devoid of any surface morphology (Goodarzi, 1984)

Figure 13a. Broadening of the fine bandings. Graptolite fragment showing the broadening of the fine bandings at curved zones of periderm in carbonate matrix, (200x, Oil).

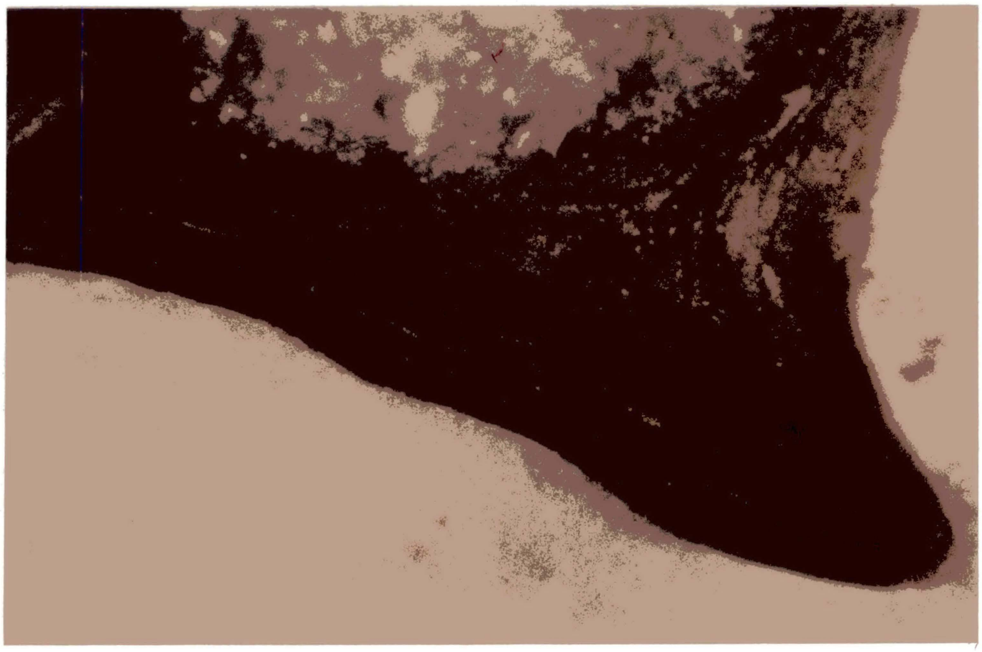


Figure 13b. Same as Figure 13a. for a shaly matrix.

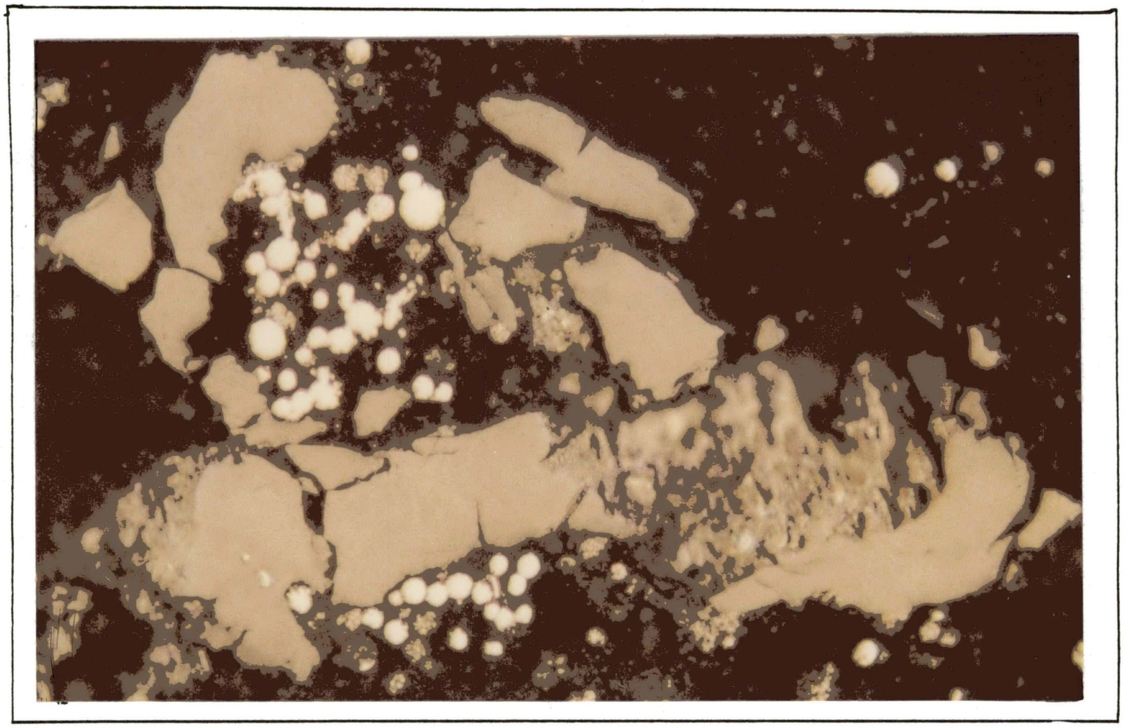


Figure 14. Smooth and non-granular texture of graptolite fragments from a shale matrix (100x, oil)

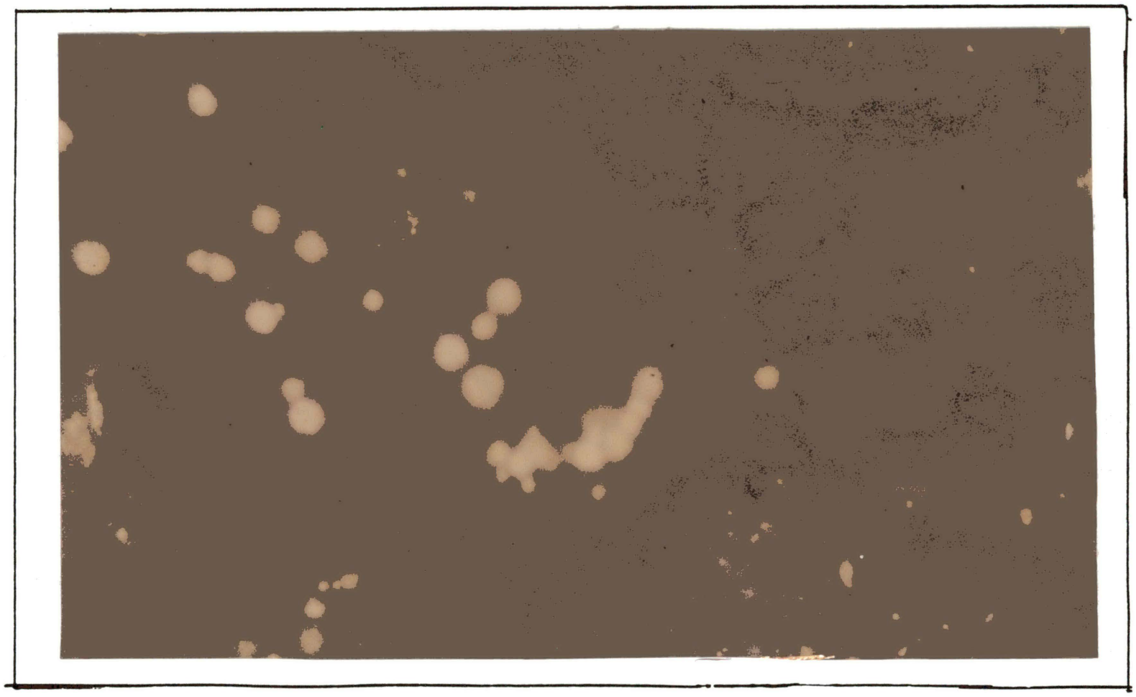


Figure 15. Granular texture of the periderm, exhibitted by graptolite fragments from carbonate matrix. (100x, oil).

CHAPTER V

RESULTS AND INTERPRETATIONS

Results Of The Study

The data gathered for the 25 samples (A-Y) used in this present study are shown in Figure 16 and Table 4. The 20-60 maximum reflectance measurements (Ro max.) taken on each sample are presented in the form of histograms (Figure 16), and the mean values for each sample were calculated (Table 4). Mean values for minimum reflectance (Ro min.) and values of bireflectance were also calculated.

The graptolite samples show a definite, marked increase in minimum and maximum reflectivity with increasing C.A.I. values. Mean maximum reflectance of the 25 samples ranges from 0.199 to 8.56 %. The C.A.I. values for these samples range from 1 to 5 and represent a paleotemperature range of <50° C to >300° C.

The reflectance histogram (Figure 16), constructed for each sample approximates a Gaussian curve, thus showing a normal distribution of reflectance values. The histograms tend to broaden at higher reflectance values. Except for a few samples, most samples show a unimodal distribution of maximum reflectance (Figure 16). Samples with a maximum reflectance of less than 1% have a narrower distribution range of reflectance. The histograms broaden considerably

TABLE IV.

OPTICAL PROPERTIES OF GRAPTOLITES

S.I NO.	C.A.I.	REFLECTANCE (OIL)		BIREF	LITHOLOGY	TEXTURE
		MINIMUM	MAXIMUM			
A*	1	0.163	0.199	0.036	LMST	G
B	1	0.320	0.362	0.042	LMST	G
C	1	0.856	0.915	0.059	LMST	G
D	1	0.386	0.449	0.063	LMST	G
E	1	0.651	0.694	0.043	LMST	G
F*	1	0.427	0.523	0.096	LMST	G
G	1	1.44	1.80	0.36	LMST	G
H	1	0.383	0.428	0.04	LMST	G
I	1	0.331	0.391	0.06	LMST	G
J*	1.5	0.460	0.567	0.107	SHALE	NG
K	1.5	0.836	0.930	0.094	SHALE	SG
L	1.5	0.682	0.689	0.061	SHALE	G
M	1.5	0.657	0.812	0.155	LMST	G
N	2	0.988	1.75	0.672	LMST	G
O	2	0.654	0.693	0.039	SHALE	NG
P	2.5	1.03	1.53	0.50	LMST	NG
Q	2.5	1.016	1.340	0.324	LMST	NG
R	3	1.39	1.47	0.09	SHALE	SG
S	3.5	1.104	1.866	0.762	SHALE	NG
T	4	3.04	3.49	0.45	SHALE	NG
U	4	1.233	1.442	0.209	LMST	SG
V	4	1.26	1.31	.05	SHALE	NG
W	5	6.99	8.56	1.56	SHALE	NG
X	5	3.81	5.08	1.27	SHALE	NG
Y	5	4.15	5.80	1.65	SHALE	NG

* R max. calculated from random reflectance values using Ting's (1975) equation R max = 1.066 Re, where Re is random reflectance. G = granular, NG = nongranular, SG = slightly granular

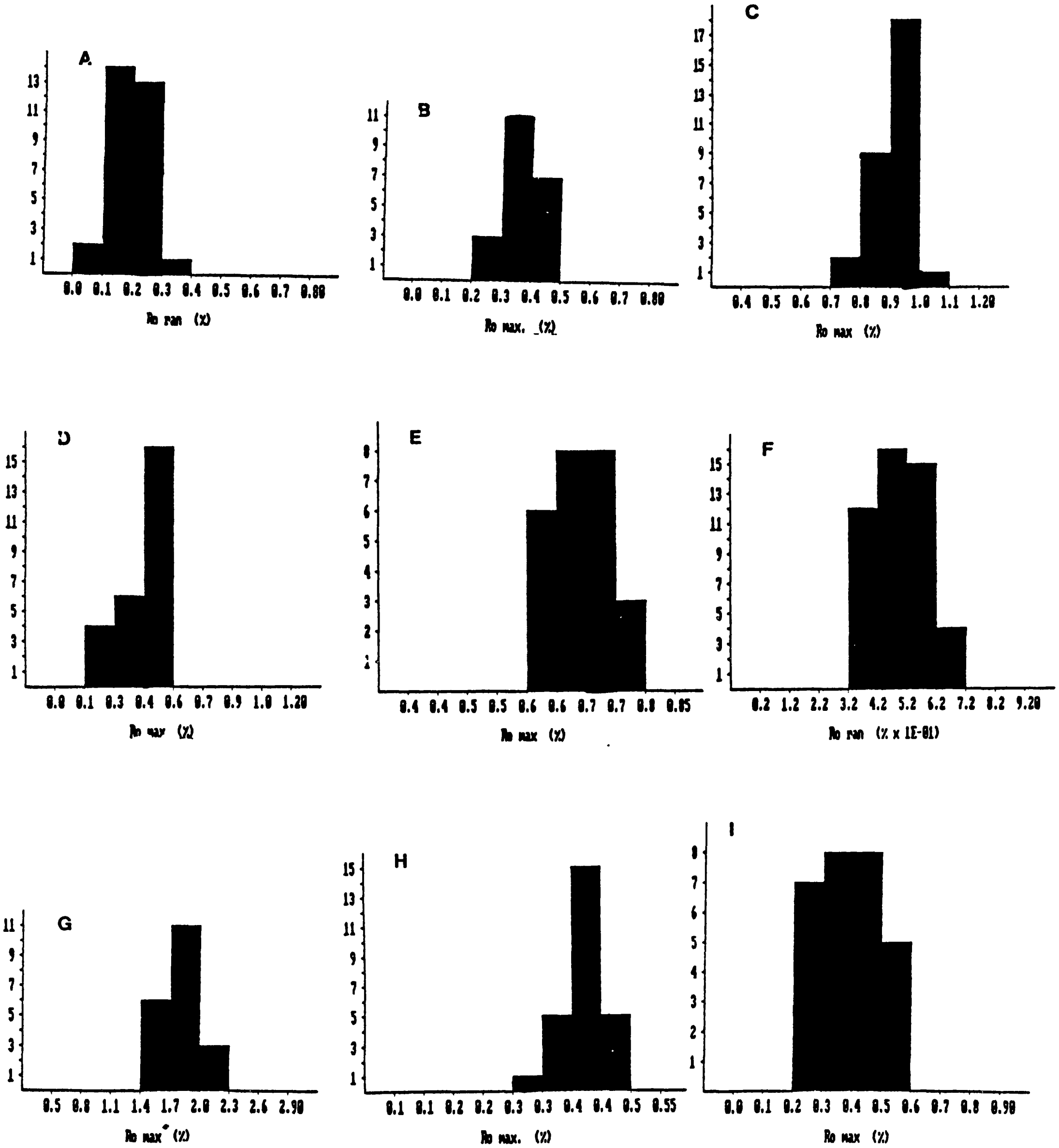


Figure 16. Histograms showing distribution of maximum reflectance for graptolites. (sample no. same as in Table IV).

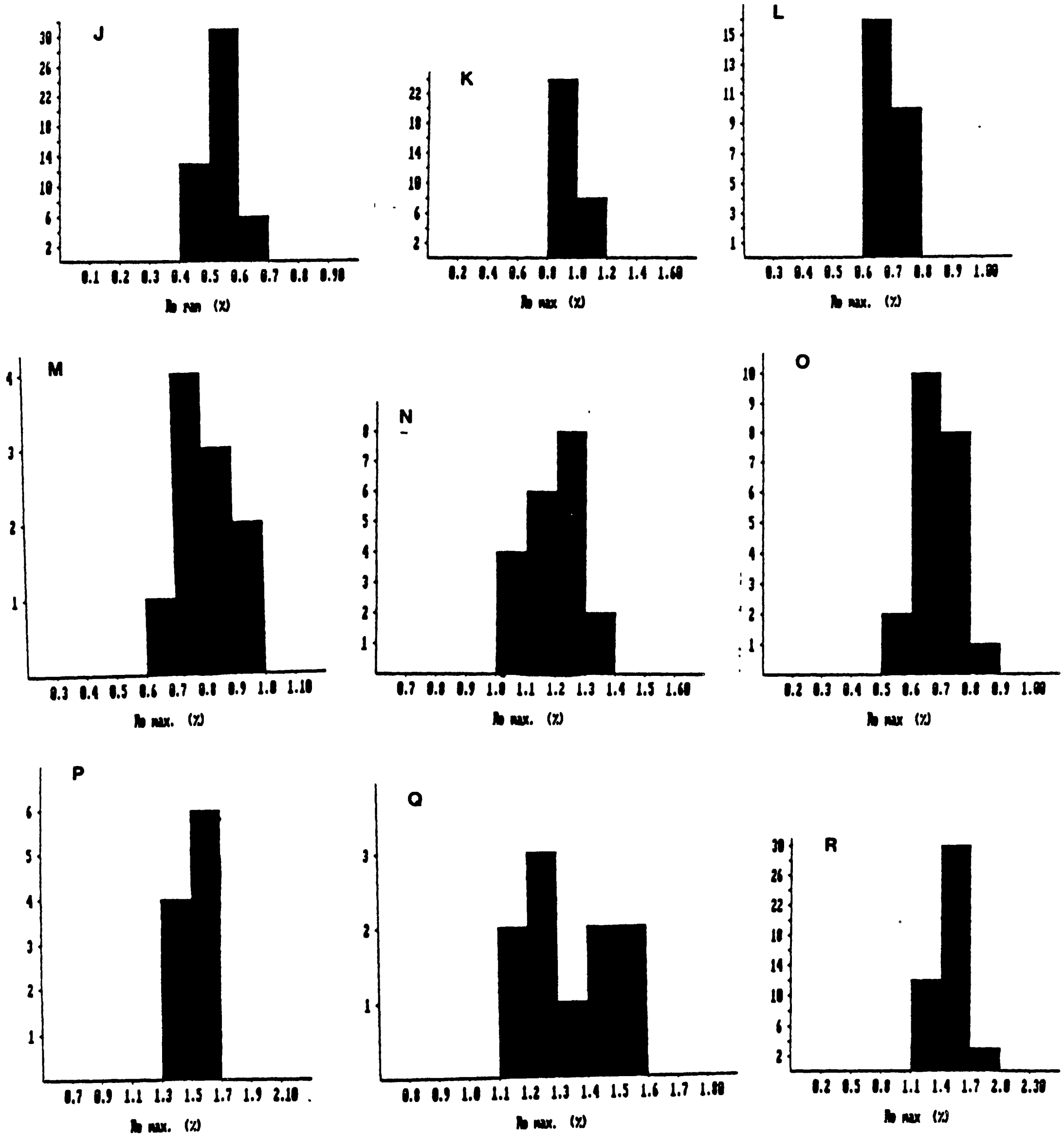


Figure 16. (continued)

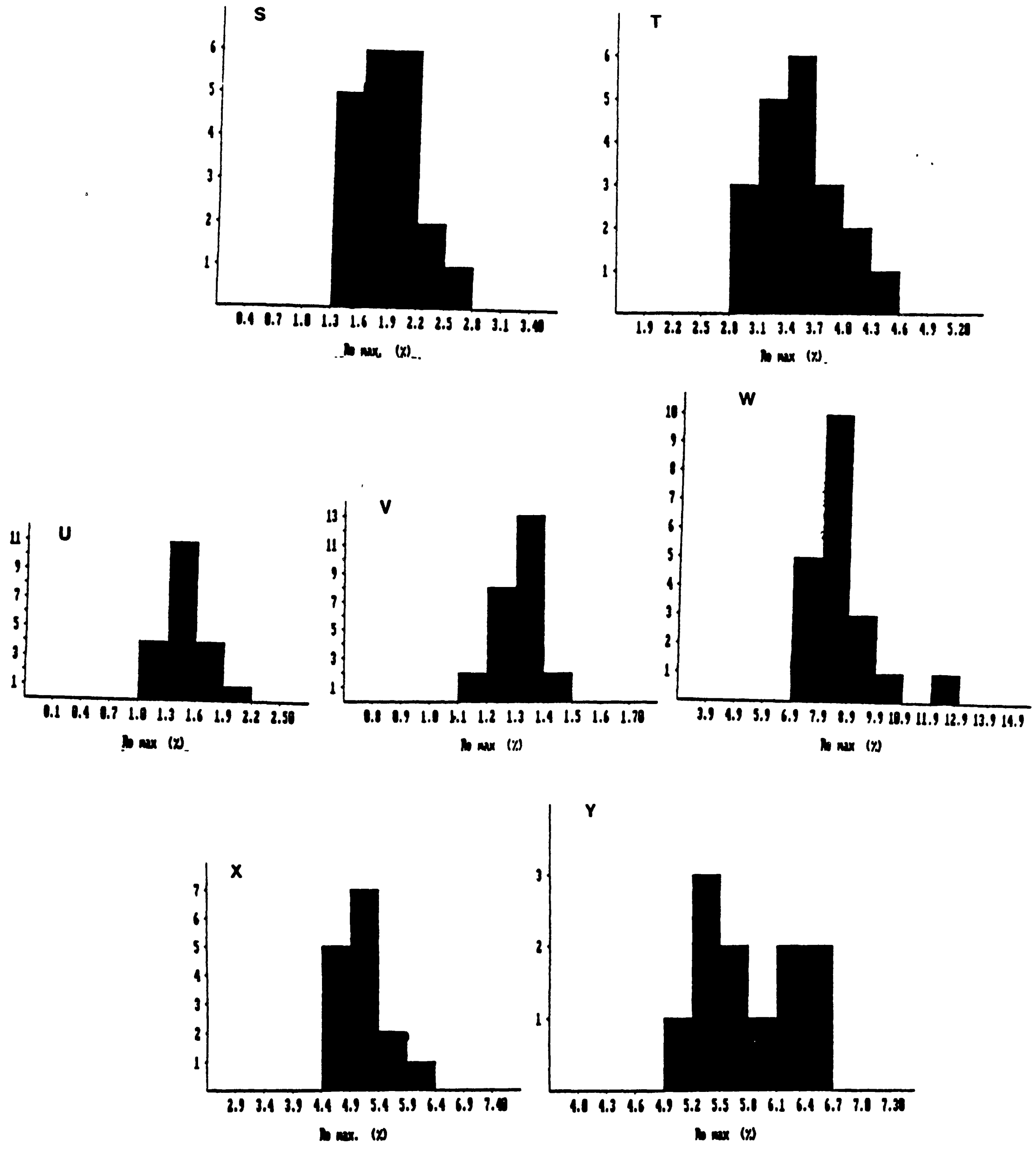


Figure 16. (continued)

for reflectance values above 2 %. Samples Q, W and Y show a bimodal distribution with a clearly defined mean. These samples have conodont alteration indicies of 2.5, 4 and 5 respectively.

Mean maximum and minimum reflectance value were plotted against conodont alteration index (Figure 17 and 18). An increase in reflectivity of graptolites is observed with increasing conodont alteration index, and thus with increasing paleotemperatures. Reflectance values gradually increase from conodont alteration index 1 to 3. The maximum and minimum oil reflectance of graptolites suddenly increase at a conodont alteration index of 4 (Figures 17 and 18). Maximum reflectance of 1.31 to 3.49% was observed for a conodont alteration index of 4. The reflectance jumps from 5.08 to 8.56% for a conodont alteration index of 5. This sudden increase in reflectance also holds true for minimum reflectance and bireflectance (Figures 18 and 19). Relative to other samples, sample A and G have unusually low and high Ro max. values for the conodont alteration index of 1. The low value of sample A (Ro max. = .199.%) is due to the poor polishing character of the sample. The unusually high value for sample G (Ro max. = 1.80%) is due to this sample being mineralized to a large extent. Pyrite nodules are present throughout the specimen.

The graptolite specimens exhibit bireflectance under cross polarized light and thus are anisotropic (Table 4). Although bireflectance values are widely scattered in the

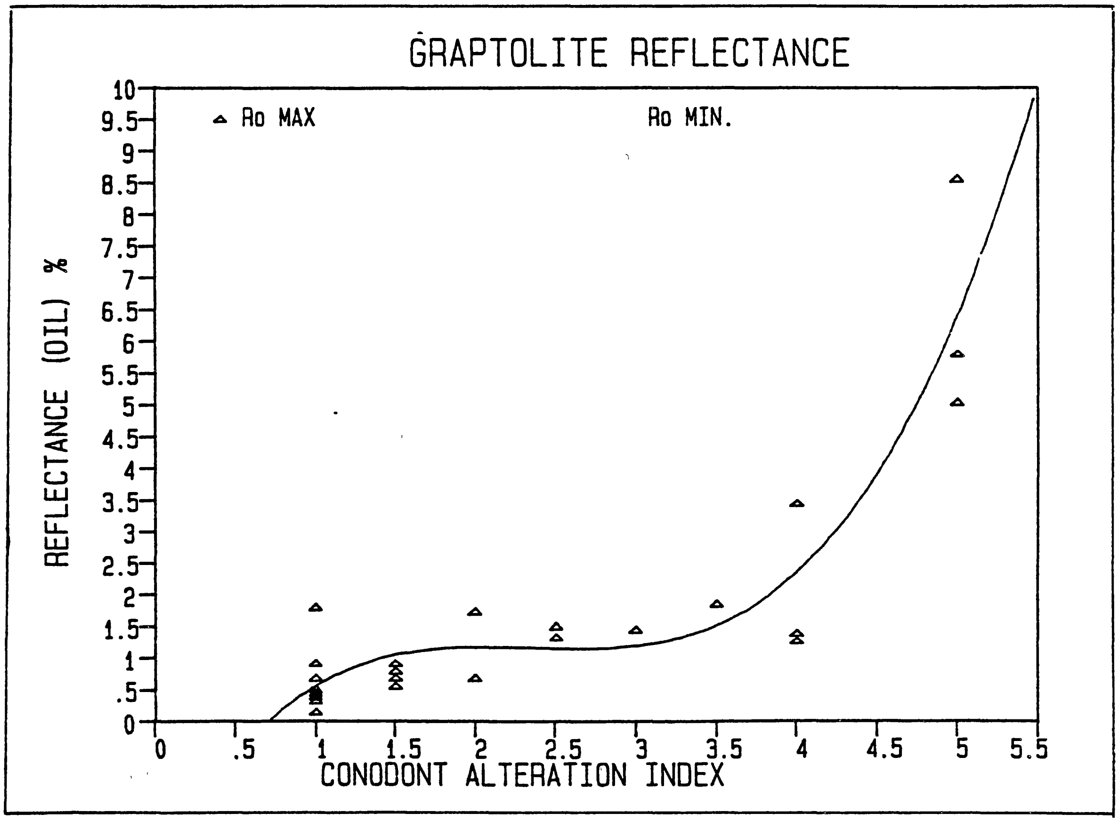


Figure 17. Maximum reflectance of graptolites plotted against CAI.

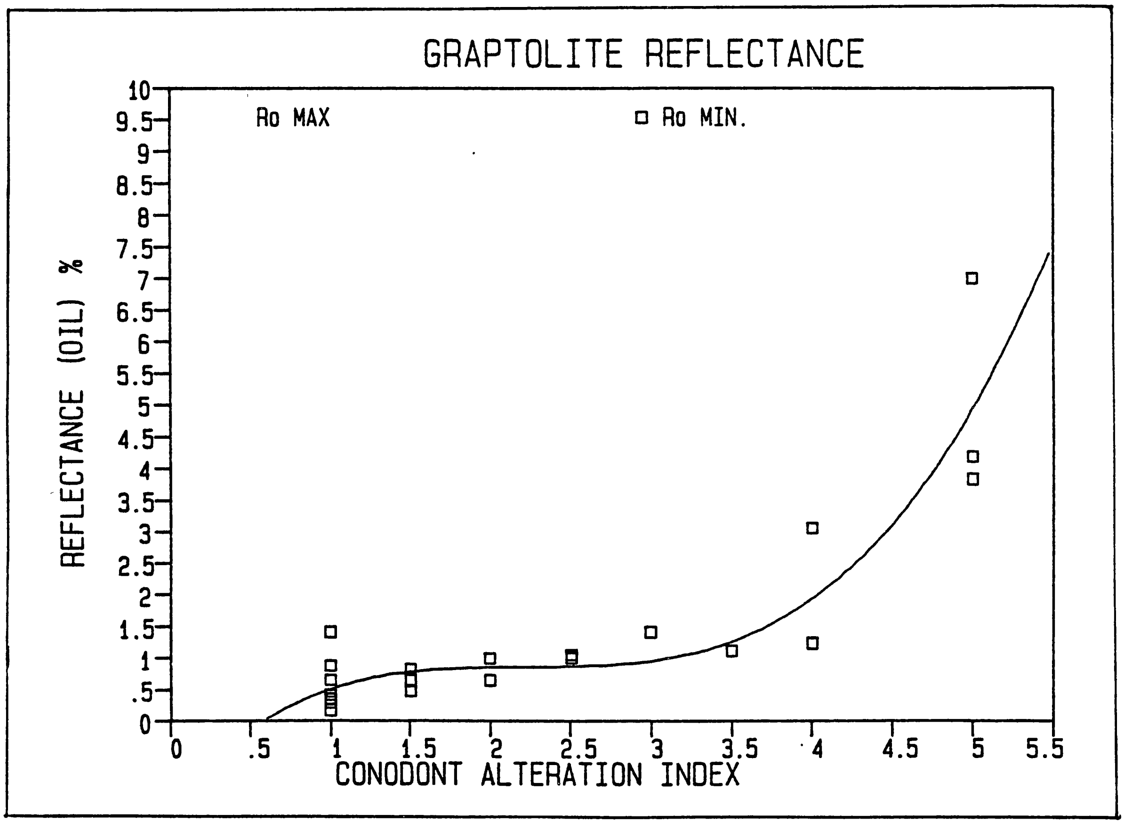


Figure 18. Plot of minimum reflectance ofgraptolites plotted against CAI.

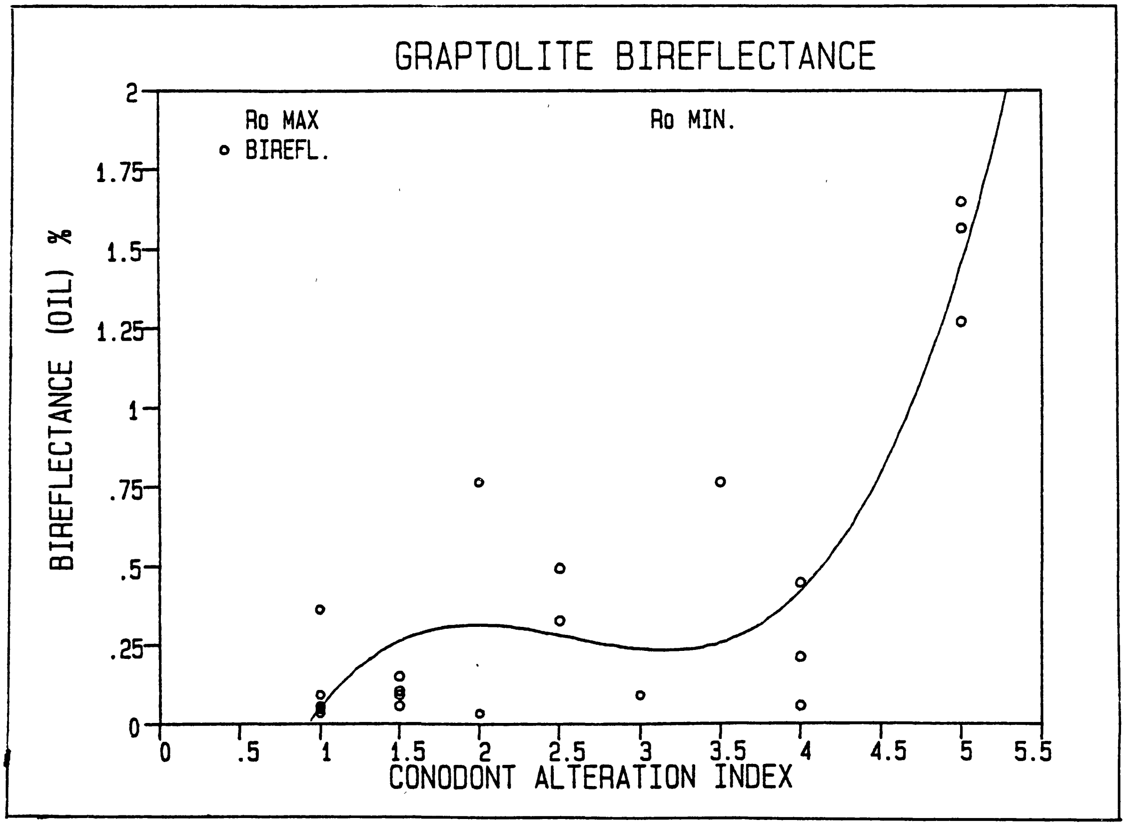


Figure 19. Bireflectance of graptolites plotted against CAI.

C.A.I. range of 2-3.5, bireflectance generally increases with increasing conodont alteration indicies (Figure 19).

Graptolite reflectance varies with lithology (Figure 20). Most specimens preserved in limestone matrix have a lower reflectance values than those preserved in shale for the same conodont alteration index. Reflectivity is also dependent on the orientation of the specimen. Samples parallel to the bedding surface of the rock matrix have higher maximum and minimum reflectance values than those oriented perpendicular (Figure 21).

Interpretation of the Results

Optical properties of graptolites obtained during this study are plotted against the corresponding conodont alteration indicies and thus with paleotemperatures (figs.17-19). A major problem encountered during plotting was that samples with the same C.A.I. can have maximum reflectance values showing a difference of as much as 2%. This is probably due to the fact that a single C.A.I. value can represent a temperature range of 80o C. The variation of reflectance values for samples with the same C.A.I reflect the fact that these samples represent paleotemperatures that differ by as much as 80o C, a condition that conodont-color alteration cannot detect.

The graptolite specimens examined in this study show an increase in reflectance with increasing C.A.I. values and thus with increasing paleotemperatures (Table 4).

Graptolites reflectance slowly and gradually increases up to a conodont alteration index of 3. Samples with a C.A.I. of 1-3 exhibit reflectance values in range of 0.36 - 1.80% Ro max. and represent a paleotemperature range of <50° C to about 200° C. Above a C.A.I. of 3 the reflectance suddenly increases, and for C.A.I of 4 the reflectance values range from 1.31-3.94 %. The scatter of reflectance increases at higher conodont alteration indicies (Figure 16). This increase in reflectance and scatter with increasing rank is also noted in vitrinite (Teichmuller and Teichmuller, 1984a, Hunt, 1979; Koch, 1970). The increase in graptolite reflectance can be attributed to the irreversible changes in the molecular structure of the periderm. The chemical reactions in which the rate increases exponentially with temperature are responsible for changes in the molecular structure. Consequently, reflectance, which measures these maturation changes, increases exponentially with a linear increase in temperature (Hunt, 1979).

The graptolite periderm is anisotropic and exhibits bireflectance. The development of bireflectance in graptolites starts at a lower maximum reflectance than that of vitrinite (Goodarzi and Norford, 1985). Graptolites show an increase in bireflectance with increasing conodont alteration index. The scatter of bireflectance also increases with higher reflectance values. A similar pattern of increased scatter of bireflectance is observed in vitrinite from the meta-anthracite to the graphite stage of

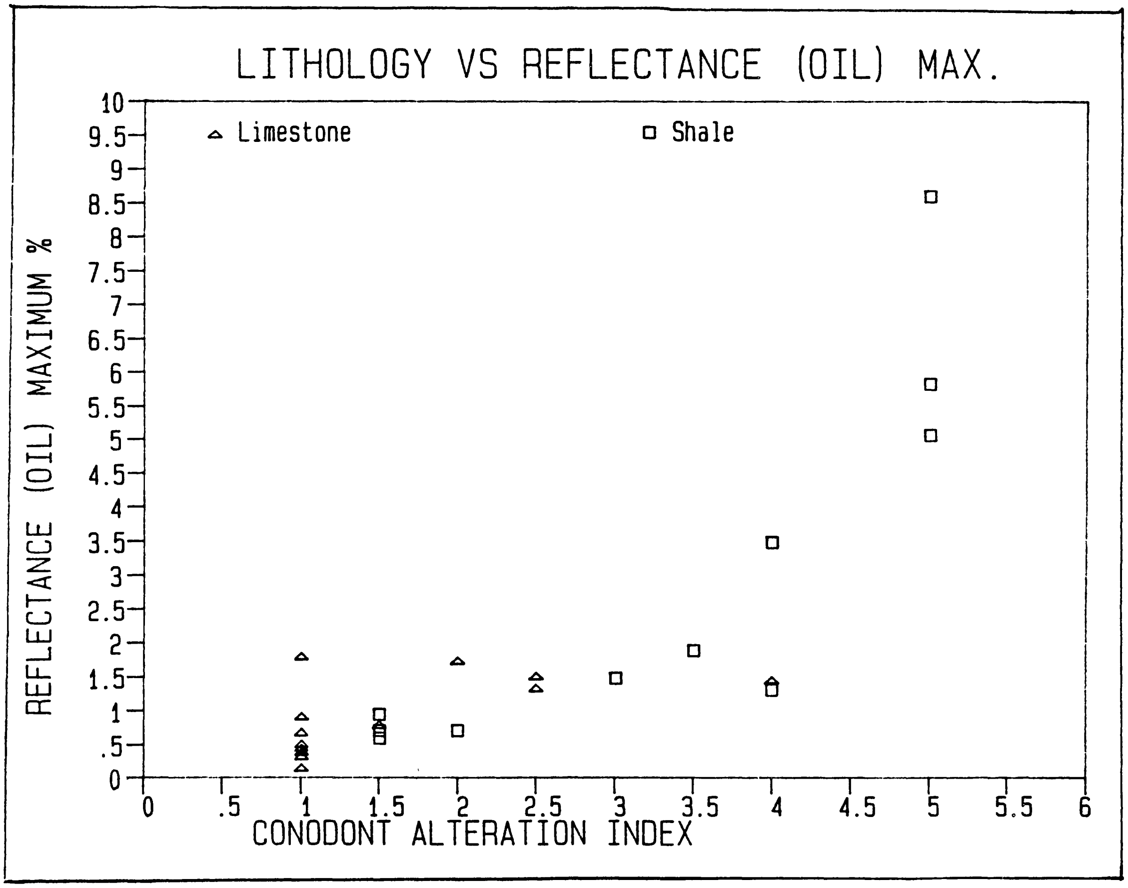


Figure 20. Difference in reflectance of graptolite with lithology of the sample.

coalification (Teichmuller and Teichmuller, 1984a). Graptolites show a linear increase in minimum reflectance with increasing maximum reflectance (Figure 22).In contrast,the minimum reflectance of vitrinite decreases after Ro max. has reached 6% (Figure 23).

The coalification trend of graptolites was determined by plotting Ro max. against Ro min. (Figure 23). With such a plot, changes in the optical properties of graptolites from this study and those studied by Goodarzi (1984) and Goodarzi and Norford (1985) can be compared to those of coal, heat-effected coal and bitumin across the coalification range of lignite to graphite. Graptolites show a coalification range of bituminous to semi-anthracite coals. Graptolite specimens in a carbonate matrix fall in the bituminous to semi-anthracite range of coalification. The reflectance of these samples is similar to that of coals. Specimens preserved in a shale matrix exhibit a coalification range of anthracite to meta-anthracite and correspond closely to the curve for bitumen.

Graptolite reflectance is dependent upon lithology (Figure 20). Specimens preserved in a carbonate matrix have a lower reflectance trend than those preserved in shale. A similar trend is followed by vitrinite (Jones et al., 1972). This difference is attributed to the different thermal conductivities of limestone and shales. Shale exhibits a lower thermal conductivity than limestone and thus may be influenced by the same temperatures to a greater

S. NO.		LITHOL	R max %	R min %	BIREF
K	Perpendicular	SHALE	0·86	0·81	.05
	Parallel		0·93	0 83	.09
F	Perpendicular	LIMESTONE	0·503	0·411	.091
	Parallel		0·523	0 427	.096

Figure 21. Difference in reflectance of graptolite fragments depending on the orientation of the sample.

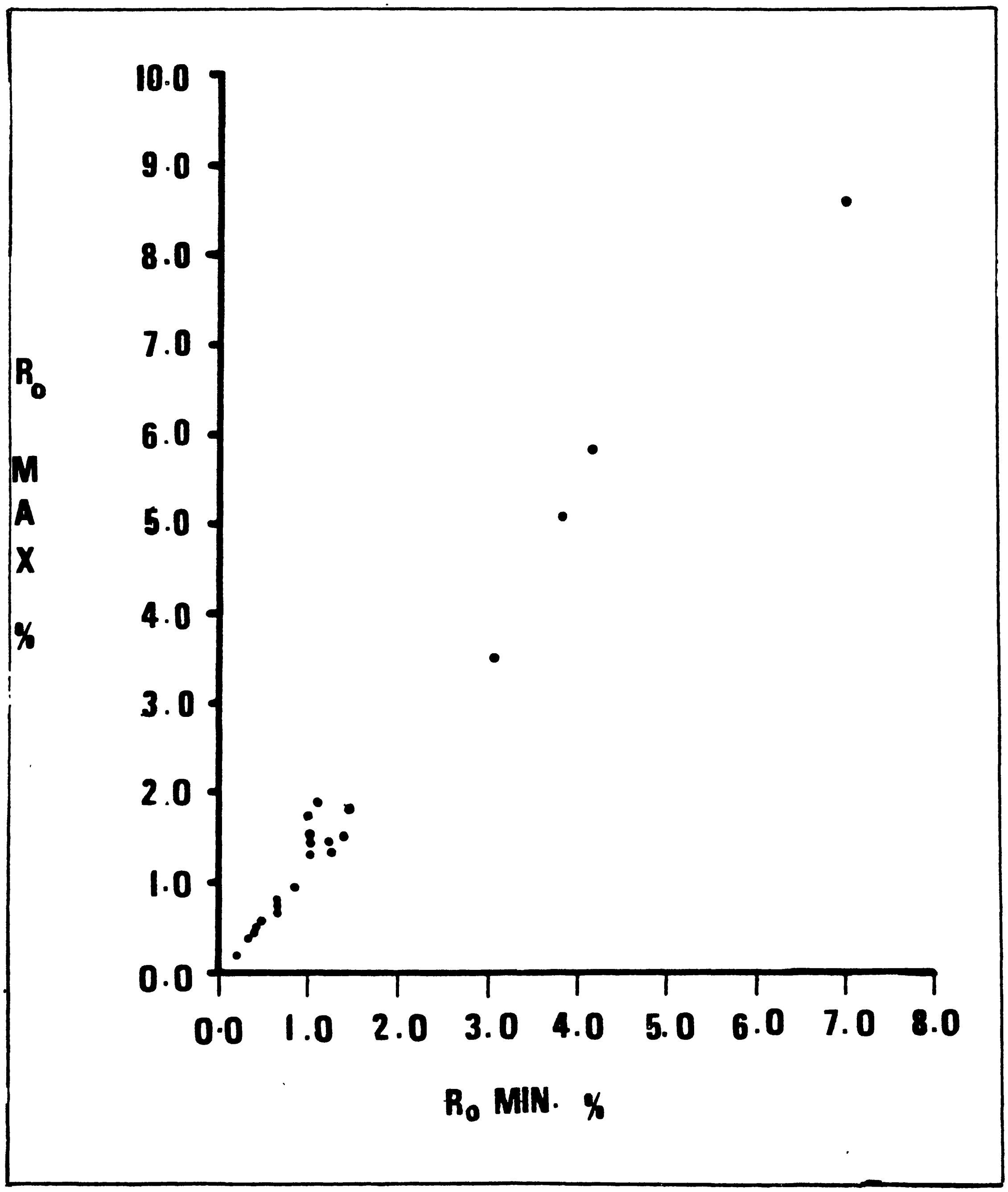


Figure 22. Relation of mimimum reflectance to maximum relectance of the graptolites.

degree (Bostick and Foster, 1975; Jones et al., 1972; Stach, 1982).

An attempt was made to correlate values of graptolite reflectance from this study and that from Goodarzi and Norford (1985) with vitrinite reflectance and paleotemperature (Table 5). This was done by means of C.A.I. values obtained in this study and that of Goodarzi and Norford (1985) and was made possible by the fact that C.A.I. values were calibrated against vitrinite reflectance and paleotemperatures by Epstein et al. (1977). Graptolite reflectance values tend to be higher than those for vitrinite for the same paleotemperatures. The reflectance values do overlap somewhat, but this is probably due to the wide temperature range represented by each conodont alteration index.

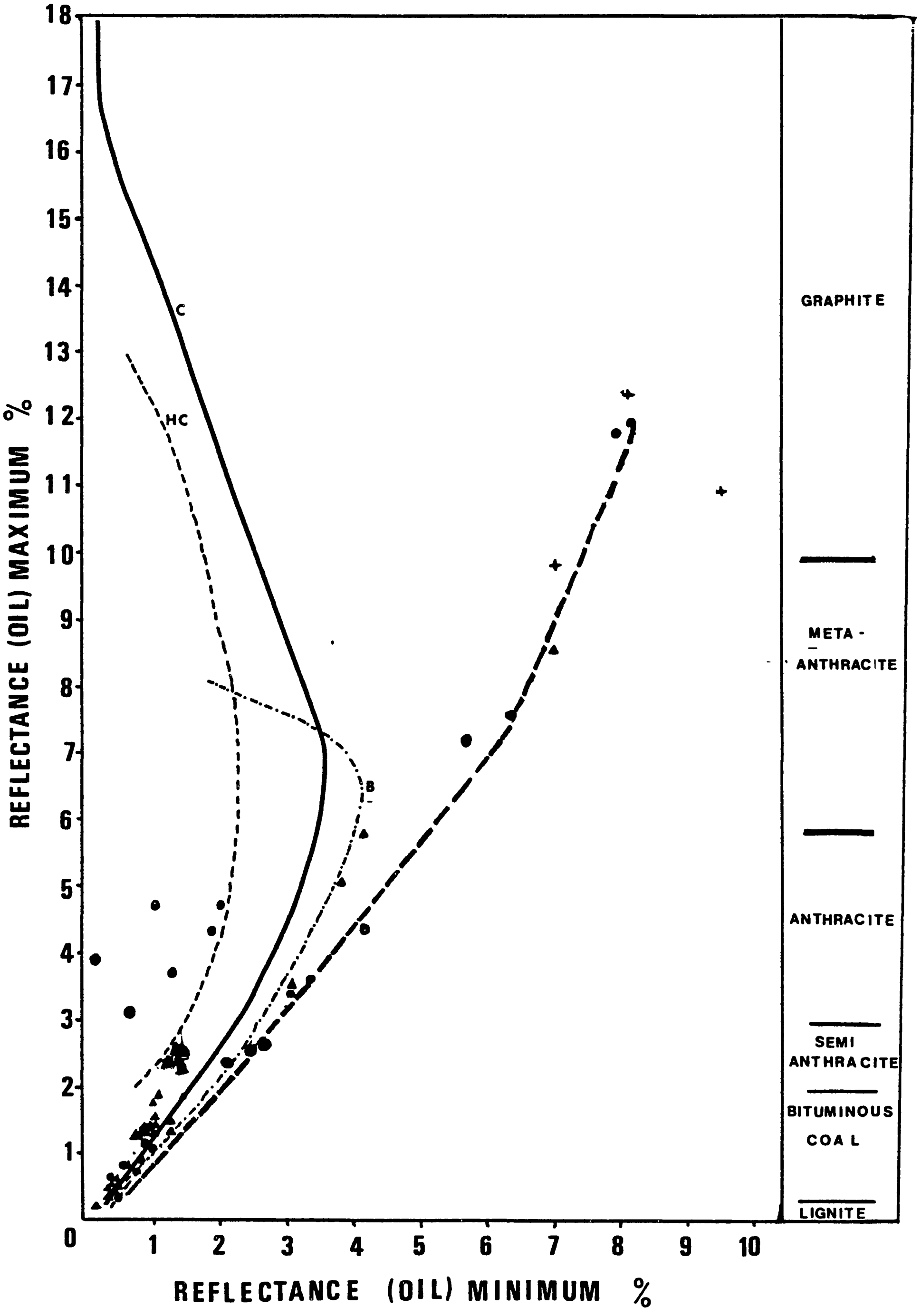


Figure 23. Coalification trend of the graptolites. Anisotropy of graptolites from this study and previous studies compared to vitrinite from coal(C), heated coal (HC), and bitumen (B). Goodarzi and Norford (1985) and Goodarzi (1984)(•), Clausen and Teichmuller (1982)(+), Kurylowicz et al. (1976)(⟵), this study (▲). (Modified after Goodarzi and Norford, 1985).

CHAPTER VI

DISCUSSIONS

The graptolite specimens examined in this study show an increase in reflectance with increasing C.A.I. values and thus with paleotemperature. All of the samples with high C.A.I. values were collected from surface exposures. The rocks at these exposures were heated to high temperatures by burial or tectonic activity. When later exposed at the surface by erosion, they cooled to low temperatures and have remained at a low temperature for many 10's to 100's of million years. The fact that graptolite reflectance values are still high and represent high paleotemperature indicate that the heat induced reflectance is irreversible. This conclusion is strongly supported by the facts that conodont alteration is irreversible and that the graptolite reflectance and C.A.I. values in this study are very consistent. Thus the reflectivity of the graptolites can provide a consistent and reliable indicator of paleotemperatures and organic maturation.

Graptolite fragments are easily distinguished in the rock matrix and polished pellets because of their characteristic internal texture and external morphology. Under cross polarized reflected light they exhibit a layered structure representing the cortical and fusellar tissues of the periderm. Their laminated ultrastructure distinguish them from other sedimentary organic matter.

Under cross polarized light, graptolite fragments exhibit bireflectance and are anisotropic. The reflectance of graptolites, when calibrated against conodont color alteration, increases with increasing C. A. I., and thus paleotemperatures (Figures 17, 18,and 19). Graptolite reflectance and bireflectance gradually increases in the lower ranks of the conodont alteration index. A sudden increase of reflectance occurs at higher ranks, above a temperature of 200° C (C.A.I. = 3). Maximum reflectance and bireflectance also exhibit a scatter at higher ranks of thermal maturation. This increase in the scatter of reflectance and bireflectance values is attributed to the reordering of the molecular structure of the periderm. The increase in temperature causes ordering of the aromatic stacks of the periderm. This molecular reordering causes a decrease in the interlayer spacing and thus an increase in reflectance (Stach et al. 1982). The sudden jump in the optical properties beyond the C. A. I. 3 could mean that a critical temperature required for the rearrangement of the molecular structure of the graptolite periderm is reached between the temperature of 190° C and 300° C. The wide scatter of reflectance is caused by the wide temperature range a single C. A. I. represents. The bireflectance of the graptolites exhibits a wide scatter for the lower ranking specimens, but shows a better correlation at higher ranks. The development of strong anisotropy in graptolites and its optically biaxial nature (Clausen and Teichmuller, 1982) suggest that the maximum reflectance is a better representative of increasing metamorphic grade than minimumm reflectance or bireflectance.

The influence of lithology and mineralization on the reflectance of graptolites was also examined (Figure 20). Graptolites exhibit variations in texture and optical properties for different lithologies. Specimens in a shale matrix show a better, continuous and higher development of reflectivity than those preserved in carbonates. The reason for this difference is not yet clearly understood, but it is speculated that the differences arise from differing thermal conductivities of the rocks. Shales are poorer conductors of heat than limestones and thus retain heat much longer. This prolonged retention of heat is then manifested in the graptolite fragments by higher reflectivities (Bostick and Foster, 1975; Jones et al., 1974; Stach, 1982)

Mineralization can also effect the reflectance of graptolites. Sample G has an anamolously high value of reflectance for its corresponding C. A. I. (Table 4). This sample is highly pyritized. Pyrite when present in large quantities seems to increase the reflectance of the surrounding periderm.

The effect of local and regional tectonic setting could not be clearly established in the present study. However it can be speculated that the reflectance of a sample from a

TABLE V.

CORRELATION OF GRAPTOLITE REFLECTANCE WITH CONODONT ALTERATION INDEX AND VITRINITE REFLECTANCE

		REFLECTANCE R (OIL) MAX (%)		
Conodont Alteration Index (EPSTIEN, 1977).	TEMPERATURE °C	GOODARZI (1985)	THIS STUDY	VITRINITE (EPSTIEN, 1977).
1	50-80	0.64-.87	0.36-0.91	<0.8
1.5	80-90	0.70	0.56-.93	0.7-0.85
2	60-140	2.46-2.73	0.69-1.75	0.85-1.3
3	110-200	3.63-7.20	1.47-1.86	1.4-1.95
4	190-300	1.86-7.93	1.31-3.94	1.95-3.6
5	+300	7.10-11.90	5.08-+8.56	+3.6

tectonically active zone will show a high reflectance. This increase in reflectance would be due to the increasingly higher temperatures associated with the tectonic activity.

The present data is not sufficiant to adequately establish a relationship of depth versus reflectance. However, samples N and M, from the Viola limestone in the Dillard 8-20 core exhibit a variation in reflectance with depth. These samples have a maximum reflectance of .812 % and 1.75 % for depths of 5628 feet and 5930 feet, respectively. Conodont alteration indicies of 1.5 and 2 were determined for these samples, and represent paleotemperature ranges of 50° to 90° C for sample M and 60° to 140° C for sample N. The graptolite reflectance of these samples indicate a temperature of about 85° C for sample M and about 140° C for sample N. It appears that graptolite reflectance gives a more precise temperature value than the corresponding C. A. I.. Thus graptolite reflectance might be a more precise criteria than the conodont alteraton index for the determination of maturity with increasing depths for sediments lacking vitrinite.

By means of C.A.I. values, graptolite reflectance is compared to paleotemperatures and vitrinite reflectance (Table 5, Figure 24). The data clearly indicate that graptolites develop reflectance and anisotropy at lower temperatures than vitrinite. Goodarzi and Norford (1985) reported that for reflectance of 2.5% vitrinite needs a

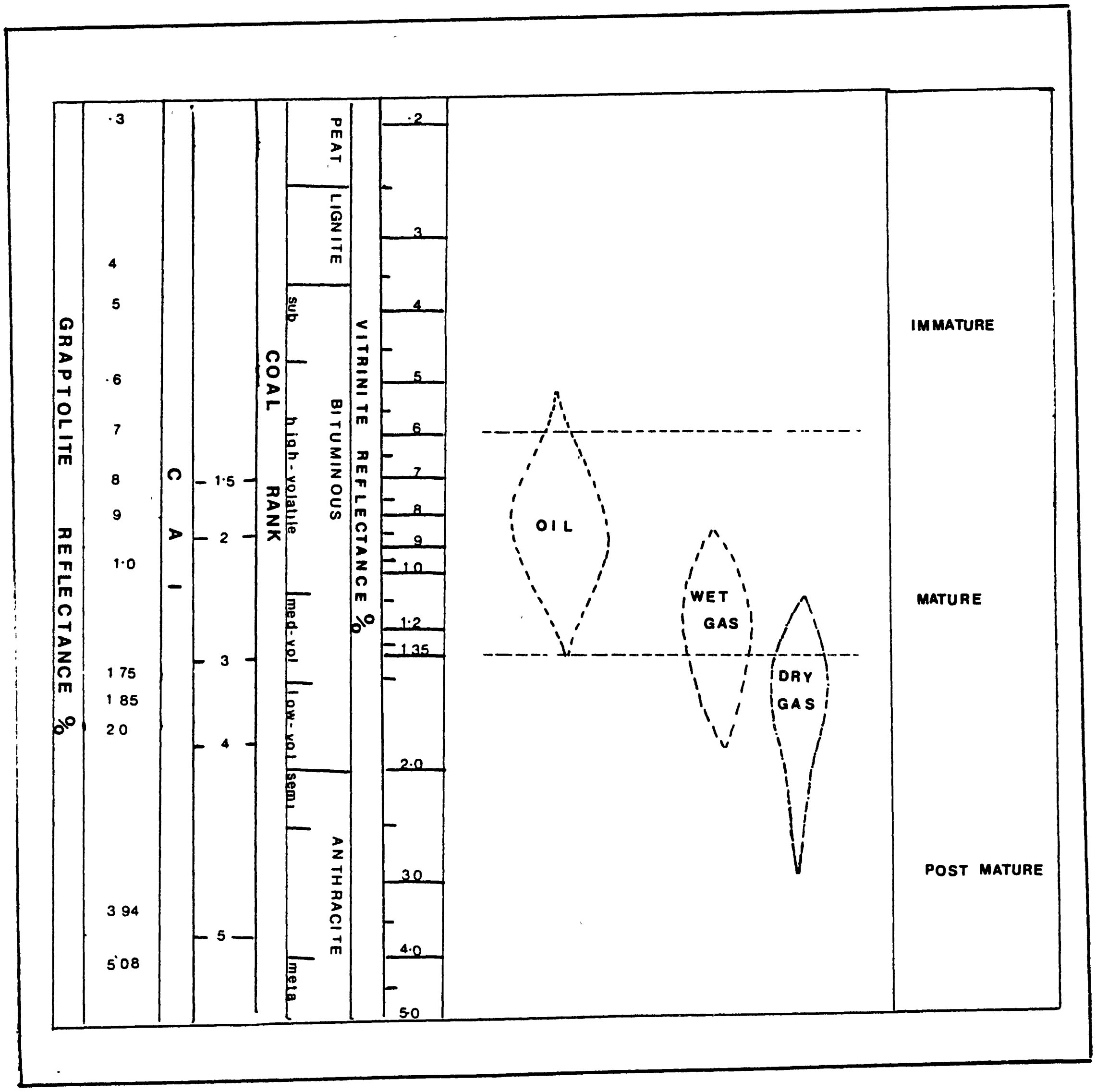


Figure 24. Correlation of graptolite reflectance to CAI, vitrinite reflectance, and stages of maturity. (Modified after Dow, 1982).

temperature of 130° C, but in graptolites 100° C will develop the same reflectance. The present data also show that the optical properties of graptolites are more sensitive to increasing temperature than conodont color alteration.

The reflectance of graptolites can be applied as a tool for assesment of paleotemperatures and maturation of the sediments. A correlation of organic maturity stages to graptolite reflectance is presented in Figure 24.

Further work needs to be done for the development of a more accurate scale of maturation based on graptolite reflectance. A more detailed study of a single basin with graptolites from varying depths and lithologies is recommended. Problems exist with the calibration of reflectivity of graptolites to conodont color-alteration. The conodont alteration index is a very subjective tool, with wide overlaps of temperature ranges. A more precise method of caliberating graptolite reflectance to paleotemperatures would be to examine changes in chemical composition of the graptolite periderm with laboratory induced heating. Calibration could be accomplished by determining the ratio of oxygen and hydrogen to carbon content of the periderm.

CHAPTER VII

CONCLUSIONS

1. Graptolite periderm exhibits an irreversible increase in maximum reflectance with increasing paleo temperatures. Paleotemperatures in turn may be directly related to depth of burial and magmatic or tectonic heating of the host rock.

2. Optical properties of the graptolite periderm can be used to determine the maximum paleotemperature the graptolite and its host rock has experienced, and thus its thermal maturity.

3. Graptolite periderm exhibits bireflectance and thus is anisotropic.

4. The development of reflectivity is gradual at lower maturity ranks and increases rapidly above a temperature of 200° C.

5. Graptolite develop reflectance and anisotropy at lower temperatures than vitrinite.

6. Particles of graptolite skeleton can be easily recognized by their finely layered structure observed under reflected light. They can be differentiated from other organic material present in sedimentary rocks by their characteristic peridermal structure.

7. The graptolites exhibit two types of periderm texture , i.e. nongranular and granular, depending on the lithology of the sample.

8. Lithology infuences the development of reflectance. Samples preserved in shale matrix have a higher reflectivity than those from limestones at the same paleotemperatures.

9. Localized mineralization and tectonic events increases the maximum reflectivity of the graptolites.

10. A scale of graptolite reflectance is calibrated with conodont alteration index. This scale (Table 5) lists the graptolite reflectance corresponding to the conodont alteration index for a particular paleotemperature the graptolite sample has experienced.

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