UNIVERSITA' DEGLI STUDI "ROMA TRE" SCUOLA DOTTORALE IN GEOLOGIA DELL'AMBIENTE E DELLE RISORSE (SDIGAR) SEZIONE GEOLOGIA DELLE RISORSE NATURALI

- XXVIII CICLO-



NEW INTEGRATED APPROACH TO ASSESS THERMAL

MATURITY OF SEDIMENTARY SUCCESSIONS BY MEANS

OF ORGANIC AND INORGANIC INDICATORS

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A.A. 2015/2016

TABLE OF CONTENT

ABSTRACT	1
CHAPTER 1 - Introduction	4
1.1 Aims and methodologies	4
1.2 Evolution of this study	5
1.3 Outline of the thesis	7
CHAPTER 2 - Methodologies	9
2.1. Kerogen characterization	9
2.1.1 Pyrolysis Rock Eval and TOC	11
2.1.2 Organic Petrography	13
2.1.2.1 Samples preparation	14
2.1.2.2 Analysis in reflected light and reflectance measurements	15
2.1.2.2.1 Vitrinite reflectance	16
2.1.2.2.2 Paleozoic organoclast	17
2.1.2.2.3 Graptolites	19
2.1.2.3 OM analysis in transmitted light	23
2.1.3 Infrared (IR) spectroscopy	24
2.1.3.1 Theory	24
2.1.3.2 Fourier transform infrared spectroscopy (FT-IR) analysis	
for dispersed organic matter	24
2.1.4 Raman spectroscopy analysis	27
2.1.4.1 Theory	27
2.1.4.2 The Raman Spectrometer	28
2.1.4.3 Band assignment for Raman spectra in dispersed organic matter	29
2.2 Inorganic fraction of sediments	33
2.2.1 X-Ray Diffraction of clay minerals	33
2.2.1.1 Samples preparation	33
2.2.1.2 Thermal maturity interpretation	36
2.2.2 Low temperature thermochronology	38
2.2.2.1 Theory	38
2.2.1.2 Samples preparation and Apatite (U-Th)/He dating	40
2.3 Thermal modeling	41

СН	APTER 3 - Overcoming pitfalls in the assessment of thermal maturity in fan-delta	
sys	tems: the case history of the Lower Congo Basin	44
	3.1 Introduction	44
	3.2 Geological setting	45
	3.2.1 Western Africa offshore: from rifting to passive margin evolution	45
	3.2.2 Stratigraphic evolution of the Lower Congo Basin	46
	3.3 Materials	48
	3.4 Results	48
	3.4.1 Organic matter optical analyses	48
	3.4.2 Mineralogical data	49
	3.4.2.1 Whole rock and clay mineral content	49
	3.4.2.2 Stacking order and illite content in mixed layers illite-smectite	52
	3.4. 3 Thermal modelling	52
	3.4.3.1 Pressure and temperature data	52
	3.4.3.2 Patterns of organic matter maturation and smectite illitization	54
	3.5 Discussion	56
	3.6 Conclusion	60
СН	APTER 4 - Thermal evolution of Mesozoic-Cenozoic successions of the Carpathian	
oro	genic system (central sector - Ukraine)	62
	4.1 Introduction	62
	4.2 Geological setting	62
	4.2.1 Carpathians Orogenic system and Ukraine Outer Carpathians	62
	4.3 Sampling and Materials	64
	4.4 Results	66
	4.4.1 Pyrolysis Rock Eval	66
	4.4.2 Organic petrography and vitrinite reflectance	67
	4.4.3 Thermal modelling	68
	4.5 Discussions	71
	4.5.1 Implication in HC generation	71
	4.5.2 Implication in Carpathians thermal history	75
	4.6 Conclusions	76

(Poland) by means of new and old datasets of indicators of temperature exposure	78
5.1 Introduction	78

5.2 Geological setting	80
5.2.1 Stratigraphy	80
5.2.2 Tectonic setting	83
5.2.3 Previous thermal maturity data collection and interpolation	84
5.2.3.1 Cambrian –Ordovician	84
5.2.3.2 Silurian	85
5.2.3.3 Devonian	85
5.3 Materials	87
5.4 Results	89
5.4.1 TOC and Pyrolysis Rock-Eval	89
5.4.2 Clay mineralogy data	91
5.4.3 Analysis on the Organic matter: Raman spectroscopy and Graptolites	
and vitrinite Reflectance data	93
5.4.4 Burial and thermal modeling	97
5.5 Discussion	99
5.5.1 Source rocks evaluation by Pyrolysis Rock Eval	101
5.5.2 Thermal maturity assessment	101
5.5.3 Paleographic implication	103
5.6 Conclusion	103
CHAPTER 6 - Burial and exhumation of the western border of the Ukrainian Shield	105
6.1 Introduction	105
6.2 Geological Setting	106
6.3 Materials	107
6.4 Results	108
6.4.1 Clay mineralogy	108
6.4.2 Organic matter reflectance data	110
6.4.3 Thermochronology	110
6.4.4 Burial modelling	112
6.5 Discussion	115
6.5.1 Maximum Burial estimate	115
6.5.2 The Late Triassic-Early Jurassic exhumation	116
6.6 Conclusions	118

CHAPTER 7 - Characterization of dispersed organic matter in Oligocene to	Upper Miocene drilled
successions in the Lower Congo Basin (offshore Angola)	120
7.1. Introduction	120

7.2. Results	120
7.2.1 KBr-FTIR analyses on bulk kerogen LIRA	120
7.3 Discussions	124
7.4 Conclusions	127
CHAPTER 8- Raman spectrosopy characterization of dispersed organic matter at low	
diagenetic stages	129
8.1. Introduction	129
8.2. Material and methods	131
8.2.1 Source rocks and kerogen	131
8.2.2 Curve fitting	132
8.2.3 Raman thermal maturity parameters	133
8.3 Raman analyses results for differents materials and case histories	134
8.3.1 Raman analyses on powder of bulk kerogen	134
8.3.1.1 Malembo Formation – Lower Congo Basin (age: Tertiary) (LIRA)	134
8.3.1.2 Carpathians fold and thrust belt	
(Age: Mesozoic and Cenozoic)(PL)	143
8.3.1.3 Holy Cross Mts.(HCM) and Podolia region (PO)	
(age: Paleozoic)	146
8.3.2 Micro-Raman on polished sections on different kinds of macerals	150
8.3.2.1 Micro-Raman on vitrinite in Carpathians fold and thrust belt	
(Age: Mesozoic and Cenozoic)	150
8.3.2.2 Micro-Raman analyses on polished sections on Paleozoic graptoli	tes from
Holy Cross Mountains (age: Paleozoic)	153
8.3.3 Final correlation against Raman parameters and R_o % or R_o % equivalent	157
8.4 Discussions on Raman parameters variations	160
8.4.1 Distance between D and G bands	161
8.4.2 Full Width at Half Maximum of the G band	162
5.4.3 Area and width ratio parameters (D/G area, RA2, D/G width)	164
8.5 Conclusion	166
CHAPTER 9 Conclusion	170
References	180

"O Tempo pergunta ao tempo quanto tempo o tempo tem, o Tempo responde ao tempo que o tempo tem tanto tempo quanto tempo o tempo tem. Mas o tempo não para, eu ja dei volta ao mundo, toquei berimbau e o tempo não para... "

Brazilian popular song

Acknowledgements

First of all, I would like to express my gratitude to my supervisor, Prof. Sveva Corrado, whose every day enthusiasm, inspiration and constant support, allows me to develop this research project. I thank her, for her teaching, precious advices and for solving my problems with patience and always with a smile.

I'm extremely indebted to Dott. Luca Aldega, without his help, support and precious advices this work would not have been possible. He help me all the times and teach me with patience and great competence how to use in basin analysis clay mineralogical tools.

Prof. Claudia Romano and Dott. Domenico Grigo are greatly acknowledged for their help. Prof. Romano for introduce me to lab work in Raman analyses and Dott. Grigo to Petroleum System Modelling.

I am greatly indebted with the Italian Society of Hydrocarbons Exploration and Production, ENI, for providing me great part of the materials studied in this Thesis, with special regard to cuttings of a well drilled in the Lower Congo Basin and for financing the field trips that allowed us to sample in Ukraine and Poland. Furthermore I wish to thank ENI also for the past and future permission to publish most of the results achieved by my work in collaboration with ENI personnel.

Lea di Paolo, Chiara Caricchi, Roberta Maffucci, Danilo Di Genova and Alessandro Vona have been a great working team that supported me during each phase of my work. Thanks to all.

I am thankful to the Istitute of Earth Sciences of the University of Porto, to Dr. Alexandra Guedes and Dr. Bruno Valentim for the facilities given for conducting the research on organic matter by means of Raman and organic petrography analyses during my period of study in Portugal. Further thanks are due to Dr. Alexandra Guedes for the stimulating review she made of my Thesis.

Thanks also to the further two reviewers of my work, Prof. Stefano Mazzoli and Dr. William Sassi for their helpful and positively critical reviews.

Thanks are also due to Prof. Massimiliano Zattin, Dr. Benedetta Andreucci and Dr. Ada Castelluccio for proving me with thermochronological data produced in Padua Laboratories, for the discussions on the burial and exhumation history on the Podolia region and for their help during the field trip in the Holy Cross Mountains.

Special thanks are also due to Rafal Szaniawski and Leszek Jankowski for their help and hospitality during the fieldwork in Ukraine and Poland..

I also want to thank Dr. Sergio Lo Mastro for the time spent on XRD samples scanning.

I'm thankful to Aida Conte and Laura Medeghin from CNR for the help given in performing FT-IR analyses on the organic matter c/o IGAG-CNR laboratories.

Donato Barbieri and Javier Cuadros are kindly acknowledged for stimulating discussions on organic matter and smectite-illitization thermal evolution.

In these years I worked rounded by people that gave me always the good mood. Gabriele, Riccardo and Martina, first of all. Don't worry my friends, everything will be alright.

Special thanks to "my generation crew", Mario, Giulia, Ines, Giorgia, Andrea, Antonio, Chiara, the new entry Ileana and also to Gabriele, Marco, Francesco, Stefano, Matteo, Silvia, Gaia and all PhD students. All good people, I've been lucky to study and spend my time with you all.

My friends in Rome, my classmates Giuseppe, Federica, Stefania, Michele, Mirko, Giansandro, Arianna and my cousins Ilaria, Sara, Roberta and Marta have been my first support since I live here in Roma. And then Marco, Valentina, Paola, Memè, Enrico, Maria, Mariassunta, Eddy gave me the best company during these years.

Great thanks to my best friends, that are far but always with me, Marco, Alessandro, Francesco, Ferran and all the Spanish, the Portuguese and Leccesi.

My parents, you are the first to thank. You supported me during this time, you'll support me always. My grandmother, thank you for thinking to me all the time and to remember me what is really important in life.

Marco and Diletta, my little brothers, thank you for staying with me.

And finally, thanks to you, my "pekeña educadora especial" for sustain me every day and share your life with me.

CHAPTER 1

Introduction

1.1 Aim and Methodologies

Sedimentary basins are defined as 'regions of prolonged subsidence on the Earth surface' (Bally and Snelson, 1980). They are classified in terms of the type of lithospheric substratum, their position with respect to the plate boundaries and the type of motion nearest to the basin (Miall, 2013).

The driving mechanism of subsidence are intimately related to the motion of the slab within the lithosphere and to the convection flow of the underlying mantle. Furthermore variation in the nature and amount of sediment supply is also strongly connected with the processes acting on the surface (e.g. sea level and climate and environmental change changes).

Therefore investigate the evolution of sedimentary basins is a key argument in many field of geological investigation such as sedimentary and structural geology, geodynamics and geomorphology.

Evaluating the subsidence is crucial also for the exploration of fossil resource, whose occurrence approximately corresponds to the location of sedimentary accumulation greater than about 1 km thick (Allen and Allen, 2013).

One of the main ways for evaluation of basin subsidence is the assessment of the thermal maturity of the sedimentary successions. During subsidence, in fact, sediments are gradually subjected to higher temperatures and pressures that can be recorded by a series of thermal indices obtained from the analyses on either the dispersed organic matter (OM) or minerals (e.g., fission tracks He dating or clay mineralogy).

In hydrocarbon (HC) exploration, the reliable assessment of thermal maturity of sedimentary successions is a key topic for the quantitative evaluation of hydrocarbons generation/expulsion and more in general for basin analyses studies. In particular, uncertainties in thermal maturity assessment, linked to input data to calibrate thermal modelling, can negatively influence decisions on the development of HC prospects.

Vitrinite reflectance is by far the better calibrating indicator of thermal maximum exposure and was adopted since the '50 as a measure of thermal maturity for organic matter dispersed in sediments. Nevertheless several problems linked to its application on dispersed organic matter still exist, especially when exploring targets that are devoid of vitrinite and/or are poor in organic matter, such those in Lower Paleozoic successions. Moreover, other several pitfalls exist (see Cardott, 2013 for a review), related to organic matter complexity (Petersen et al., 2009), such as identification of indigenous vitrinite in dispersed organic matter (DOM), or related to high hyrdrogen content in the whole organic matter (Petersen and Rosenberg, 1998), or due to the effect of overpressure (Carr, 1999; McTavish, 1978).

In order to overcome these problems in vitrinite reflectance application, in this thesis we tested a multimethod approach to assess thermal maturity in sedimentary basins based on thermal indicators carried out from a series of analyses on both the organic and the inorganic fraction of sediments and their modelling. The inorganic fraction has been analysed by means of: 1) X-Ray Diffractions of fine grained fraction of sediments and 2) low-temperature thermochronology. Organic matter dispersed in sediments have been analysed by means of: 1) organic petrography; 2) pyrolysis Rock Eval; and 3) spectroscopy (FT-IR and Raman). Raman spectroscopy, in particular, is a novel technique to study the composition and thermal evolution of the organic matter in a range of temperature typical of the metamorphism (200–700°C). But its application to lower temperatures, typical of hydrocarbons generation/expulsion windows, has not been yet explored with the production of robust datesets of parameters and satisfactory correlations with other thermal indicators (first of all vitrinite reflectance).

We present four case histories: two pertain to Mesozoic and Cenozoic successions and two to Paleozoic successions.

In detail, analyses and their interpretation through modelling were performed on:

- 33 cuttings from an Oligocene to Upper Miocene succession drilled in the Lower Congo Basin in the offshore of Angola (chapter 3);
- 2) 19 samples from Lower Cretaceous-Miocene sections, collected in the Outer Carpathians fold and thrust belt (Ukraine) (chapter 4);
- 3) 30 samples form the Cambrian to Devonian succession outcropping in the Holy Cross Mountains (Poland) (chapter 5);
- 4) 18 samples from the Ordovician to Devonian succession collected in the Carpathians foreland (Podolia region, Ukraine) (chapter 6).

Each of these case histories shows some of the before mentioned limitations related to vitrinite reflectance: in particular, the absence of vitrinite in the dispersed organic fraction of sediments in Lower Paleozoic rocks, the scarce reliability of measured vitrinite reflectance values in highly complex organic facies or overpressured sections and even the almost totally absence of organic matter dispersed in sediments.

Thus reliable thermal maturity was assessed though the critical application of other methods and their possible correlations and use for calibrating thermal models.

Results allowed to define new scenarios for the burial and thermal history of sedimentary successions representative of each case history, for HC generation/expulsion and tectonic evolution of the studied areas. Finally a new promising geothermometer in diagenesis based on Raman spectroscopy on organic matter has been proposed on the base of a robust dataset of highly variable organic matter content.

1.2 Evolution of this study

The first months of the first year were spent reviewing the existing literature on the different techniques for thermal maturity assessment. In particular a careful bibliography research was dedicate to the application of Raman spectroscopy in the characterization of organic matter in sedimentary rocks and coals. At the same time the preparation of samples for laboratory analyses started: this consisted in preparation of plugs for optical analyses, samples for XRD analyses on bulk rocks and <2 μ m grain size fraction and kerogen concentration for FT-IR and Raman spectroscopy.

Analyses started from the samples of the Carpathian fold and thrust belt (PL) and of the Podolia region (PO) that were collected in a field trip a few months before the beginning of the PhD period. In addition Pyrolysis Rock Eval data (produced in ENI's laboratories) were also collected for these two dataset. Before the end of the first year, analyses on these sets of samples were fully perfomed and preliminary interpreted. In the Podolia area, pyrolysis data were discarded because of the scarcity of organic matter. Whereas optical and mineralogical data obtained were used to perform a burial/thermal model, in collaboration with Dr. Benedetta Andreucci and Prof. Massimiano Zattin from the University of Padua that provided thermochronological data (apatite fission tracks and He dating on apatites) on the same dataset we adopted. For the Carpathian fold-and-thrust belt, analyses on the organic matter of samples PL revealed a very

complex macerals composition and in particular FT-IR analyses on bulk kerogen of this samples were discarded.

Because of the scarcity of the organic matter found in Paleozoic samples from Podolia, a new area in which Paleozoic sedimentary successions crops out in northern Europe was identified in the Holy Cross Mountains (Poland) and a field trip was organized at the end of June 2012 (HCM samples).

In the first months of the second year, HCM samples have been prepared and analysed by means of optical and mineralogical analyses and thermal models were performed.

Subsequently FT-IR and Raman spectroscopy and mineralogical analyses were perfomed on the whole set of samples coming from the offshore Angolan well. FT-IR data provided good insight on the OM composition and mineralogical results were used to calibrate a thermal model using the kinetic equation of smectite illitization provided by Cuadros et al., (2006). The comparison of this model to optical analyses that had been previously performed by ENI laboratories led to unravel correctly the thermal evolution of the succession drilled in the Angolan well. The calculated thermal maturities for each depth were then correlated to parameters obtained by Raman spectroscopic analyses.

The last four months of the second year were spent at the IES laboratory at the Department of Sciences of the University of Porto (Portugal), as a visiting scholar. Here samples collected in the Carpathians and in the Holy Cross Mountains were analysed by means of optical observation and Raman spectroscopy in collaboration with Dr Alexandra Guedes and Dr Bruno Valentim.

The third year was spent comparing thermal maturity data collected with those carried out from Raman spectroscopy and studying the existing literature on the band assignment of carbon materials (e.g. graphite, coal, disordered graphite, anthracite, graphene, fullurene, carbon nanotubes) in order to explain the correlations found between thermal evolution and changes in the Raman spectra of kerogen. In addition also a thermal models of the sector of the Carpthians fold and thrust belt was developed.

Throughout the duration of this study, poster presentations were given at national and international conferences:

- 1) Riunione annuale Gruppo Informale Geologia Strutturale, October 2013, Milan
- 2) Petroleum Geoscience Research Collaboration Showcase, November 2014, London
- 3) AAPG Europe Region Conference, May 2015, Lisbon.

1.3 Outline of the thesis

Chapter 1 presents a general introduction with main aims of the work, the methodologies used and evolution of this research (Fig. 1.1).

It briefly describes the importance of thermal maturity studies and their implication in geological studies and hydrocarbon exploration. In addition describes some of the main problems that can be encountered with the best known calibrating indicator of thermal maximum exposure in sedimentary rocks (e.g. vitrinite reflectance).

Chapter 2 introduces theoretical aspects and analytical procedures of the applied methodologies.

Chapter 3 describes the approach to the assessment of the thermal maturity profile in the Angolan well in the Lower Congo Basin. It outlined the pitfalls found in vitrinite reflectance profile and how to overcome them with the use of indicators from clay mineralogy analyses.

Chapter 4 focusses on the thermal evolution and characterization of source rocks in a sector of the Charpatian fold and thrust belt assessed by means of optical analyses and pyrolysis Rock Eval.

Chapter 5 deals with the thermal evolution of the Holy Cross Mountains. In this chapter we describe the quality of the Paleozoic source rocks in the area and unravel the thermal evolution of the two tectonic blocks in which the Holy Cross Mts are geologically organised by means of optical analyses on Paleozoic organoclasts and clay mineralogy and their modelling. In addition we constrain the maturity of Cambrian organic matter using Raman spectroscopy.

Chapter 6 presents the thermal evolution of the Podolia area constrained by mineralogical indixes and thermos-chronological data.

In *Chapter* 7 we analysed the organic matter of the each depth interval of the Angolan well using FT-IR spectroscopy thermal parameters. These analyses were performed to understand whether the maturation of the OM followed the maturation patter outlined by clay mineralogy assessed in Chapter 3.

Chapter 8 we present the correlation between thermal maturity (expressed as vitrinite reflectance) and parameters obtained from Raman investigation. In the last part of this chapter we provide an articulated discussion on the observed variations in the Raman spectra according to the existing literature that deal with Raman analyses on kerogen or more in general with carbon materials.

In *Chapter 9* we draw the general conclusions of this work on the base of the main results obtained in the four case histories with the proposed multi-method approach.

MAIN PHASES OF THE RESEARCH



Focusing on aims and methodologies

Definition of the scientific problem, bibliographic research on methodologies and analytical techniques, definition of the workflow (Chapters I and II)





Lab work

- Organic petrography and analysis of vitrinite/organoclasts reflectance (ALBA, Department of Sciences, University of "Roma Tre"; IES Lab Department of Science, University of Porto; ENI laboratories)

- X Ray Diffraction of fine grained sediments (Department of Geological Sciences, University of "Roma Tre")

- FT-IR analysis of organic matter (FT-IR Laboratory, C.N.R. Roma)

- Raman analyses of organic matter (EVPLab Department of Sciences, University of "Roma Tre"; IES, Department of Science, University of Porto)

Correlation among different thermal maturity parameters and calibration of thermal modelling for each study area integrated with low T thermochronology (Chapter 3-7)

Correlation between thermal maturity parameters and Raman new thermal proxy (Chapter 8)

Figure 1.1 Diagram showing the study evolution and thesis organization

Chapter 2

Methodologies

In this Chapter the methodologies used in this work to study the thermal evolution of the sampled sedimentary successions.are described

In detail the Chapter begins with a general introduction on kerogen and its classification, followed by a description of the main methods adopted in this work, the sample preparation and the characteristics of the instruments.

2.1 Kerogen characterization

Most organic matter (OM) in rocks represents the solid, usually dark coloured, remains of plants or animals which lived at the time of deposition (Taylor et al., 1998). Many rocks contain only a little amount of OM, while others, such as coals, are made up almost totally of organic matter.

At the time of deposition the organic matter dispersed in sediment is composed of a mixture of organic compounds of various origin and composition. In particular, aquatic organisms contribute mainly proteins, lipids and carbohydrates while higher plants contribute resins, waxes, lignins and carbohydrates in the form of cellulose (Barnes et al., 1990). These basic chemical constituent or their hydrolysis product (amino acids, long-chain fatty acids and sugar) are mostly microbially degraded in the water column and in the upper part of the sedimentary column. The principal processes involving the degradation of OM are aerobic respiration , bacterial sulphate reduction and methanogenesis as well as the reduction of manganes oxides, nitrates and iron oxides (Henrichs, 1993). An exception to this rules is lignin, a complex, partly aromatic macromolecule, concentrated in the inner cells walls of vascular plants, that can be hardly degraded by microorganisms with the exception of some aerobic fungi acting in the soil (Taylor et al., 1998).

OM that is not degraded in these processes is incorporated in sediments and the insoluble part of these materials is called kerogen (Durand, 1980). Starting from this point, further degradation will be primarily associated with temperature changes. In particular, it is usual to distinguish three zones that with increase in temperatures are called: diagenesis, catagenesis and metagensis. In these zones, kerogen progressively converts into hydrocarbons (primary oil in catagenesis and gas in metagenesis) leading to the formation of new constituent such as bitumen, pyrobitumen, exsudatinite or micrinite (Taylor et al., 1998).

A first kerogen classification can be made by the use of bulk parameters, such as the H/C and O/C atomic ratios, obtained from elemental analyses (Fig. 2.1). On the basis of these ratios, four types of kerogen have been defined which follow distinct diagenetic pathways.

Type I kerogen has high initial H/C and low O/C ratios. The source material is mainly algal, or a combination of algal lipids and waxes from higher plants (Fig. 2.2). It forms part of the liptinite macerals in coal.

Type II kerogen has intermediate initial H/C and O/C ratios, and larger contributions by aromatic and carboxylic acid groups than type I kerogen. Ester bonds are abundant, as are medium-length aliphatic hydrocarbon chains and naphthenic rings. Both algal and higher plant sources appear to contribute to type II kerogens (liptinite macerals).



Figure 2.1 Van Krevelen diagram showing maturation pathways for Types I to IV kerogen as traced by changes in atomic H/C and O/C ratios. The progressively darker shaded areas approximately represent diagenesis, catagenesis, and metagenesis stages, respectively (from http://www.falw.vu/~rondeel/grondstof/oil/oil-total-web.html#_Toc531067567)

Type III kerogen has an initial H/C ratio less than 1, an initial O/C ratio of 0.2 to 0.3, and is derived dominantly from terrestrial plants. It consists mainly of aromatic groups formed from lignins and humic compounds, and represents the huminite/vitrinite fractions of coal petrography. Oxygen is present as carboxylic acids, ketones and ethers rather than in ester bonds.

Type IV kerogen has the H/C ratio less than 0.5 and contains mostly decomposed organic matter and highly oxidized material of various origins and represents the inertinite group (Fig.2.2).

A palynological classification on the base of transmitted light analysis for a rapid assessment of hydrocarbon potential can be performed according to Tyson (2012). This classification is primarily designed for routine

source rock 'kerogen typing' with the aim to identify the relative proportions of inert, gas-prone, oil-prone and very oil prone material within the total kerogen assemblage (Tyson, 2012).

In general, more detailed characterizations are needed, which can be performed by means of optical and chemical indicators related to the changes in kerogen composition. With increasing maturity, kerogen looses

Kerogen Type (according to IFP)	Principal biomass	Environment (general)	Original Hydrogen Index	Sulphur incorporation	Hydrocarbons generated and expelled (1)
Туре І	algae, bacteria	tectonic non-marine basin	> 700	low	oils
Туре ІІ	marine algae, bacteria	marine	400-700	moderate	oils
Type II S (sulphur rich)	marine algae, bacteria	marine, carbonatic environment	400-700	high	oils
Type III "H"	spores, pollens, cuticles, resin, lignin, bacteria	, fluvial-lacustrine, coastal plains	300-600	low	waxy oils
Type III	lignin	coastal plains, deltaic, turbiditic	50-250	low	gas and light oils (gas traces when HI < 100)
Type IV	lignin	coastal plains, deltaic	< 50	low	none
(1) Also depending by	kerogen maturity le	evel.			

Figure 2.2 The main kerogen types, origin and pyrolysis indexes, from Scotti 2003

first preferentially O to produce CO_2 and H_2O , then H to produce hydrocarbons. Changes in the molecular structure have effect in the:

- 1) maximum temperature of the S2 band registered by Pyrolysis Rock Eval (Tmax);
- 2) petrographic detection of the constituents that can be observed in reflected and transmitted light;
- 3) molecular changes reflected mainly in the decrease aliphatic chains with respect to aromatic rings and changes in the spatial distribution of the aromatic rings. All these variations can be measured through Fourier Transform Infrared Spectroscopy (FT-IR) and Raman spectroscopy.

These are the thermal maturity indicators used in this work whose principles and applications will be discussed in the text below.

2.1.1 Pyrolysis Rock Eval and TOC

Pyrolysis Rock Eval and TOC measurements were perfumed at ENI laboratory (Milan-Italy) using: Rock Eval 6 equipment.

Total organic carbon (TOC) refers to the weight percent (wt %) of the organic carbon present in 100g of rock (Langford and Blanc-Valleron, 1990).

Total organic carbon is measured from 1g samples of pulverized rock that are combusted and converted to CO or CO₂. According to Hunt et al. (2002) value of approximately 0.5% total organic carbon by weight percent is considered the minimum for an effective source rock.

Pyrolysis is a widely used degradation technique that allows breaking a complex substance into fragments, by heating it under an inert gas atmosphere (Vandenbroucke, 2003). In this technique, a sample is firstly heated at 300°C and the free hydrocarbons are volatilized and measured as the S1 peak. In general a S1>1 mg/g may be indicative of oil.

Then the temperature is increased from 300° to 550°C (at 25°C/min) and leads to the volatilization of the very heavy hydrocarbons compounds as well as the cracking of no volatile organic matter. The hydrocarbons released from this thermal cracking are measured as the S2 peak that, thus, is an indication of the quantity of hydrocarbons that the rock has the potential of producing, should burial and maturation continue.

The temperature at which S2 reaches its maximum, depends on the nature and maturity of the kerogen and is called Tmax. Tmax is directly related to the stage of maturation of the organic matter.

The CO_2 issued from kerogen cracking is trapped in the 300°-390°C range. The trap is heated, and CO_2 is released and detected on a TCD during the cooling of the pyrolysis oven (S3peak) (Fig.2.3). This peak is an indication of the amount of oxygen in the kerogen and is used to calculate the oxygen index.



Figure 2.3 S1 and S2 peaks after Pyrolysis heating for samples with different starting thermal maturity

The type and maturity of organic matter in petroleum source rocks can be characterized from Rock Eval pyrolysis data using the following parameters:

HI = hydrogen index (HI = [100xS2]/TOC). HI is a parameter used to characterize the origin of organic matter. Marine organisms and algae, in general, are composed of lipid- and protein-rich organic matter,

where the ratio of H to C is higher than in the carbohydrate-rich constituents of land plants. HI typically ranges from ~100 to 600 in geological samples.

OI = oxygen index (OI = [100xS3]/TOC). OI is a parameter that correlates with the ratio of O to C, which is high for polysacharide-rich remains of land plants and inert organic material (residual organic matter) encountered as background in marine sediments. OI values range from near 0 to ~150.

PI = production index (PI = S1/[S1+S2]). PI is used to characterize the evolution level of the organic matter.

2.1.2 Organic Petrography

OM in coals or dispersed in sedimentary rocks is usually highly heterogeneous firstly because it has various origins (from plant, plant organs and less commonly animals), and also because its components suffered modifications of various degree and in different ways before and after deposition (Taylor et al., 1998). The best way to describe the OM heterogeneity is using a light or, even more, an electron microscope. Through these techniques to classify qualitatively and quantitatively the component of the OM on the basis on their origin, nature and properties gets possible.

The base of this classification is the "maceral concept" that, according to Taylor et al. (1998), defines macerals as the microscopically (through the use of light, especially reflected light, microscopy) recognized individual constituents of OM. The word 'maceral' referred to the selective oxidative treatment of OM used in paleobotany and are derived from the latin verb 'macerare' which means 'to soften'.

Macerals represent, at least partly, the remains of plants whose form and/or structure have been preserved in coal and other rocks, while other macerals are degradation products which are so altered that their plant origin cannot be determined.

All macerals have the suffix '-inite', and are classified into three main groups:

- vitrinites: are coalification products of humic substances, which essentially originate from the lignin and cellulose of plants cell walls. They are characterized by high oxygen and aromatic fraction content;
- liptinites: derive from relatively hydrogen-rich plant remains such as sporopollenin, resins, waxes and fats. It differs from vitrinite for a higher aliphatic (paraffin) fraction and a correspondingly higher hydrogen content;
- 3) inertinites: are characterized by relatively high carbon content, low hydrogen content and a much increased level of aromatization. Most inertinite have the same origin of vitrinite and liptinite but they experienced a different primary transformation due to various processes (e.g. charring, oxidation or fungal attack).

Vitrinite is the standard reference material for reflectance measurements for determining the level of organic maturation. This technique is well known and widely used as it provides consistent and reliable thermal maturity assessment with high resolution degree.

In the same sample, the three group can coexist but showing different reflectance values, as shown in the histograms in Figure 2.4.



Figure 2.4 – Microphotographs of different macerals at the same thermal maturity level. On the right, Reflectance random histograms, grey bins indicate the reflectance for the corresponding macerals on the left. Photos are taken from microscope with 50X magnification under oil immersion

To avoid as possible ambiguity among different macerals, the International Committee for Coal and Organic Petrology (ICCP) has established standard rules for petrographic microscopy which provide that the description of macerals should be in terms of their appearance in reflected light using oil immersion objectives with 25-50X magnification.

Fluorescence microscopy can be seen as a complementary method of examination that can help to reveal details, not otherwise visible, of the internal make-up of macerals and some of their chemical and physical properties.

2.1.2.1 Samples preparation

Sample preparation was performed at the Academic Laboratory of Basin Analysis (ALBA) of "Roma Tre" University (Italy).

Analyses were performed on concentrated kerogen using acid attack and, on dispersed OM fragment in the bulk rocks and on organoclasts (e.g., graptolites) that protruded from the rocks. When analyses were performed on the bulk rock, samples were grounded in a mortar and were hand-picked under an optical microscope (Leica zoom 2000).



Figure 2.5 Extracted kerogen particles (on the left) and Kerogen embedded in epoxy resin block (on the right)

For optical analyses both bulk kerogen, bulk rock or graptolites were mounted on epoxy resin block (Serefiex resin +hardening with a 1:20 ratio – Fig. 2.5).

Samples were polished using an automated polishing system (Struers Labopol 5), 250, 500, 1000 carborundum papers and isopropanol lubricant. After washing samples in order to remove debris, three polishing laps were used with alumina powders of decreasing grain size (1.00, 0.30, 0.01 µm) and samples polished for a few minutes (Fig. 2.6).

Extraction of kerogen was performed at the Academic Laboratory of Basin Analysis (ALBA) of "Roma Tre" University (Italy) and in the laboratory of the Institute of Earth Sciences (IES) of Science Faculty of the



Figure 2.6 Automated polishing system

University of Porto (Portugal).

In this thesis kerogen was extracted using wet-chemical acid demineralization according to Robl and Davis (1993) and Schimmelmann et al. (1999). Samples were crushed using the mixer ball mill. Removal of carbonates was done adding HCl on the dried samples. The HCl was added in small increments to prevent excessive foaming. The acid digestion process was done at 50-60°C in a water bath to facilitate removal of carbonates.

The acid was removed with pipette and disposed in plastic containers with

neutralizing limestone gravel under a fume hood. Digestion of inorganic matter was done by hydrofluoric acid (HF). For 5 g of powder sample a mixture of 50% distilled water and 50% HF was added (45 ml). Samples were placed on a shaker table for 2 hours at regular intervals. The samples were finally washed 5-6 times with distilled water.

2.1.2.2 Analysis in reflected light and reflectance measurements

Optical analyses were performed at the Academic Laboratory of Basin Analysis (ALBA) of "Roma Tre" University (Italy) for analyses of chapter 5 and 6, in the laboratory of the Institute of Earth Sciences (IES) of Science Faculty of the University of Porto (Portugal) for analyses of chapter 4 and at ENI's laboratory (Milan- Italy) in the capther 3. At ALBA laboratory we used a Zeiss Axioskop 40 A, equipped with a tungsten-halogen lamp (12V, 100w), an Epiplan-Neofluar 50x/1.0 oil objective, in incident filtered ($\lambda = 546$ nm) non-polarized light under oil immersion (n = 1.518) at about 23°C (Figure 2.7). The microscope is equipped with the MPS 200 detection system by J & M Analytik AG (web site: http://www.j-m.de).



Figure 2.7 Zeiss Axioskop 40 A microscope equipped with MPS detection system

On each sample measurements were performed on unaltered fragments. Mean reflectance values (Ro%) were calculated from the arithmetic mean of these measurements with a standard deviation, identifying the indigenous population.

Microphotographs of specimens fragments were taken using a microscope-mounted Canon Power Shot G6. In the IES laboratory measures were conducted on a reflected light Leitz microscope coupled to a Diskus-Fossil System, and oil immersion objectives. The reflectance measurements were made using a combined magnification of objective and oculars of 20 and 50×.

At ENI's laboratory mean random vitrinite reflectance (Ro%) was measured on concentrated OM prepared using the traditional HF–HCl method (Robl and Davis, 1993). Samples were first mounted in epoxy resin and polished. Vitrinite reflectance analyses were then performed on randomly oriented grains using a Zeiss Axioplan MPM400 microscope equipped with J&M Analytik Tidas S 800 spectrometers CCD UV/NIR 2098. We used conventional microphotometric methods, under oil immersion (v = 1.518) in reflected monochromatic non-polarized light ($\lambda = 546$ nm). Reflectance standards (Spinel Ro%=0.427 and 0.905) were used for calibration. In most cases a population of a few tens of readings per sample was collected on fragments only slightly fractured and/or altered (Borrego et al., 2006).

2.1.2.2.1 Vitrinite reflectance

Mean vitrinite reflectance (VRo%) is measured as the percentage of the incident light intensity which is reflected from the polished surface of vitrinite macerals fragments relative to a standard substance (e.g.,

glass, sapphire, etc.). This measurement uses immersion oil and is related to the refractive index and absorptive index of immersion oil and standards which follows the Fresnel-Beer equation:

$$R_{o} = (\mu - \mu_{o})^{2} + \mu^{2}k^{2}/(\mu + \mu_{o})^{2} + \mu^{2}k_{o}^{2}$$

where: μ , μ_o = refractive index of vitrinite and immersion oil, respectively; k, k_o = absorption index of vitrinite and immersion oil, respectively.

These indexes are wavelength dependent, thus a green monochromatic non-polarised light ($\lambda = 546$ nm) is chosen for R_o% measurements.

In diagenesis and in the first stages of catagenesis (R_0 % <1.5), vitrinite is optically isotropic and the aromatic clusters present in the organic structure have no preferred orientations. In metagenesis instead, vitrinite behaves like an anisotropic material because of the orientation of aromatic clusters (Oberlin et al., 1980). When tectonic stress affects the thermal maturity of sediments, vitrinite macerals can turn out to be biaxial (Levine and Davis, 1989) (Fig. 2.8).



Figure 2.8 - Increase of vitrinite reflectance (% Rmax, Rm and Rmin) with depth in the Münsterland I borehole (Germany) showing the increase of anisotropy (difference between Rmax and Rmin) with increasing depth and rank stage (from M. Teichmüller, 1982)

2.1.2.2.2 Paleozoic organoclast

Vitrinite is absent in Lower Palaeozoic rocks until the advent of significant terrestrial floras in Silurian times. However, marine organoclasts may abound in sequences that are devoid of vitrinite macerals. Thermal maturation in these sequences can be acquired measuring reflectance on such organoclasts (e.g., scolecodonts, chitinozoans and graptolites) or on bitumen.

Furthermore alteration color semi-quantitative assessment in transmitted light on spores, conodonts and acritarchs may be coupled with reflectance analyses to provide a reliable evaluation of thermal maturity.

Comparison between these two techniques underlines that quantitative reflected light analyses are generally more reliable than semi-quantitative ones in transmitted light (Tricker et al., 1992).

Reflectance analyses on marine organoclasts have been successfully used in regional maturation studies in lower Paleozoic successions (Bertrand, 1990a, b, 1991; Bertrand and Malo, 2001; Bertrand and Malo, 2012; Clausen and Teichmüller, 1982; Goodarzi, 1982; Goodarzi, 1984, 1985a, b; Goodarzi and Norford, 1985; Kurylowicz et al., 1976; Roy, 2004; Wilson et al., 2004).

Reflectance values of organoclasts and bitumen can be converted into equivalent reflectance values of standard vitrinite using following equations, derived by Bertrand (1990, 1993), Bertrand and Malo (2001) and Tricker al. (1992) (Fig.2.9):

- $R_o\% eq = 0.8873 * R_o chitinozoan + 0.0124$
- $R_0\% eq = 0.9376*R_0 = 0.0278 \text{ or } R_0 = 0.9686*R_0 = 0.9819$
- $R_o\% eq = 0.6493 R_o hydroid + 0.2126$
- $R_o\% eq = 1.2038 * R_{o-scolecodon}^{0.6824}$
- $R_o\%eq = 0.8113*R_o-migrabitumen (shale-marl)^{1.2438}$
- $R_o\% eq = 1.2503 * R_{o-migrabitumen}$ (limestones) ^{0.904}



Figure 2.9 Correlation reflectance scale among different kinds of organoclasts: vitrinite (collotelinite), chitinozoans, graptolites, hydroids and scolecodonts, spores and migrabitumen (as a function of lithology). Thermal Alteration Index scale is also reported. From Bertand and Malo, (2012)

In Chapters 5 and 6 we measured reflectance of all types of dispersed marine organoclasts and correlate measured reflectance values to the equivalent reflectance of the standard vitrinite using Bertrand and Malo's equations (2012).

The analysed samples from pre-Devonian successions in our sets of samples generally contain vitrinite-like and graptolite fragments. In particular our analyses were focused on the latter groups because show a greater abundance and is more easily recognizable. The main features of the last cited group are briefly reviewed in the following paragraph on the base of the most recent literature.



Figure 2.10 Incident light photomicrographs on graptolites (from Cole, 1994)

2.1.2.2.3 Graptolites

Graptolites represent planktonic to epi-planktonic colonial animals that occur in Lower Paleozoic (Ordovician–Lower Devonian) marine sediments (Goodarzi, 1984, 1985b). The graptolite skeleton (periderm) is composed of a chitinous substance (Duran, 1980), or a collagen-like protein (Crowther and Rickards, 1977; Towe and Urbanek, 1972). During the increase in maturity, graptolites undergo similar molecular structural changes than vitrinite-huminite group macerals, for example an increase in aromaticity and ordering of aromatic carbon with increased thermal maturity (Cole, 1994; Goodarzi, 1984).

Graptolites generally exhibit optical properties in reflected light similar to that of vitrinite macerals (Goodarzi and Norford, 1987; Hoffknecht, 1991). For this reason measurements of the optical properties of graptolites may provide a valid alternative method for assessing the level of OM maturation of pre-Devonian sediments that are devoid of vitrinite (Bustin et al., 1989; Goodarzi, 1982).

The colours of graptolites, microscopically observed on polished surfaces, range from medium grey to light grey

(Fig. 2.10). Distinct morphological features of graptolite fragments have been described in detail in a series of earlier studies (Hoffknecht, 1991; Link et al., 1990; Suchý et al., 2002; Teichmüller, 1978).

Suchy et al., (2002) analysed the Barrandian shales, cut perpendicular to bedding, observing that the most common features include graptolite cortical tissues, common canals, and/or layered walls of the periderms. If cortical tissues are thick enough, graptolites can be recognized by their finely laminated structure (Fig. 2.11).



Figure 2.11 Silurian shales. Sections perpendicular to bedding. A–D: Graptolite fragments [A—fragment of graptolite showing the periderm wall (P), common canal (CC), and an apartural spine (As). A section of the branching from the upper part of the common canal. B- Non-granular graptolite fragments of a colony of "rooted dendroids". C—Graptolite fragment displaying cortical laminated tissue. D—Transverse section of a graptolite stipe showing fusellar tissue which has the form of complete tubes. Some tubes were filled with brightly reflecting sulfide minerals. From Suchy et al., 2002

Graptolites show two types of textures under reflected light; a) non-granular fragments which appear hard, brittle and often show fine structural details, for example laminations, b) granular which is fine granular to reticular. The non-granular fragments show higher anisotropy than the granular fragments (Goodarzi 1984). Goodarzi and Norford (1985) described the morphology of a range of Canadian graptolites found in sedimentary rock: shales, marls, limestones, cherty lithotypes, also in weathered and heat affected rocks. They observed that graptolites in carbonates were granular (Fig. 2.12a) but those in shale were often non-granular (Fig. 2.12b).



Figure 2 a) Fragment with granular surface, lower Silurian argillaceous limestone, Cape Phillips Fm., Canadian Arctic. Plane polarized scale bar is 50 μm, b) Non-granular fragments, middle Ordovician shale, Glenogle Shales. British Columbia. Partially crossed polars. From Goodarzi and Norford (1985)

In a few cases, however, where optical properties of both graptolite types were measured in identical samples, the reflectance of the non-granular type was found to be systematically higher than those of the granular type (Goodarzi, 1984; Suchy et al., 2002) (Fig. 2.13).



Figure 2.3 Plot of non-granular versus granular graptolite reflectance. Note the almost perfect linear correlation between the two variables. From Goodarzi and Norford (1985)

Goodarzi (1984) and Goodarzi and Norford (1985), Goodarzi et al. (1985b) have compared the morphology of fragmentary graptolites to those of arcritarchs, bitumen, chitinozoans and sclecodonts. Graptolite fragments showed higher anisotropy than other dispersed organic material in the same sediments.

Optical properties of graptolites have been studied by Kurylowicz et al. (1976), Teichmüller (1978), Clausen and Teichmüller (1982), Goodarzi (1982, 1984, 1985b), Goodarzi and Norford (1985). Kurylowicz et al.(1976), Teichmüller (1978) and Clausen and Teichmüller (1982) have determined the reflectance and bireflectance of a range of graptolite. Kurylowicz et al. (1976) have examined graptolites found in some central Australian sediments (Ordovician- Devonian). The maximum range of reflectance in oil was 0.80-2.37% with bi-reflectance of 0.35-1.05. Teichmüller (1978) determined the reflectance of graptolite cortex found in the Ordovician of a borehole in NW-Germany (5.1-10.0% Rmax) as well as from graptolites found in boulders from the Baltic Sea (0.8% Rmax), from Brittany (1.7% Rmax), from Thuringia (8.2% Rmax) and from Spain (9.2% Rmax). Clausen and Teichmüller (1982) found that the maximum oil reflectance of graptolites from the borehole in NW Germany increases with depth. They also report reflectance values of a range of graptolites from Sweden. The Swedish graptolites had reflectances of 0.36-0.72% Rm, whereas the reflectances for graptolites from the borehole Soest-Erwitte 1/la ranged from 6.0- 0.5% Rmax. Goodarzi (1982, 1984) determined the reflectance and bireflectance of Turkish graptolites (Ordovician-Silurian) and found that the reflectance of graptolites increased with depth and also that graptolites had higher reflectance than natural bitumen or chitinozoans (Goodarzi 1984, 1985b). Furthermore, Goodarzi (1984) determined the dispersion of maximum and minimum oil reflectances of graptolites from Turkey parallel and perpendicular to bedding to determine the optical character of graptolites (Figure 2.14 and 2.15). Goodarzi (1985b) found



Figure 2.4 Dispersion curve of maximum and minimum oil reflectance for nongranular (NG) and granular (G) graptolite fragments. Redrawn after Goodarzi, 1984

that the dispersion of oil reflectance of both granular and non-granular graptolite epiderm for sections both parallel and perpendicular to bedding increased with increasing wavelength, similar to anthracite. The granular graptolites appear to be softer, lower reflecting and show weaker anisotropy, whereas the non-granular graptolite fragments are hard and brittle, high reflecting and exhibit strong optical anisotropy. However, both the maximum reflectances and bi-reflectances of non-granular graptolites were higher than those of granular graptolites.

The relation between the granular and nongranular fragments is complex and different opinions exist (see Goodarzi and Norford, 1985; Link et al., 1990 for a review). Non-granular fragments may represent the remains of the graptolite exoskeleton, whereas the granular fragments may form parts of the soft body of the graptolite that once occupied the common canal (Goodarzi, 1984; Riediger et al., 1989). They

may also represent the cortical tissue composing the outer layer of the periderm (Link et al., 1990).



Figure 2.15 Principal reflectance axis of vitrinite A) graptolites are invariably observed on bedding planes because of their shape; B) Principal reflectance axis of biaxial indicating surface of graptolite shown in section cut parallel and perpendicular to the bedding. Ra= Ro max Rb= Ro intermediate Rc=Ro minimum (Bustin et al., 1999).

Graptolites settled on the sea bottom with their largest dimension horizontal and, therefore, the largest surface areas for the determination of optical properties are often present in sections parallel to bedding. In this orientation graptolites show true maximum reflectance, while the true minimum reflectance and the strongest bi-reflectance are observed on sections perpendicular to bedding (Goodarzi and Norford, 1989; Hoffknecht,1991; Suchy et al., 2002).

2.1.2.3 OM analysis in transmitted light

Another approach to the study of OM in sedimentary rocks is the use of microscope in transmitted light using kerogen concentrate (Teichmüller, 1986) whose advantage is a better identification of palynomorphs with respect to the incident light techniques. In particular the use of fluorescence-light techniques allows liptinite occurrences to be distinguished from the less fluorescent component of kerogen, and the individual liptinite macerals to be differentiated one from another (Fig. 2.16). Applied to hydrocarbon exploration transmitted light analysis has the advantage to estimate directly all factors which are decisive for oil and gas proneness like type, abundance distribution and substance.

This analysis has been used in Chapter 3 to quantitatively assess the kerogen composition according to the ENI classification that propose 4 classes:

- 1) AOM: amorphous organic matter;
- 2) MPH: marine phytoplankton;
- 3) CWF: continental wooden organic matter;
- 4) CHF: continental herbaceous fragments.

Reflected light



Transmitted light



Figure 2.6 Two microphotographs showing the same liptinite fragment observed under: a) reflected light and b) transmitted light

2.1.3 Infrared (IR) spectroscopy

2.1.3.1 Theory

Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions. In IR spectroscopy, an organic molecule is exposed to infrared radiation. When the radiant energy matches the energy of a specific molecular vibration, absorption occurs.

The bond of a molecule experiences various types of vibrations and rotations. This causes the atom not to be stationary and to fluctuate continuously. Vibrational motions are defined by stretching and bending modes. These movements are easily defined for diatomic or triatomic molecules. This is not the case for large molecules due to several vibrational motions and interactions that will be experienced. When there is a continuous change in the interatomic distance along the axis of the bond between two atoms, this process is known as a stretching vibration. A change in the angle occurring between two bonds is known as a bending vibration. Four bending vibrations exist namely, wagging, twisting, rocking and scissoring (Fig.2.17).

For a molecule to show infrared absorptions, it must possess a specific feature, i.e. an electric dipole moment of the molecule must change during the vibration. This is the selection rule for infrared spectroscopy. The dipole moment is determined by the magnitude of the charge difference and the distance between the two centers of charge. As the molecule vibrates, there is a fluctuation in its dipole moment; this causes a field that interacts with the electric field associated with radiation. If there is a match in frequency of the radiation and the natural vibration of the molecule, absorption occurs and this alters the amplitude of the molecular vibration.

IR spectroscopy is a great method for identification of compounds, especially for identification of functional groups. Therefore, we can use group frequencies for structural analysis. Group frequencies are vibrations that are associated with certain functional groups. It is possible to identify a functional group of a molecule by comparing its vibrational frequency on an IR spectrum to an IR stored data bank.



Figure 2.17 Vibrational motions for a triatomic molecule

2.1.3.2 Fourier transform infrared spectroscopy (FT-IR) analysis for dispersed organic matter

Infrared (IR) spectroscopy records changes in dipole moment resulting from bond vibration upon absorption of IR radiation, thus allowing the identification of functional groups in organic samples (Mastalerz and



Figure 2.18 Classification of kerogen-types and maturation according to FT-IR ratio of the intensities of aliphatic/aromatic bands (A-Factor) and FT-IR ratio of the intensities of carboxyl and carbonyl/aromatic bands (C-Factor) and the vitrinite reflectance equivalent grid from Ganz et al. (1990)

Bustin, 1996). Fourier Transfomr Infrared (FT-IR) measurements of IR absorbance simultaneously over the entire infrared spectrum. As a result, many spectra can be collected and summed, which reduces random noise and enhances absorbance peaks.

FT-IR has been widely used to provide insight into the chemical composition and structure of coal (Guo and Bustin, 1998; Ibarra et al., 1996; Iglesias et al., 1995; Mastalerz and Bustin, 1993; Painter et al., 1981; Sobkowiak and Painter, 1992) and kerogen (Ganz and Kalkreuth, 1987; Kister et al., 1990; Lin and Ritz, 1993). FT-IR studies assigned specific bands to chemical structures in complex kerogen molecules (Baruah, 1986; Painter et al., 1981; Painter et al., 1983) and proved the diagnostic value for maturity and kerogen type (Chen et al., 1998; Chen et al., 2012; Christy et al., 1989; Ganz et al., 1990; Kister et al., 1990; Lin and Ritz, 1993; Lis et al., 2005) (Fig. 2.18).

FT-IR experiments were carried out FT-IR at NR-IGG-UOS Roma, laboratory at the Department of Earth

FT-IRband assignment	
Absorption band (cm^{-1})	Band assignment
3000-3100	Aromatic C-H stretching
2960	Aliphatic C-H stretching vibrations-methyl (CH_3)
2920	Aliphatic C-H stretching vibrations-methylene (CH ₂)
2880	Aliphatic C-H stretching vibrations-methyl (CH ₃)
2850	Aliphatic C-H stretching vibrations-methylene (CH ₂)
1710	C=O stretching vibrations-carbonyl groups
1650	C=O stretching vibrations conjugated with aromatic rings
1600	C=C aromatic ring
1445	Asymmetric aliphatic C-H deformation of methylene and methoxyl
1370	Symmetric aliphatic C-H bending of methyl groups
880	Aromatic out-of-plane-aryl ring with isolated C-H groups
815	Aromatic out-of-plane-rings with 2 neighboring C-H groups
750	Aromatic out-of-plane-4 neighboring C-H groups

Sciences, Sapienza University of Rome on a Bruker Equinox 55 FT-IR spectrometer.

Table 2.1 Band assignment in the infrared spectra of kerogen



Figure 2.19 FT-IR spectrum of a concentrated kerogen. Measured band areas and peaks

The spectra were obtained covering the $4,000-400 \text{ cm}^{-1}$ range and recorded with a spectral resolution of 2 cm⁻¹ and a signal/noise ratio of 42,000:1. About 200 scans were added before Fourier transform. Two



hundred scans per sample were recorded in absorption mode from 4000 to 500 cm^{-1} with a 4 cm^{-1} resolution.

Ground kerogen was mixed with potassium bromide in the proportion of 1 mg/ 100 mg and was analysed as KBr pellets. Two hundred scans per sample were recorded in absorption mode from 4,000 to 500 cm⁻¹ with a 4 cm⁻¹ resolution. Bands were identified by comparison with published spectra (Chen et al., 2012; Lis et al., 2005; Painter et al., 1981; Sobkowiak and Painter, 1992; Wang and Griffiths, 1985) and their assignments were performed according to Drobniak and Mastalerz (2006) (Table 2.1).

Integrated band areas were measured using Omnic spectral analysis software. In particular they are: aromatic C-H stretching region (3,000-3,100 cm⁻¹), aliphatic C-H stretching region (2,800-3,000 cm⁻¹), oxygenated groups and aromatic/olefinic region (1,550-1,750 cm⁻¹), CH₂ and CH₃

bending modes (complex peak at 1,450 cm⁻¹), CH₃ absorption band (peak at 1,375 cm⁻¹), and aromatic outof-plane C-H deformation region (700-900 cm⁻¹) (Fig. 2.19). The aliphatic C-H stretching region (2,800-3,000cm⁻¹) was resolved using Fourier deconvolution (Lin and Ritz, 1993) into five spectral bands at 2,955 (asymmetrical CH₃ stretching), 2,925 (asymmetrical CH₂ stretching), 2,890 (CH stretching), 2,865 (symmetrical CH₃ stretching), and 2,850 cm⁻¹ (symmetrical CH₂ stretching) as shown in Figure 2.20.

The CH₂/CH₃ ratio was calculated using asymmetrical stretching of these bands $(2,925/2,955 \text{ cm}^{-1})$ according to(Lin and Ritz, 1993). Bands in the 1,550-1,750 cm⁻¹ region were resolved into two peaks representing carbonyl/carboxyl absorption at 1,700 cm⁻¹ and an olefinic/aromatic region at 1,600cm⁻¹.

2.1.4 Raman spectroscopy analysis

2.1.4.1 Theory

When radiation passes through a transparent medium, the species present scatters a fraction of the beam in all directions. Nevertheless, in 1928 it was found by the Indian physicist, *C. Raman*, that a small fraction of the radiation scattered by certain molecules differs from that of the incident beam and the shifts in wavelength depend on the chemical structure of the molecules responsible for scattering.

Raman spectra are obtained by irradiating a sample with a powerful laser source of monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured. The scattered radiation is of three types, namely Stokes, anti-Stokes and Rayleigh (Fig. 2.21). The wavelength of Rayleigh radiation is the same of the incident radiation, while a shift toward higher and lower wavenumbers is observed respectively for the anti-Stokes and Stokes radiation.



Figure 2.21 Jablonski energy-level diagram representing the virtual vibrational states involved in Raman inelastic diffusion and the real electronic excited states involved in fluorescence (modified from Schwartz, 2011)

The Raman effect can be described in terms of transitions between vibrational energy levels (Fig.2.21). When an energetic photon strikes a molecule in its ground state, it may raise the molecule to a higher virtual state. As this is not a stable energy state for the molecule, two things can occur. The molecule will probably return to its ground vibrational state and emit a photon with the same energy and frequency as the exciting photon (i.e. Rayleigh scattering). However, some of the excited molecules will not return to the ground state, but to some excited vibrational state. Such a molecule emits a photon, which has a lower energy than the exciting photon, the energy difference being equal to the difference between the initial and final vibrational states. This is Stokes-type Raman scattering. If a molecule, which is in the first excited vibrational state, absorbs the photon then the molecule is again raised to some high, non-stable energy state. This molecule will probably then return to the ground state, and doing so, emits a photon, which has a higher energy than the exciting photon. The difference in energy between the exciting photon and the emitted photon is equal to the energy difference between the two excited vibrational states of the molecule. This is anti-Stokes-type Raman scattering.

The relative populations of the two energy states are such that Stokes Raman is much favoured over anti-Stokes. The quantum theory of Raman scattering shows that the phenomenon results from the same type of vibrational changes that are associated with infrared (IR) absorption. Thus, the difference in wavelength between the incident and scattered radiation corresponds to wavelengths in the mid-IR region.

There are, however, notable differences between the kinds of groups that are IR active and those that are Raman active. The IR absorption requires that a vibrational mode of the molecule have a change in dipole or charge distribution associated with it. Only then can radiation of the same frequency interact with the molecule and promote it to an excited vibrational state. In contrast, scattering involves a momentary distortion of the electron distribution around a bond in a molecule, followed by re-emission of the radiation as the bond returns to it ground state. In its distorted form, the molecule is temporarily polarized, i.e. develops momentarily an induced dipole, which disappears upon relaxation and re-emission.

Each band in a Raman spectrum represents the interaction of the incident light with certain atomic vibrations. Atomic vibrations, in turn, are controlled by the sizes, valences and masses of the atomic species of which the sample is composed, the bond forces between these atoms, and the symmetry of their arrangement in the crystal structure. These factors affect not only the frequencies of atomic vibrations and the observed Raman shifts, but also the number of observed Raman bands, their relative intensities, their widths and their polarization. Therefore, Raman spectra are highly specific for a certain type of sample and can be used for the identification and structural characterization of unknowns.

2.1.4.2 The Raman Spectrometer

Micro-Raman spectroscopic analyses, were performed at the Laboratory of Experimental Volcanology and Petrology (EVPLab) of "Roma Tre" University (Italy) and in the laboratory of the Institute of Earth Sciences (IES) of Science Faculty of the University of Porto (Portugal).

At EVPLab laboratory we used a Jobin Yvon micro-Raman LabRam system in a backscattering geometry, in the range of 700-2300 cm-1 (first order Raman spectrum) using a 600 grooves/mm spectrometer gratings and CCD detector under a maximum of 50X optical power.

A laser source Neodimium-Yag at 532 nm (green laser) was used as the light source and optical filters adjusted the power of the laser (<6mW). The Raman backscattering was recorded after an integration time of 20s for 6 repetitions for each measurement. This, together with the use of green laser and optical filters, allowed to reduce the fluorescence background to optimal values. Between ten to fifteen measurements were performed for each samples to ensure reproducibility of the measurements.

Each organic grain was analysed with a 2 µm diameter spot and a 50× objective lens (Fig. 2.22).



Figure 2.22 Jobin Yvon micro-Raman LabRam system from EVPLab laboratory (Roma Tre)

In Chapter 4 and partially 6, analyses were performed at the Institute of Earth Sciences (IES) of the University of Porto, using a Horiba Jobin-Yvon LabRam Microscope XploRATM system in a backscattering geometry, in the range of 700-2300 cm⁻¹ (first order Raman spectrum) using a 600 grooves/mm spectrometer gratings and CCD detector. The instrument is equipped with 50X and 100X objective lens, and an excitation wavelength of 532 nm from a Ar⁺ laser at a power of 25 mW. Optical filters adjusted the power of the laser were used to reduce of more than 10% the output power.

2.1.4.3 Band assignment for Raman spectra in dispersed organic matter

Raman spectral signal of kerogen is concentrated in a "first order" region between 1,000 and 2,000 cm⁻¹ and "second order" region between 2,000 and 3,500 cm⁻¹. Bands in the second order region are visible only in higher thermal maturity samples (Beyssac et al., 2003) and they were never observed in our set of samples.

The first order Raman spectra for carbon materials consist of two main bands known as D and G band (Friedel and Carlson, 1972; Tuinstra and Koenig, 1970) and in other less defined bands that can vary depending on the kind of material and rank degree (Li, 2007; Potgieter-Vermaak et al., 2011).

D and G bands correspond respectively to breathing and stretching mode in sp² bonded carbon clusters (Ferrari and Robertson, 2000). In graphite, the G band is related to E_{2g} vibration mode of a crystal with D_{6h}^4 symmetry, i.e. to in-plane vibration of aromatic carbons at 1580-1600 cm⁻¹. The D band was originally observed at 1355 cm⁻¹ with a 488 Ar-ion laser and was related to the in-plane A_{1g} mode that is active only in the presence of lattice defect of polycrystalline graphite (Pócsik et al., 1998). It's worth to note that D mode is dispersive and vary with photon excitation energy, while G peak is not dispersive (Castiglioni et al., 2004; Ferrari and Robertson, 2000; Ferrari and Robertson, 2004; Nestler et al., 2003; Pócsik et al., 1998).

Dealing with very disordered materials, the contribution of other features at 1,100-1,200 and 1,400-1,500 cm⁻¹ cannot be neglected and even the assignment of the G and D bands to specific vibrational modes is questioned. Unfortunately, very few works exist that attempt to explain the origin of these bands and the

results are often contradictory. For this reason, assignment of Raman bands for disordered material is still matter of debate.

In high-rank coals, Beyssac et al. (2002), based on literature work (Beny-Bassez and Rouzaud, 1985; Nemanich and Solin, 1979; Tuinstra, 1970) (Fig. 2.23) propose the presence of two additional bands: the D2 band, that appear as a right ned shoulder of the G band at approximately 1,620 cm⁻¹ and the D3 band, which is a wide band at approximately 1,500 cm⁻¹. The band has been attributed to out-plane defects like tetrahedral carbons by Bèny-Bassez and Rouzaud (1985), or to small crystallite size by Nemanich and Solin (1979).



Figure 2.23 Raman spectra deconvolution in the first order region according to Beyssac et al. (2002)

Working on carbon material matured at lower temperatures (about 200-320°C), Lahfid et al., (2010) (Fig. 2.24) and Sadezky et al. (2005) propose the presence of an additional band called D4 at about 1,200 cm⁻¹, attributed to sp^3-sp^2 bonds or C–C and C=C stretching vibrations of polyene-like structures.



Figure 2.24 Raman spectra deconvolution in the first order region according to Lahfid et al. (2010)

In low maturity coal, the Raman spectra of very disordered carbonaceous matter are significantly different and more complex than the spectra of highly ordered carbon materials such as those investigated by Beyssac et al. (2002) and Lahfid et al. (2010).

One of the first order band assignment for disordered materials, based on analyses on Victorian brown coal, is provided by Li et al. (2006) and Li (2007). In their work the Raman spectrum was deconvoluted into 10 bands, as illustrated in Fig. 2.25.



Figure 2.25 Raman spectra deconvolution in the first order region, according to Li et al. (2007)

In their work the authors proposed the assignment of the G band (1,580-1,600 cm⁻¹) to aromatic quadrant ring-breathing mode with little contribution from graphitic structures and the D band (1,300 cm⁻¹), not to defects, as previously proposed for highly ordered carbonaceous matter, but to disorder of fused benzene rings having more than six rings, but less than graphite. Li et al., (2007) attributed the band at about 1,700 cm⁻¹ (Gl band) to carbonyl group C=O, while the Gr (1,540 cm⁻¹), V1 (1,465 cm⁻¹) and Vr band (1,380 cm⁻¹) that represent the "overlap" between D and G are assigned to semi-circle breathing of 3-5 membered aromatic rings and methylene or methyl aromatic rings with mixed sp²- sp³ structures. At lower wavenumbers they found that the S band (1,185 cm⁻¹) band together with Sl band (~1,220 cm⁻¹) act as the shoulder of the D band (1,230 cm⁻¹= aryl-alkyl ether; para-aromatics) and mainly representing C_{aromatic}–C_{alkyl}, aromatic rings. Finally S_R band (1,060 cm⁻¹) is assigned to C-H on aromatic rings and benzene ring and the R band (960-800 cm⁻¹) C-C to alkanes and cyclic alkanes and/or C-H on aromatic rings.

More recently based on analyses on carbon nanotubes Rebelo et al. (2015) proposed new assignments on the first order deconvoluted peaks in which the "D region" is deconvoluted with a central Lorentzian D band at
1,350 cm⁻¹ and two satellites Gaussian band called Dl and Dr (left and right) respectively at ~1,250 and ~1,400 cm⁻¹ (Fig. 2.26).



Figure 2.26 Raman spectra deconvolution in the first and second order region . Redrawn after Rebelo et al. (2015)

D band corresponds to vibration with A_{1g} symmetry associated with interlayer arrangement. DI and Dr are assigned to identical vibration of the D band, but in low size aromatic domains. For higher Raman shift values the G band is fitted with a Lorentzian shape at ~1,580 cm⁻¹ surrounded by a Lorentzian Gr peak at ~1,610 cm⁻¹ and a Gaussian Gl peak near 1,500 cm⁻¹ (Heise et al., 2009).

The G band corresponds to vibrations with E_{2g} symmetry from in-plane aromatic graphene sheets and Gr band to the same vibration in low size aromatic domains. A further band, called S band, was used to fit a relative small feature in the left side of the spectra, at about 1,120cm⁻¹ Bands S and Gl were assigned to a fingerprint of polyacetylene like structures or areas of conjugated double bonds mainly present in the border of structures were aromaticity has been broken upon functionalization (Shirakawa et al., 1973). For highly functionalized materials, other bands can arise at 1,180 cm⁻¹ (Sr) and at 1,480 cm⁻¹ (Gv).

For a further understanding of disorder, it is important to obtain appropriate correlations between the spectral features and effects arising from covalent functionalization, (transformation of sp^2 aromatic carbon into sp^3 carbon) and distinguish them from other structural effects and deviations to the perfect graphite structure, namely, the curvature in carbon nanotubes or nanofibers, the reduction of the graphitic crystals size in few layer graphene and edge structures, or the presence of amorphous carbon.

2.2 Inorganic fraction of sediments

2.2.1 X-Ray Diffraction of clay minerals

2.2.1.1 Samples preparation

In the Academic Laboratory of Basin Analysis (ALBA) of "Roma Tre" University, the procedure described by Moore and Reynolds (1997) and modified by Giampaolo and Lo Mastro (2000) was adopted to analyze the $<2 \mu m$ grain size fraction of sediments (equivalent spherical diameter).

About 20 g of the whole-rock sample were slightly crushed by hand in an agate mortar and put in a flask with 150 ml of distilled water (Fig. 2.27). Samples were disaggregated in distilled water by swinging the clay-rich mixture at 200 oscillation/min (Fig. 2.28).

Then, 50 ml of the suspension was put in a plastic tube and centrifuged to separate the $<2 \mu m$ fraction according to standard procedures which take into account water temperature and the centrifuge radius (Figure 2.29). After centrifugation, the suspension containing $<2 \mu m$ were separated, pipetted, and dried at room temperature on glass slides to produce a thin highly oriented aggregate (Fig. 2.30, Giampaolo and Lo Mastro, 2000).



Figure 2.27 Crushed rock samples in distilled water

Qualitative and semi-quantitative analyses were performed with a Scintag X1 X-ray system (CuK α radiation) at 40 kV and 45 mA (Figure 2.31). Oriented mounts were analysed in air-dried and ethylene glycol solvated forms (saturation in ethylene-glycol atmosphere at room temperature for 24 h) in the 1 to 48°20 and 1 to



Figure 2.28 Clay-rich mixture swinging at 200 oscillations/min



Figure 2.29 Centrifuge up to 4,000rpm

30°20 ranges respectively with a step size of 0.05°20 and a counting time of 4 s per step. The illite content in mixed-layer I–S was determined by the delta two-theta method after decomposing the composite peaks between 9–10°20 and 16–17°20 (Moore and Reynolds, 1997) and by modeling X-ray diffraction patterns using Pearson VII functions and the DMSNT Scintag associated program. The I–S stacking order (Reichweite parameter, R; Jagodzinski, 1949) was determined by the position of the I 001–S 001 reflection between 5 and 8.5°20. Kübler index (KI) measurements were made by first subtracting the background from the raw data, and then applying a profile fitting method (Lanson, 1997). From the fitted data, KI was measured by the FWHM (full-with-half-maximum) parameter of the program. Half-peak widths were calibrated using Warr and Rice's standards (1994). Peaks in relative close position were selected for clay



Figure 2.30 Air-dried oriented slides



Figure 2.31 Scintag X1 X-ray system

mineral quantitative analysis in order to minimize the angle-dependent intensity effect. Integrated peak areas were transformed into mineral concentrations by using mineral intensity factors as a calibration constant (for a review, see Moore and Reynolds, 1997). Non-clay minerals were not taken in account in the $<2 \mu m$ grain-size fraction quantitative analysis.

2.2.1.2 Thermal maturity interpretation

The study of clay mineralogy has provided several useful tools for diagenesis and very low-grade metamorphism by providing information on the burial and thermal history of sedimentary sequences (Aldega et al., 2007a; Aldega et al., 2010; Aldega et al., 2007b; Botti et al., 2004; Corrado et al., 2005; Di Paolo et al., 2012). Clay minerals in shales and sandstones undergo diagenetic and very low-grade metamorphic reactions in response to sedimentary and/or tectonic burial. Reactions in clay minerals are irreversible under normal diagenetic and anchizonal conditions, so that exhumed sequences generally retain indices and fabrics indicative of their maximum maturity and burial (Merriman and Frey, 1999).



Figure 2.32 Calculated XRD patterns of illite-smectite mixed layers with different illite content and stacking order: A) random ordered I-S; B) short range ordered I-S; C) long range ordered I-S. After Pollastro (1990)

An important reaction occurring in shales during burial diagenesis and in hydrothermal settings is the gradual conversion of smectite to illite through I-S mixed layers as intermediate phases. The progressive trend ranging from early diagenesis to epizone includes the following series: dioctahedral smectite - disordered mixed layers (R0) - ordered mixed layers (R1 and R3) - illite dioctahedral white K-mica (muscovite). This prograde series is characterized by various crystal structural changes as the decrease of proportions of swelling phases and the increase of ordering in mixed layers. The layers are stacked along a direction parallel to the c-axis in random, partially regular, or regular sequences. The classical terminology for the stacking order is based on the term R (Reichweite; Jadgozinski, 1949) that expresses the probability, given a layer A, of finding the next layer to be B. The R parameter may range from 0 to 3. R=0 means that there is no stacking order and illite and smectite layers are stacked randomly along the c-

axis, R=1 indicates that a smectite layer is followed by an illite layer and a stacking order appears in the interstratification sequence, R=3 means that each smectite layer is surrounded by at least three illite layers on each side.

In this report, I-S structures will be described by means of the Reichweite nomenclature using R1 to mean R=1, R3 for R=3, etc. (Figure 2.32).

The most common approaches utilizing I-S "geothermometer" in diagenetic studies are vertical profiles from wells and outcrops and thermal maturity mapping at local and regional scale. In the first case, illitization



Figure 2.33 Correlation scheme among clay mineral geothermometers, vitrinite reflectance data, hydrocarbon and metapelitic zones and paleo-temperatures. After Merriman and Frey (1999)

reaction profiles are generally produced. They are compared to the present geothermal gradient profile and organic matter maturity profiles in order to determine the temperature range in a particular point of the well correlating them to hydrocarbon generation phases (Pollastro, 1993; Merryman and Frey, 1999, Figure 2.33). Although the conversion to paleotemperatures depends on more than one factor (e.g., heating rate, protolith, fluid composition, permeability, fluid flow), Pollastro (1990; 1993) summarized the application of two simple time-temperature models for I-S geothermometry studies based primarily on the duration of heating (or residence time) at critical I-S reaction temperatures. The first model was developed Hoffman (1979) for long-term, burial diagenetic settings that can be applied to most geologic and petroleum studies of sedimentary rocks and basins of Miocene age or older. In this model the major changes from R0 to R1 and from R1 to R3 occur in the temperature range of about 100-110 °C and of 170 °C-180 °C respectively and a minimum heating duration of 2 My is generally placed (Hoffman and Hower, 1979). The second model, which was developed for short-lived heating events, applies to young basins or areas characterized by relatively recent thermal activity with high geothermal gradients, or to recent hydrothermal environments.

Such settings are those where relatively young rocks were subject to burial temperatures in excess of 100 $^{\circ}$ C for <2 My. In this model the conversion from R0 to R1 and from R1 to R3 ordering occurs at about 130-140 $^{\circ}$ C and 170-180 $^{\circ}$ C respectively (Jennings and Thompson, 1986) . Many authors have studied the use of illite-smectite reaction as a measurement of temperature. Bibliographic data of approximate temperatures for changes in mixed layer illite/smectite, relative to different geological settings, are reported in Table 2.2.

%l in l-S	0-20% (smectite to R0)	30-60% (R0)	60-80% (R0 to R1)	80-90% (R1 to R3)	90-95% (R3)	100% (illite)
(R number)			, , , , , , , , , , , , , , , , , , , ,			
Hoffman &						
Hower	50-60°C		100-110°C	170-180°C		210°C
1979						
Jennings &			120 140%	170 100%		
1 nompson			130-140°C	170-180°C		
1900						
Broekstra		90-130°C (only		200°C	250-280°C	
1984		40% I)		200 C	250 200 C	
Merriman						
& Frey	<100°C		100°C		200°C	300°C
1999						
Jaboyedoff						
& Thelin	<100°C		100-130°C		200-250°C	
1999						
Uysal et al.			115-120°			
2000			113-120			

Table 2.2 Approximate temperature ranges derived from mixed layer illite/smectite composition and stacking order (according to different authors: left column)

2.2.2 Low temperature thermochronology

2.2.2.1 Theory

Apatite fission-track analysis on sedimentary successions provides an evaluation of the thermal history, giving information on both temperature of burial and time of exhumation (Zattin et al., 2002). Unlike other burial indicators (e.g. vitrinite reflectance or %I in I-S) apatite fission-track (FT) analysis is a reversible indicator because the sample age and the track length distribution can reflect multiple cooling and heating events.

FT dating is based on the spontaneous fission of 238U which produces a damaged zone or a linear defect (spontaneous track) in the crystal lattice (Fleischer et al., 1965). FT dating is very similar to other isotopic dating methods based on the decay of an unstable parent to a stable daughter atom. The age is function of the proportion between the abundance of the new stable isotope and the parent unstable atom. In FT dating methodology, these two quantities are substituted by the number of observable tracks and the amount of uranium present in the sample. The uranium content is determined by the number of induced tracks obtained by irradiation with a known dose of thermal neutrons in a nuclear reactor. This irradiation causes the fission

of 235U which isotopic ratio with 238U is constant in nature. Therefore, the age of the sample can be estimated by the ratio between spontaneous and induced tracks.

The most important parameter affecting the stability of tracks is temperature. As temperature increases, a decreasing of the number of tracks and a reduction of their length is visible. This process is known as annealing. The FT annealing rate depends on the chemical composition of apatite (Green et al., 1986) and on cooling or heating rate (Gleadow and Duddy, 1981). It generally occurs between about 60 °C and 125 °C for heating time of about 10 My and can be used to reconstruct the thermal history of basins, from deposition and burial of sediments through subsequent cooling related to uplift and erosion.

The temperature range in which reduction of lengths occurs is known as Partial Annealing Zone (PAZ; Wagner and Van den Haute, 1992). According to this concept, temperatures of any geological setting can be divided into three zones with respect to fission-track annealing: - the total annealing zone, in which spontaneous tracks are immediately erased after any fission event; - the partial annealing zone, in which reduction of lengths occurs with the increase of temperature; - the stability zone, where tracks are stable. FT record the age of cooling and the exhumation rate of rocks from the total annealing zone, evaluate the thermal history of a sedimentary succession in the partial annealing zone and assess the age of the source rock in the stability zone giving information on the provenance of the sediments. As it is possible to see in the Arrhenius diagram (Fig. 3.34), the annealing temperatures depend on the rate of the geological process and the PAZ temperature range cannot be univocally defined.



Figure 2.34 Reduction of the FT density as a function of temperature in drill-hole samples from the Otway Group sandstones, after Gleadow and Duddy (1981)

For apatite, temperatures between 140 and 120 °C are cited for the bottom whereas 70 to 40 °C for the top of the PAZ. More precisely, Gleadow and Duddy (1981), on the basis of data obtained from drill holes samples in the Otway basin, suggest a PAZ between 145 and 80 °C for heating events 1 My long, and between 110

and 45 °C for events 1 Gy long. The cooling range in the PAZ has been simplified in a single temperature value to which the age has to be referred. This temperature value was defined by Dodson (1973) as the closure temperature. Wagner and Reimer (1972) suggest that the closure temperature correspond to temperature at which 50% of the track are retained. In conclusion, the best assessments of the closure temperature are 128 °C, 112 °C, 98 °C and 85 °C for cooling rates of 100 °C/My, 10 °C/My, 1 °C/My and 0.01 °C/My, respectively (Brandon et al., 1998). Most of the methodological limitations are due to the young age of sediments (less than 10 My). In fact in this short period of time, the accumulation time of tracks can be too short to produce a good number of measurable tracks with a "normal" uranium content (about 35 ppm) causing relevant errors in the age determination (Zattin, 2003). A different problem derives from the relationships between the apatite chemistry and the annealing degree. In terrigenous rocks, it is very probable to analyse, in the same sample, apatites coming from different source rocks with different chemical composition. Finally, different source areas may have different cooling times and, as a consequence, the predepositional history of detrital apatites cannot be the same for the single grains in the samples and therefore quantitative modelling of data can be very difficult given the heterogeneity in the thermal history of single grains. Radial plots and/or peak-fitting statistical method can be used to discriminate different inherited populations and overcome this problem (Gailbraith, 1988; Brandon and Vance, 1992; Brandon et al., 1998; Fig. 3.35).



Figure 3.35 Graphical methods for visualization of FT data. a) Radial plot: each single cross represents a crystal; age can be read on the intersection between the line linking the origin with the point along the arc; the x coordinate is the precision of the age which increases towards the arc; the error ±2, represented by the bar on the origin, is easily detected superimposing the bar on the selected point. b) Probability density plot: the thicker line represents the observed distribution whereas different tones of grey are assigned to the individual peaks obtained by binomial peak-fitting method from Zattin (2003)

2.2.1.2 Samples preparation and Apatite (U-Th)/He dating

In this work low-temperature thermochronological analyses were performed by Prof.. Massimiliano Zattin and dr. Benedetta Andreucci at the University of Padova.

In detail, apatite grains were separated after careful crushing using heavy liquids and magnetic separation techniques. Mounts of apatites in epoxy were ground and polished to expose planar surfaces within the grains and then etched with 5N HNO3 at 20°C for 20 seconds to reveal spontaneous fission tracks. Samples

then were irradiated with thermal neutrons in the reactor at the Radiation Center of Oregon State University with a nominal neutron fluence of 9 x 1015 n cm-2. The CN-5 dosimeter was used to measure neutron fluence. After irradiation, induced fission tracks in the low-U muscovite that covered apatite grain mounts and glass dosimeter were revealed by etching in 40% HF at 20°C for 40 minutes. Apatite Fission Track (AFT) dates were calculated using the external-detector and the zeta-calibration methods (Hurford and Green, 1983) with IUGS age standards (Durango, Fish Canyon and Mount Dromedary apatites; Hurford 1990) and a value of 0.5 for the $4\pi/2\pi$ geometry correction factor. The analyses were subjected to the χ 2 test (Gailbraith, 1981) to detect whether the data sets contained any extra-Poissonian error. A χ 2 probability of less than 5% denotes a significant spread of single grain dates.

Apatite (U–Th)/He dating (AHe) was carried out at the University of Arizona He dating laboratory. Apatite grains which satisfied quality requirements (e.g., no inclusions, $> 60 \mu m$ in minimum dimension, etc.; see Ehlers and Farley, 2003) were extracted from heavy mineral separates and up to five crystals measured for alpha-ejection correction following methods described in Reiners et al. (2007).

Single crystals were loaded into 0.8 mm Nb tubes, and degassed under vacuum by heating with a Nd-YAG laser. The concentration of 4He was determined by 3He isotope dilution and measurement of the 4He/3He ratio through a quadrupole mass spectrometer. U, Th and Sm concentrations were obtained by isotope dilution using an inductively coupled plasma mass spectrometer.

2.3 Thermal modeling

Basin and Petroleum System Modeling allows geoscientists to examine the dynamics of sedimentary basins and their associated fluids to determine if past conditions were suitable for hydrocarbons to fill potential reservoirs and be preserved there.

Basin modelling allow to assess:

- 1) The burial history of the basin (back-stripping)
- 2) The thermal history of the basin
- 3) The maturity history of the source rocks.

In this work basin modelling was performed using Basin Mod-1D software for Windows (1996) and e-simba software by ENI. These softwares allow reconstructing the burial and thermal evolution of sedimentary sequences both in undeformed and deformed conditions from geological data (e.g., age of sedimentary sequences and tectonic/erosional events, pure and mixed lithologies, thicknesses, porosity, permeability and thermal conductivity of sedimentary sequences).

These data derive from the integration between the database of physical features provided by the libraries available of the modelling software and the geological information coming from the regional literature and the stratigraphic and structural data collected in the field or wells. Burial curves were corrected for decompaction according to the Sclater and Christie's method (1980). Sea level changes were neglected, as sediments thickness, more than water column controls the thermal evolution (Butler, 1992).

The evaluation of the maturation pattern for kerogen is carried out both in Basin Mod and in esimba software using the EASYR_o% kinetic model proposed by Sweeney and Burnham (1990). EASYR_o% model adopts the Arrhenius first-order parallel equation based on changes in vitrinite composition with time and temperatures. Using a distribution of activation energies, the model calculates the extent to which a series of products are generated from vitrinite during maturation (Eqs. 1 and 2). Choosing an A value of 1.10^{13} s⁻¹ and an *Ea* distribution, the extent of the reaction (Eq. 3) is then applied to calculate vitrinite reflectance (Eq. 4):

$$dw/dt = -kw \tag{1}$$

$$k = \operatorname{Aexp}\left(Ea/R\mathrm{T}\right) \tag{2}$$

$$\mathbf{F} = 1 - w/w_0 \tag{3}$$

$$\%R_{o} = -\exp(3.7F - 1.6) \tag{4}$$

where *w* is the amount of unreacted component, w_0 the initial concentration of total reactant, *k* the reaction rate, A the Arrhenius (frequency) factor, *Ea* the activation energy, *R* the universal gas constant (kJ mol⁻¹ K⁻¹) and T the absolute temperature.

Vitrinite reflectance values carried out as outputs from the EASYRo% model, can be compared with measured values and the model can be adjusted to improve the match.

Other thermal maturity indicators used in this work, such as Tmax or %illite in I-S mixed layers, have been converted into vitrinite reflectance equivalent and used to calibrate thermal modelling with Basin Mod software (Chapters 4-5-6).

Moreover, in Chapter 3 where paleo-pressure data were available and ages are better constrained, different equation were used in order: 1) to model the vitrinite reflectance maturation pattern including the effect of pressure in a overpressure interval and 2) to model the smectite-illitization using a properly kinetic equation proposed by Cuadros and Linares (1996).

The alternative kinetic equations PresRo[™] (Carr, 1999) and T-P-Ro (Zou et al., 2001) have been used to verify the effect of pressure on vitrinite maturation.

Carr's model (1999) model differs from the EASYRo% in the calculation of the Arrhenius factor (A) that in the PresRo[™] is modified by overpressure according the equation:

$$A = 1.10^{13} \exp(-p/c)$$
(5)

where p is overpressure expressed in psi and c is a constant equal to 590. The so calculated A value is then replaced in equation 2 and vitrinite reflectance is finally calculated using Eqs. 3 and 4.

The T-P-Ro model (Zou et al., 2001) modifies Ea in Eq. 2 using an activation energy Ep (in Eq.6) that varies as a function of the difference between hydrostatic and pore pressure.

$$Ep = E_0 + \beta (\mathbf{P} - \mathbf{P}_0) \tag{6}$$

were β is a pressure factor empirically assumed to be 130 cal mol⁻¹, P the total pore pressure (MPa) and P₀ is the hydrostatic pressure (MPa). Vitrinite reflectance is then calculated using Eqs. 3 and 4.

The two models were run modifying either the Arrhenius factor or the activation energies in the $EASYR_0\%$ model on an Excel spreadsheet.

Smectite to illite reaction was modelled using the kinetic equation 7 proposed by Cuadros and Linares (1996).

$$-dS/dt = kK^{0.25}S^5$$
(7)

where *S* is the proportion of smectite layers in I-S mixed layers, *t* is the time expressed in days as a function of sedimentation rate, *k* is the rate constant and *K* is the concentration of potassium. *k* is temperature dependent through the equation suggested by Cuadros (2006) with $k = 1.213 \times 10^{-9} \text{ T}^2 - 6.608 \times 10^{-8} \text{ T} - 2.033 \times 10^{-7}$ where T is expressed in Celsius degree (°C).

A Matlab code was developed in ALBA laboratory (at Roma Tre University) to model the smectite illitization process where input data for each stratigraphic interval of the well are: smectite content in mixed layers I-S, sedimentation rate, geothermal gradient and K availability.

Chapter 3

Overcoming pitfalls of vitrinite reflectance measurements in the assessment of thermal maturity: the case history of the Lower Congo Basin

3.1 Introduction

Vitrinite reflectance (R_0 %) has been proven to be the most reliable technique in evaluating thermal maturity of sediments as it is highly sensitive to temperature and is not affected by retrograde metamorphism (Teichmüller 1987). However, several limitations arise when exploring targets that are devoid of vitrinite macerals (e.g., Lower Paleozoic rocks; Caricchi et al., 2016) and/or are poor in organic matter content.

In addition, high hydrogen contents in kerogen and aliphatic-rich vitrinite may suppress reflectance measurements (Petersen and Rosenberg, 1998; Carr, 2000). Suppression occurs from very shallow depths and goes on with burial until the hydrogen is completely removed from the kerogen structure (Carr, 2000).

Suppression phenomena were widely reported in the North Sea (Petersen et al., 1998; Senftle and Landis, 1991), in the Carnarvon Basin in Western Australia (Wilkins et al., 1995) and in the Malay Basin in the Vietnam offshore (Petersen et al., 2009).

Moreover, other pitfalls in vitrinite reflectance measurements can occur in geological environments characterized by rapid sediments supply as fast sedimentation may generate overpressure and retard organic matter maturation (Carr, 1999; Dalla Torre et al., 1997; McTavish, 1978).

Retardation phenomena refers to a thermochemical reduction in reaction rate resulting from the effects of overpressure in a sedimentary basin. Carr (1999) and Uguna et al. (2012, 2015) pointed out that overpressure appears to restrict the release of volatiles from vitrinite structure. Thereby vitrinite retains lower reflectance values than those expected at the same temperature under hydrostatic pressure. Retardation processes due to overpressure have been extensively recognized in the North Sea (MacTavish, 1978), in the Yinggehai Basin (Hao et al., 1995, 2007) and in the Niger paleodeltas (McTavish, 1998)

In these cases, the use of other thermal maturity indicators derived from the analysis of the organic (e.g., TAI, Tmax) and/or the inorganic fraction of sediments (e.g., fluid inclusions, apatite fission tracks and mixed layer illite-smectite; e.g., Aldega et al., 2014; Cantarelli et al., 2013; Caricchi et al., 2015a, b; Di Paolo et al., 2014) may overcome these issues.

The need to drastically reduce the errors caused by a misinterpretation of thermal maturity is of particular relevance in the exploration of deepwater plays where drilling costs are significantly high (Levell et al., 2016).

In this work we unravel, using a multimethod approach, the thermal history of the Malembo Fm in the Lower Congo Basin which is one of the worldwide main targets for deepwater oil exploration (Anderson et al., 2000; Anka et al., 2009; Gay et al., 2004; Uenzelmann-Neben, 1998; Valle et al., 2001). Vitrinite reflectance profile throughout a 5 km deep well drilled in the basin presents an unusual trend with respect to the expected paleo-geothermal gradient since Oligocene times as also reported by Anka et al. (2013) in the same stratigraphic interval.

For this reason we combined mixed layer illite-smectite (I-S) and vitrinite- and bitumen-reflectance (R_0 % and R_{oeq} %) to model the thermal evolution of the sedimentary succession by using different kinetics approaches (Carr, 1999; Cuadros and Linares, 1996; Sweeney and Burnham, 1990; Zou et al., 2001). Models were discussed on the base of present-day temperature and pressure conditions measured in the well.

In this paper, we pointed out that in case of retardation and/or suppression, the classical Sweeney and Burnham's (1990) thermal model fails in assessing hydrocarbon generation/expulsion windows. Thus, thermal and burial models should be calibrated using appropriate kinetic equations (Carr, 1999; Dalla Torre et al., 1998; Zou et al., 2001) or complementary inorganic thermal indicators (e.g., mixed layer I-S) whose maturation patterns do not seem to be affected by retardation phenomena in case of overpressure (Colten-Bradley, 1987).

3.2 Geological Setting

3.2.1 Western Africa offshore: from rifting to passive margin evolution

Western African continental margin formed as a result of Gondwana break-up in the early Cretaceous (Brice et al., 1982; Standlee et al., 1992). First continental rifting occurred since the end of the Late Jurassic-Neocomian (~140-150 My) (Binks and Fairhead, 1992; Davison, 1999; Dupré et al., 2011) whereas crustal separation and onset of oceanic spreading took place ~133 My ago (Dupré et al., 2011) and remained active until the Late Aptian (Brice et al., 1982; Dupré et al., 2011; Karner et al., 1997; Lavier et al., 2001). Various deep underfilled lacustrine basins formed during rifting in Early Cretaceous times (Anderson et al., 2000). Continental sedimentation went on until Aptian times when it evolved to shallow marine conditions driven by thermal subsidence of the passive margin (Anderson et al., 2000; Séranne, 1999; Valle et al., 2001). Currently the basins forming the western Africa Passive margin are: the Gabon, the Lower Congo and the Kwanza Basins (Fig.3.1).



Figure 3.1 Simplified map of the basins forming the West African margin and extension of the Miocene fan-delta complex. Redrawn after Anderson et al., (2000)

3.2.2 Stratigraphic evolution of the Lower Congo Basin

The Lower Congo Basin is one of the sub-basins developed on thinned continental crust along the Western Africa passive margin. It is located between the Gabon Basin to the north and Kwanza Basin to the south (Fig.3.1).

The sedimentary infill is organised into three megasequences (Ala and Selley, 1997; Brice et al., 1982; Valle et al., 2001): 1) the "syn-rift megasequence" (Late Jurassic-Early Cretaceous), 2) the "transitional/early drift megasequence" (Aptian) and 3) the "drift megasequence" (Albian-Holocene).

"Syn-rift" sedimentation in the Early Cretaceous is related to different phases of rifting (de Matos, 1999; Karner and Driscoll, 1999) which led to the generation of deep, underfilled lacustrine basins (pre-salt sediments of the Lucula and Bucomazi formations, Fig. 3.2).

The end of rifting is recorded in the Early Aptian by a transgressive clastic succession composed of fluvial sandstones and marine shales (Chela formation, Fig. 3.2) overlain by the evaporitic levels of the Loeme formation (Anka et al., 2009) (Fig. 3.2). Due to halokinetic movements, the Loeme formation shows large

Chronostra-		Formations and Depositional environments					
tigraphy		Slope Shel					
Quaternary							
NEOGENE	Miocene	ALEMBO	MARINE	channelling erosion of shelf and slope and deposition			
	Oligo- cene	W	and fans				
OGENI	sne				<u></u>		
PALEC	Eoce	ANA	LANDANA	channelling erosion of shelf and slope and depositior of turbidite			
	Paleo- cene	LANDA					
E CREATACEOUS	Maes- tricht	IABE MARINE	NE	and fans			
	Santonian/ Coniacian		occasional turbidites				
LAT	Cenomanian						
EOUS	Albian	PINDA MARINE	trasgressive				
12	c	LOE	ME	evaporites	^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^ ^		
RET	Aptia	CHELA		transitional			
EARLY C	an Barre- mian	JCOMAZI	la	custrine			
	Neocomia	ULA BL					
JUR. Tithonian		ti la	uvio- icustrine				
Mudstone and shale Limestone Siltstone Calcareous mudstone Sand, Sandstone Salt and evaporites							



thickness variations, from nearly zero to up to 1,000 m along Congo and Angola margins (Anderson et al., 2000; Valle et al., 2001).

The "drift" group consists of the Pinda, Iabe, Landana and Malembo formations (Fig.3.2).

The Late Albian Pinda Formation is composed of shallow marine clastic/carbonate shelf facies evolving to deep open marine shales and mudstones (Lavier et al., 2001).

Lithologies of the Iabe and Landana formations consist of marine shales and minor silt layers deposited during a phase of intense channeling erosion on the shelf and slope and the deposition of turbidite fans (Gay et al., 2004).

The Early Oligocene is characterized by a major erosion phase (Lavier et al., 2000) linked to the "Oligocene unconformity" recognized along the whole West African margin (Teisserenc and Villemin, 1989). During this time, a significant increase in terrigenous supply led to the development of the Congo deep-sea fan in the abyssal plain (Anka and Séranne, 2004).

During the Early and Late Miocene, two events of uplift were recorded. The first occurred 22 My ago as a result of seaward margin tilting (Anka et al., 2009; Brice et al., 1982; Valle et al., 2001),

whereas the second was a minor event occurred in Tortonian times (Lavier et al., (2000; 2001).

The main tectonic feature in the Lower Congo Basin is the gravitational spreading of post-rift sediments above the "decollement" layer made up of Aptian

evaporites (Duval et al., 1992; GyöRgy Marton et al., 2000; Spathopoulos, 1996). As a consequence, the post-rift sediments underwent thin-skinned extension to the east whereas thin-skinned compressional structures dominate to the west (Anderson et al., 2000).



Figure 3.3 Well stratigraphy and sampling location. Black dots indicate the depth intervals where cuttings have been collected.

3.3. Materials

Samples derive from cuttings from a well drilled in the northern sector of the Lower Congo Basin. Drilled succession, from depths between 1,290 and 4,950 m, range in age from the Upper Miocene to the Oligocene and belong to shales and near shore to deep water sandstones of the Malembo formation (Fig.3.3). The Upper Miocene has a thickness of about 800 m and only one sample is available for this interval (collected between 1,290 and 1,300 m). Four samples were collected in the Middle Miocene section, whose bottom lies at depth of 1,750 m and ten more samples are from the 1,950 m-thick Lower Miocene sediments. In the Oligocene portion of the succession, seventeen samples were collected at depths between 3,700m and 4,950m (Fig.3.3).

3.4. Results

3.4.1 Organic matter optical analyses

The Oligocene-Upper Miocene sedimentary succession shows differences in organic matter composition throughout the well. Vitrinite-huminite fragments are dominant up to depths of 4,000 m, whereas amorphous organic matter was observed from 4,000 down to 4,200 m (Table 3.1).

Reliable samples for R_0 % analyses are located at shallow depths (1,290, 1,390, 1,600 m), at the transition between the

Middle Miocene and Lower Miocene (between 1,800 and 2,200 m) and in the Lower Miocene (between 2,900 and 3,400 m).

In the Upper Miocene, the only suitable sample shows a mean reflectance value of 0.35%. In the Middle Miocene, a slight increase in thermal maturity as function of depth was observed

with mean values of 0.33 R_o% at 1,390 m to 0.38 at 1,800 m. In the upper part of the Lower Miocene section



Figure 3.4 Distribution of vitrinite and bitumen reflectance against depth..Black dots indicate average reflectance values measured on vitrinite, grey dots indicate average reflectance values measured on bitumen and then converted into vitrinite reflectance equivalent values values using Schoenherr's et al., equation (2007).

between 1,950 and 2,200 m, R_0 % values are constant at about 0.39 R_0 %, whereas they range from 0.42 to 0.52 R_0 % (between 2,920 and 3,360 m) in the lowermost Miocene (Fig. 3.4).

Bitumen reflectance measurements are from depths between 3,900 and 4,580m showing a range of R_{oeq} % values between 0.82 and 1.31% according to different equations (Tab. 3.2).

Bitumen shows typical morphology and texture as described by Barker and Bone (1995) and does not display any fluorescence. Bitumen reflectance, measured on polished sections, was converted to vitrinite reflectance (Roeq%) values by using published equations (Jacob, 1989; Landis and Castaño, 1994; Schoenherr et al. (2007) (Table 2). Schoenherr

et al.'s (2007) equation has been preferred as it includes both Jacob's (1989) and Landis and Castaño's (1994) datasets.

3.4.2 Mineralogical data

3.4.2.1 Whole rock and clay mineral content

Semiquantitative analysis of randomly oriented whole-rock powders for the Oligocene to Upper Miocene sediments of the Malembo formation is shown in Table 3.1. Phyllosilicates are major minerals and their amount range between 57 and 85%. Quartz shows contents in the range of 3-7% for depths shallower than 3,000 m, whereas its average weight percent is about 8% for greater depths, except for the interval between 4,100 and 4,300 m where it increases up to 16%. Plagioclase, pyrite and siderite are present in every sample and their abundance span respectively between 1-11%, 1-7% and 1-8%. Calcite occurs in minor amounts (1-4%) with maximum contents at the bottom of the well. K-feldspar never exceeds 2%.

X-ray diffraction analysis of the $<2\mu$ m grain-size fraction shows a substantially homogeneous composition of clay minerals throughout the well. The fraction is dominated by kaolinite and illite which prevail on chlorite and mixed layers illite-smectite (Tab. 3.1).

Depth	٨٥٥	Organic matter	Ro% ± s.d.	R parameter	XRD analysis	
interval (m)		composition	(n.meas.)	(%l in l-S)	<2µm	Whole rock
1290	Upper Miocene	AOM ₁₀ CHF ₂₅ CWF ₆₅	0.35 ± 0.04 (3)	R0 (35)	I_9I -S $_8K_{80}Ch_3$	Qtz _{6.2} Cal _{1.0} Kfs _{0.4} Plg _{1.8} Ph _{80.2} Sid _{3.9} Pyr _{6.5}
1390-1400	Middle Miocene	AOM ₅ MPH ₅ CHF ₃₀ CWF ₆₀	0.33 ± 0.03 (16)	R0 (35)	$I_{10}I-S_8K_{79}Ch_3$	Qtz _{5.5} Cal _{1.7} Kfs _{0.4} Plg _{1.5} Ph _{75.8} Sid _{8.3} Pyr _{6.8}
1500-1510	Middle Miocene	AOM ₈₀ CHF ₁₅ CWF ₅	-	RO (35)	$I_{17}I-S_{10}K_{71}Ch_2$	Qtz _{4.1} Cal _{0.8} Kfs _{0.5} Plg _{2.8} Ph _{78.3} Sid _{6.3} Pyr _{7.2}
1600-1610	Middle Miocene	AOM ₇₀ CHF ₂₀ CWF ₁₀	0.36 ± 0.02 (5)	RO (35)	$I_{13}I-S_9K_{77}Ch_1$	Qtz _{3.5} Cal _{1.6} Kfs _{0.5} Plg _{1.3} Ph _{85.3} Sid _{2.9} Pyr _{4.9}
1700-1710	Middle Miocene	AOM ₇₀ CHF ₂₅ CWF ₅	-	R0 (42)	$I_{13}I-S_2K_{84}Ch_1$	Qtz _{3.9} Cal _{1.0} Kfs _{0.5} Plg _{2.1} Ph _{84.3} Sid _{3.1} Pyr _{5.1}
1800-1810	Middle Miocene	AOM ₁₀ MPH ₅ CHF ₂₅ CWF ₆₀	0.38 ± 0.04 (26)	RO (35)	$I_{17}I-S_{10}K_{72}Ch_1$	Qtz _{5.2} Cal _{0.7} Kfs _{0.6} Plg _{4.5} Ph _{81.8} Sid _{3.4} Pyr _{3.8}
1950-1960	Middle Miocene	AOM ₂₀ MPH ₁₀ CHF ₂₅ CWF ₄₅	0.39 ± 0.03 (21)	R0 (42)	$I_{20}I-S_{17}K_{62}Ch_1$	Qtz _{4.9} Cal _{1.5} Kfs _{0.4} Plg _{2.1} Ph _{84.8} Sid _{3.0} Pyr _{3.3}
2120-2130	Lower Miocene	AOM ₆₀ CHF ₁₅ CWF ₂₅	0.39 ± 0.04 (13)	R0 (40)	$I_{21}I-S_{12}K_{67}Ch_1$	Qtz _{5.9} Cal _{1.2} Kfs _{0.5} Plg _{2.9} Ph _{80.7} Sid _{2.8} Pyr _{6.0}
2260-2270	Lower Miocene	AOM ₁₀ MPH ₁₀ CHF ₁₅ CWF ₆₅	0.39 ± 0.04 (8)	R0 (45)	$I_{26}I-S_5K_{68}Ch_1$	Qtz _{4.3} Cal _{1.2} Kfs _{0.2} Plg _{9.8} Ph _{77.6} Sid _{1.6} Pyr _{5.3}
2460-2470	Lower Miocene	AOM ₈₀ MPH ₅ CHF ₁₀₀ CWF ₅	-	R0 (52)	$I_{21}I-S_2K_{76}Ch_1$	Qtz _{3.5} Cal _{1.1} Kfs _{0.2} Plg _{1.9} Ph _{85.0} Sid _{2.7} Pyr _{5.6}
2600-2620	Lower Miocene	AOM ₉₀ CHF ₅ CWF ₅	-	R0 (50)	$I_{23}I-S_2K_{75}Ch_1$	Qtz _{4.9} Cal _{0.8} Kfs _{0.3} Plg _{2.1} Ph _{83.8} Sid _{3.1} Pyr _{5.0}
2780-2790	Lower Miocene	AOM ₈₀ MPH ₅ CHF ₁₀ CWF ₅	-	R0(45)+R1(72)	$I_{26}I-S_5K_{66}Ch_3$	Qtz _{5.5} Cal _{0.5} Kfs _{0.3} Plg _{2.0} Ph _{81.0} Sid _{3.2} Pyr _{7.5}
2920-2930	Lower Miocene	AOM ₄₀ CHF ₂₀ CWF ₄₀	0.47 ± 0.03 (12)	R0(45)+R1(72)	$I_{30}I-S_{10}K_{58}Ch_1$	Qtz _{4.0} Cal _{0.6} Kfs _{0.1} Plg _{10.6} Ph _{75.7} Sid _{2.5} Pyr _{6.5}
3060-3070	Lower Miocene	AOM ₉₀ CHF ₅ CWF ₅	0.42 ± 0.04 (3)	R0(45)+R1(74)	$I_{28}I-S_{16}K_{56}Ch_1$	$Qtz_{5.4}Cal_{0.4}Kfs_{0.4}Plg_{2.0}Ph_{81.1}Sid_{4.6}Pyr_{6.1}$
3180-3190	Lower Miocene	AOM ₂₅ CHF ₃₅ CWF ₄₀	0.52 ± 0.06 (16)	R0(45)+R1(73)	$I_{33}I-S_{16}K_{50}Ch_1$	Qtz _{7.0} Cal _{0.4} Kfs _{0.3} Plg _{3.0} Ph _{80.8} Sid _{3.7} Pyr _{4.8}
3360-3370	Lower Miocene	AOM ₃₅ CHF ₁₅ CWF ₅₀	0.52 ± 0.04 (27)	R1(73)	$I_{51}I-S_{15}K_{25}Ch_9$	Qtz _{13.5} Cal _{0.5} Kfs _{0.1} Plg _{11.5} Ph _{68.9} Sid _{3.0} Pyr _{2.5}
3600-3610	Lower Miocene	AOM ₆₀ CHF ₂₅ CWF ₁₅	-	R0(45)+R1(74)	$I_{39}I-S_{14}K_{46}Ch_1$	Qtz _{7.1} Cal _{0.2} Kfs _{0.1} Plg _{3.3} Ph _{81.4} Sid _{3.2} Pyr _{4.7}
3700-3710	Oligocene	AOM ₈₀ MPH ₁₀ CHF ₅ CWF ₅	-	R0(45)+R1(74)	$I_{33}I-S_{15}K_{52}Ch_1$	$Qtz_{4.0}Cal_{0.5}Kfs_{0.2}Plg_{1.3}Ph_{85.2}Sid_{3.2}Pyr_{5.6}$
3820-3830	Oligocene	AOM ₉₀ CHF ₅ CWF ₅	-	R1(74)	I ₃₆ I-S ₂₀ K ₄₂ Ch ₃	Qtz _{10.1} Cal _{1.0} Kfs _{0.2} Plg _{6.1} Ph _{74.4} Sid _{4.1} Pyr _{4.1}
3900-3910	Oligocene	AOM ₁₀ CHF ₂₀ BIT ₇₀	0.82 (15)*	R1(74)	$I_{31}I-S_3K_{49}Ch_{16}$	Qtz _{16.2} Cal _{0.2} Kfs _{0.1} Plg _{2.6} Ph _{74.7} Sid _{4.3} Pyr _{1.9}
4010-4020	Oligocene	AOM ₈₅ CHF ₁₅	-	R1(75)	$I_{36}I-S_4K_{59}Ch_1$	$Qtz_{5.6}Cal_{0.6}Kfs_{0.1}Plg_{2.9}Ph_{82.0}Sid_{5.5}Pyr_{3.3}$
4100-4110	Oligocene	AOM ₁₀₀	-	R1(70)+R3(83)	$I_{28}I-S_{23}K_{46}Ch_3$	Qtz _{17.6} Cal _{0.3} Kfs _{0.1} Plg _{4.6} Ph _{74.7} Sid _{1.4} Pyr _{1.3}
4120-4130	Oligocene	-	0.90 (4)*	-	-	-
4210-4220	Oligocene	-	-	R1(70)+R3(85)	$I_{43}I\text{-}S_7K_{46}Ch_4$	$Qtz_{21.4}Cal_{1.1}Plg_{7.6}Ph_{63.9}Sid_{4.3}Pyr_{1.7}$
4270-4280	Oligocene	AOM ₁₀₀	-	R3(86)	$I_{27}I-S_3K_{67}Ch_3$	Qtz _{12.8} Cal _{0.4} Kfs _{0.2} Plg _{4.2} Ph _{79.3} Sid _{1.0} Pyr _{2.1}
4380-4390	Oligocene	-	0.92 (3)*	-	-	-
4510-4520	Oligocene	AOM ₁₀₀	-	R3(84)	$I_{45}I\text{-}S_1K_{52}Ch_2$	$Qtz_{6.4}Cal_{0.8}Kfs_{0.1}Plg_{1.8}Ph_{82.8}Sid_{4.0}Pyr_{4.1}$
4570-4580	Oligocene	-	1.03 (10)*	R3(84)	$I_{37}I-S_6K_{56}Ch_1$	Qtz _{8.9} Cal _{0.9} Kfs _{0.2} Plg _{3.9} Ph _{77.3} Sid _{6.8} Pyr _{2.0}
4600-4610	Oligocene	AOM ₁₀₀	-	R3(84)	$I_{33}I-S_{21}K_{43}Ch_3$	$Qtz_{21.5}Cal_{4.4}Kfs_{0.1}Plg_{4.6}Ph_{64.2}Sid_{1.7}Pyr_{3.5}$
4680-4686	Oligocene	AOM ₁₀₀	-	R3(84)	$I_{36}I-S_4K_{57}Ch_3$	Qtz _{8.9} Cal _{2.9} Plg _{5.3} Ph _{77.2} Sid _{1.7} Pyr _{4.0}
4780-4790	Oligocene	AOM ₁₀₀	-	R3(85)	$I_{54}I\text{-}S_{3}K_{42}Ch_{1}$	Qtz _{7.9} Cal _{2.4} Kfs _{0.1} Plg _{2.9} Ph _{76.6} Sid _{2.9} Pyr _{7.2}
4810-4820	Oligocene	-	-	R3(88)	$I_{48}I-S_5K_{46}Ch_1$	$Qtz_{7.3}Cal_{1.9}Kfs_{0.1}Plg_{1.6}Ph_{80.3}Sid_{1.9}Pyr_{6.9}$
4880-4890	Oligocene	AOM ₁₀₀	-	R3(85)	$I_{58}I-S_3K_{36}Ch_3$	Qtz _{10.7} Cal _{1.4} Plg _{5.4} Ph _{76.5} Sid _{2.3} Pyr _{3.7}
4940-4950	Oligocene	AOM ₁₀₀	-	R3(87)	I65I-S2K28Ch6	Qtz _{11.2} Cal _{0.9} Plg _{7.0} Ph _{75.5} Sid _{2.0} Pyr _{3.4}

Table 3.1 Organic matter composition, X-ray diffraction analyses and related vitrinite reflectance and illite content in mixed layer I-S data. Acronyms: AOM— amorphous organic matter; MPH— marine phytoplankton; CHF— continental herbaceous fragments; CWF— continental wooden fragments; Ro%— vitrinite reflectance; s.d.— standard deviation; n.meas.— number of measured fragments; % I in I-S— illite content in mixed layer illite-smectite; R parameter—stacking order of mixed layers I-S; I— illite; I-S - mixed-layer illite-smectite; K— kaolinite; ChI— chlorite; Qtz— quartz; CaI— calcite; Kfs— K feldspar; PIg— plagioclase; Ph— phyllosilicates; Sid— siderite; Pyr— pyrite. Subscript numbers correspond to mineral and organic matter weight percentages. Asterisk beside vitrinite reflectance data indicates Roeq% from bitumen.



Upper and Middle Miocene samples are constituted by illite (values between 9 and 17%), high expandability mixed layers illite-smectite (8-10%), chlorite (1-3%) and large amounts of kaolinite (71-80%). The Lower Miocene succession is composed of illite (mainly 20-33%), random and short-ordered mixed layers illite-smectite (2-16%), kaolinite (50 and 76%), and chlorite (mainly 1-3%). In the Oligocene section a substantial increase in illite (27-65%) and decrease in kaolinite (36-67%) contents are observed in comparison with younger strata, followed by long-range ordered mixed layers (1 and 23%) and chlorite (1-6%).

Figure 3.5 Representative ethylene-glycol-solvated (grey line) and air-dried (black line) diffraction patterns of the <2 μ m grain-size fraction showing the progressive smectite illitization throughout the well. Acronyms: Chl—chlorite; I—illite; I-S—mixed-layer illite-smectite; K—kaolinite; Qtz— quartz. Numbers over the peaks refer to the d spacing of mixed layer I-S.

	Bitumen	Jacob, 1989 ^a	Landis and	Schoenherr et al., 2007 ^c
Depth (m)	reflectance (R _{obit} %)	(R _{oeq} %)	Castaño, 1995 [⊳] (R _{oeq} %)	(R _{oeq} %)
3910	0.68	0.82	1.00	0.88
4120	0.81	0.9	1.12	1.00
4390	0.84	0.92	1.15	1.03
4580	1.02	1.03	1.31	1.20

Table 3.2 Bitumen reflectance data and their conversion into vitrinite-equivalent reflectance values according to different Authors. a): $Ro_{eq}\%$ = 0.618 $Ro_{bit}\%$ + 0.40; b): $Ro_{eq}\%$ = ($Ro_{bit}\%$ + 0.4)/1.09; c): $Ro_{eq}\%$ = ($Ro_{bit}\%$ + 0.2443)/1.0495



Figure 3.6 Plot of illite content in mixed layers I-S and corresponding stacking order versus depth and ages. R0, R1 and R3 stacking order are indicated respectively by black, grey and white dots.

3.4.2.2 Stacking order and illite content in mixed layers illite-smectite

Mixed layers I-S display an increase of illite content and a progressive conversion from random to short-range ordered and to long-range ordered structures as function of depth, suggesting that sedimentary burial is the main factor driving smectite illitization (Figs. 3.5, 3.6 and Table 3.1).

In detail, R0 structures are dominant in the Upper and Middle Miocene units and characterize the upper part of the Lower Miocene up to depths of 2,600 m with illite contents ranging from 35 to 52%.

At 2,700 m, in the lower Miocene section, two populations of mixed layer I-S occur, and random ordered mixed layer I-S (R0) progressively converts to short-range ordered structures (R1).

R0 mixed layers display illite contents of 45% whereas low-expandable R1 mixed layers I-S are characterized by illite contents of 72-75%. From 3,820 m to 4,010 m in the Oligocene section, only R1 mixed layers I-S were observed with an illite content of about 75%.

Both R1 and R3 structures are present at depths ranging between 4,100 and 4,200 m. R1 mixed layers I-S display illite contents of about 70% whereas low-expandable R3 mixed layers I-S are characterized by illite contents of 83-85%. From 4,270 m to the well bottom, the conversion from short-range to long-range ordered I-S is complete with illite contents between 84 and 88%.

3.4.3 Thermal modelling

3.4.3.1 Pressure and temperature data

Temperature and pressure data were collected during well drilling and are shown in Figure 3.7. Figure 3.7a indicates temperature of 13°C measured at the seabed and temperatures ranging between about 100 and 170°C for the depths interval of 3,500-4,500m. These data fit with a present-day geothermal gradient of about 40°C/Km.



Figure 3.7 (a) Present-day measured temperatures (black dots) plotted against different geothermal gradients. The temperature measured at depth of 358m (seabed) is reported in the upper left. (b) Present-day pressure measurements throughout the well measured by MDT (Modular Formation Dynamics Tester). The dashed diagonal line represents the increasing hydrostatic pressure as function of depth. Notice the abrupt increase of pressure at about 3,000 m when compared to the correspondent hydrostatic value.

Pressure data collected at depths of 1,290 and 1,400 m record values of 130 and 142 Kg/cm² respectively that are consistent with the hydrostatic pressure gradient (Fig. 3.7b). At depths between 3,000 and 4,200m, pressure measurements do not match the hydrostatic trend and their values range between 491 and 626 Kg/cm² delimiting an overpressured interval.



Figure 3.8 Distribution of vitrinite reflectance (Ro%) and vitrinite-equivalent reflectance data (Ro%eq) against depth, projected on different organic matter maturation trends calculated for various geothermal gradients.

Depth (m)	Measured reflectance (R _o %)	PresRo ^a	T-P-Ro [♭]
2920	0.47	0.42	0.45
3060	0.42	0.44	0.48
3180	0.52	0.48	0.52
3360	0.52	0.52	0.58

Table 3.3 Measured vitrinite reflectance data and expected values calculated using the equations proposed by (a) Carr (1999) and (b) Zou et al., (2001). See the text for explanation.

3.4.3.2 Patterns of organic matter maturation and smectite illitization

Figure 3.8 shows the distribution of R_0 % and R_{oeq} % data vs. depth plotted on organic matter maturation curves calculated for different geothermal gradients (e.g., 10, 20, 30, 40 °C/km) and average sedimentation rates. The diagram shows that Lower Miocene samples fit a paleogeothermal gradient of about 20°C/km whereas both Upper-Middle Miocene and Oligocene data fit the curve of higher paleogeothermal gradients (between 30° and 40°C/km).

A more robust calibration was performed by using the software e-simba (Fig. 3.9). The calibration is based



Figure 3.9 Distribution of vitrinite reflectance (R_o%) and vitrinite-equivalent reflectance data (R_{oeq} %),against depth projected on the organic matter maturation trend calculated by the present-day geothermal gradient. Black dots indicate average reflectance values measured on vitrinite, grey dots indicate average reflectance values measured on bitumen and then converted into vitrinite reflectance equivalent values using Schoenherr's et al.'s equation (2007). The solid line represent the organic matter maturation trend calculated by the presentday geothermal gradient using Sweeney and Burnham's model (1990); white dots indicate the expected reflectance values obtained modifying the kinetic equation according to Carr (1999) and black crosses modifying the kinetic equation according to Zou et al., (2001).

on the present-day geothermal gradient calculated from measured temperatures (Fig. 3.7 a), and on a set of selected rock properties (compaction data, density, conductivity, heat capacity and porosity).

Figure 3.9 shows that between the end of Oligocene and the end of the Lower Miocene, vitrinite reflectance values follow a deviated trajectory with respect to the calculated maturity profile with

maximum differences for samples at the boundary between Lower Miocene and Oligocene. On the other hand, reflectance data measured on bitumen fit the model.

Vitrinite reflectance values expected by Carr's (1999) and Zou et al.'s (2001) equations were calculated for the overpressured interval and are plotted respectively as white dots and black crosses in Figure 3.9. Figure 3.9 shows a good match between R_0 % values calculated including overpressure effects and R_0 % values measured in the overpressured interval.

To model smectite illitization several parameters such as geothermal gradient, sedimentation rate, and potassium concentration are required. Among them only the potassium concentration is an unknown parameter and its values were chosen to fit the model according to Cuadros (1996).

We adopted different sedimentation rates calculated using thickness values of the decompacted succession. The decompaction was calculated according to Allen and Allen (2013). Calculated sedimentation rates are: 0.17 mm/yr for Late and Middle Miocene times, 0.40 mm/yr for the Early Miocene and 0.17 mm/yr



Figure 3.10 Measured values of smectite content in mixed layers I-S (black dots) plotted against depth. The grey line indicates the modelled pattern of smectite illitization by adopting Cuadros and Linares kinetic equation using a present-day geothermal gradient of 38°C/km.

for the Oligocene. The chosen geothermal gradient value is close to the present-day one (38°C/km, Fig. 3.9). Five values of effective K concentration (expressed in Moles) were used (10⁻¹⁷ between 1290 and 1810m depth; 10⁻¹⁹ between 1810 and 2620m and between 3190 and 4110; 10⁻¹³ between 4110 and 4520m and 10⁻²¹ between 4520 and 4950m). The magnitude of these values are in the order of those adopted by Cuadros (2006) and variations were related to the change in K bearing and Ca bearing minerals (in particular K-feldspar and calcite).

The modelled smectite illitization pattern (grey line in Fig.3.10) that satisfactorily fits the experimental data shows a typical Z shape already detected by Cuadros (2006) with two abrupt changes in the proportion of smectite in mixed layers I-S at about 3 and 4 km of depth.

3.5. Discussion

Divergences in thermal maturity assessments arise when using different organic maturation kinetics and/or clay minerals reactions.

Two main vitrinite reflectance clusters can be observed in Figure 3.8. One group of R_0 % and R_{oeq} % data, corresponding to the Oligocene and Upper-Middle Miocene sediments, matches organic maturation curves calculated using a geothermal gradients of 30-40°C/km whereas a second cluster including Lower Miocene samples fits the curve generated with a geothermal gradient of 20°C/km.

Our attempt to match the distribution of R_0 % data with the present day geothermal gradient of about 37°C/Km (Fig. 3.9) clearly indicates that in the Lower Miocene interval, vitrinite reflectance data depict a deviated trajectory consistent with a lower geothermal gradient. This localized geothermal gradient decrease is unlikely for the western Africa passive margin where heat flow has been decreasing exponentially since about 130 My ago (rifting event) (Lucazeau et al., 2004; Anka et al., 2013).

We suggest that the apparent decrease in geothermal gradient during the Lower Miocene is not related to geological causes but is the result of pitfalls in vitrinite reflectance measurements.

In particular, vitrinite reflectance is not the adequate thermal indicator to calibrate thermal modelling in this case history because:

- 1) vitrinite is scarce in the whole organic facies and its measurements are not regularly distributed along the well (see Table 3.1);
- 2) high hydrogen content, reflected by a high content of amorphous organic matter (AOM) and marine phytoplankton (MPH) could have produced suppression of vitrinite reflectance;
- 3) vitrinite reflectance have been retarded in the overpressured interval.

Table 3.1 shows that most of our samples are characterized by high contents of amorphous organic matter. In particular eight out of eleven samples on which vitrinite reflectance has been measured, show a content of hydrogen rich organic matter (AOM and MPH) higher than 20% in volume.

According to Murchison et al, (1991), Petersen and Vosgerau (1999) and Hutton and Cook (1980), the minimum content in liptinite (hydrogen-rich OM) required to produce suppression varies between 10 and 35% and depends on the nature of the liptinite group macerals (e.g. presence of resinite, alginite). For these Authors, suppression can be attributed to the incorporation of lipid-derived hydrogen or bitumen into the vitrinite structure during peat deposition or during early diagenesis.

Lo (1993) described a model to correct the suppressed reflectance in a range of maturity between 0.4 and 2.0 R_0 %, using the hydrogen index (HI) values obtained from Pyrolysis Rock Eval analysis.

In our samples, the AOM and MPH contents can be approximately considered as a measure of the liptinite content. Nevertheless, Lo's model (1993) cannot be used, as most of the samples on which vitrinite reflectance has been measured show maturity values lower than 0.4 R_0 %, the HI is not available as well as the maceral composition of the liptinite group. However some influences on vitrinite reflectance measurements are highly probable, in particular on those samples with the highest AOM and MPH content.

On the other hand, Figure 3.7b shows that pressure values deviate from the hydrostatic trend in the depth interval between 3,000 and 4,000 m. Thus they could be responsible for the retarded vitrinite reflectance values found in this stratigraphic interval.

The effect of overpressure has been widely recognized to affect organic matter maturation in a series of petroleum basins such as the North Sea (McTavish, 1978) and the South China Sea (Zou et al., 2001; Hao et al., 1996) or in the products of Pyrolysis Rock Eval experiments (Dalla Torre et al., 1998; Carr et al., 2009; Uguna et al., 2012; 2015).

Carr (1999; 2009) and Uguna (2012; 2015) pointed out that volatiles products (water/hydrocarbons) of the organic matter maturation cannot be released in presence of high pore pressure. In the case of vitrinite, volatiles retention prevents the formation of the aromatic structures inhibiting the reflectance increase with depth.

A quantification of the effects of overpressure on vitrinite reflectance can be made using proper kinetic equations that describe organic maturation as a function of pressure, temperature and time. Three models have been proposed by Carr (1999), Dalla Torre et al. (1998) and Zou et al.(2001). In the first two models, the Arrhenius factor (A, Eq. 2, Chapter 2) is modified by overpressure, in the third Zou et al.(2001) modified the activation energies (*Ea*, Eq. 3, Chapter 2).

In this Chapter we applied Carr (1999) and Zou et al (2001)'s equations to evaluate the overpressure effect on our samples (Fig.3.9 and Table 3.3). Dalla Torre et al.'s (1998) model was discarded since it uses a single value instead of a distribution of activation energies as proposed by Sweeney and Burnham (1990).

Figure 3.9 shows that R_0 % values taking into account overpressure (white dots and black crosses in Fig. 3.9) well approximate measured data, suggesting that overpressure retards vitrinite reflectance.

Overpressure in the studied area probably arises as the results of the rapid increase of sedimentation rates that in our section pass from about 0.2 mm/yr in Middle Miocene times to about 0.4 mm/yr in the Lower Miocene. Such an increase is widely recognized in the Lower Congo Basin and is the result of the onset and progradation of the giant Congo deep-sea fan during Early Miocene times (Anka and Séranne, 2004; Anka et

al., 2009; Broucke et al., 2004). This event led to the deposition of large thicknesses of siliciclatic sediments, deposited in both pro-delta slope and basin floor settings (Anderson et al., 2000). As matter of fact, an analogous deviation in the trajectory of vitrinite reflectance data, with respect to organic matter maturation models has been observed in Lower Miocene and Upper Oligocene rocks also by Anka et al. (2013) in two pseudo-wells representative of the successions located in the Lower Congo Basin to the south of the submarine Congo Canyon.

In contrast, in the Lower Congo Basin no further works have been developed using inorganic thermal indicators alternative to vitrinite reflectance. For this reason we analysed two clay minerals reactions such as smectite-illitization and kaolinite-illitization, that do not seem to be affected by any retardation during thermal evolution.

Figure 3.11 shows a negative correlation between illite and kaolinite contents as function of depth. This trend



Figure 3.11 Distribution of illite (dark line) and kaolinite (dashed line) contents in the <2 μ m grain- size fraction against depth. Notice the negative correlation between the two mineral phases (see text).

is the result of the changing composition of the original sediment on which kaolinite illitization would be superimposed. We propose that at depths deeper than 3,000 m, where the kaolinite-illite trends become almost specular, kaolinite illitization is the prevailing mechanism for formation of authigenic illite.

Precipitation of discrete illite from kaolinite is a widely described phenomenon occurring in sandstone reservoirs at temperatures of 120-140°C coupled with K-feldspar dissolution in closed systems (Berger et al., 1997; Bjølykke, 1998) or with K⁺-rich fluid circulation in open systems at lower temperatures (90-95°C; Lanson et al., 2002). Taking into account the low permeability of the studied succession, the strong negative correlation from 3,000 m depth down to the well bottom seems to be linked to the reaction proposed by Bjølykke (1998) for kaolinite illitization in closed systems (Kaolinite + K-feldspar = Illite + Quartz + H₂O) suggesting paleotemperatures of at least 120°C. Such temperatures are consistent with a paleogeothermal gradient similar to the present day one

(e.g., about 40°C, see Fig. 3.7a) rather than that derived by vitrinite reflectance distribution for the Lower Miocene section (e.g., about 20°C, see Figs.3.8).

Another evidence suggesting that inorganic thermal indicators are not affected by fast sedimentation rates, derives from the increase of illite content in mixed layers illite-smectite. Figure 3.6 shows a regular trend of increase of illite layers in mixed layers I-S with depth indicating that burial was the main driving force for smectite illitization. The R0-R1 I-S conversion that approximately coincides with the onset of the oil window

(100-110°C), occurs at depth of about 2,700 m, shallower than that recorded by organic matter maturation (~0.5 R_0 % at 3,200m of depth). From depths of 2,700 m to 3,820 m, the co-existence of two populations of mixed layers illite-smectite (R0 and R1) is probably related to the K⁺ availability at the time of burial (McCarty et al., 2009). At depths of 4,100 m, the R1-R3 I-S conversion occurs and corresponds to temperatures of about 170°C according to Merriman and Frey (1999) that are in agreement with the present-day temperatures.

From these depths downwards, the formation of authigenic illite as end-member of the smectite to illite reaction could be a complementary mechanism to the kaolinite illitization process.

The role of pressure in the smectite illitization process is not as well understood as in organic matter maturation. Some Authors agree that retardation of smectite illitization can occur in overpressured intervals (Carr, 1999; Feyzullayev and Lerche, 2011), while others (Shawn et al., 1989) indicate that the reaction is not affected or even accelerated when overpressure occurs. Nevertheless these works do not take into account other factors that influence smectite illitization, such as K^+ availability, pore fluids composition and permeability.

Colten-Bradley (1987) studied the role of pressure in smectite dehydration that is different from smectite illitization. The latter process involves together with the loss of water, an increase of layer charge and uptake of K in the interlayer region. Colten-Bradley (1987) pointed out that in diagenetic conditions, smectite is stable as a two-water-layers complex, while under differential-pressure conditions, the temperature range of the water loss occurs approximately at the beginning of the smectite to illite transformation and the onset of HC generation. After dehydration, the remaining one-water layer phase becomes chemically instable with the increase of pressure and thus becomes more susceptible to transformation to illite.

Looking at our case history, the Matlab code enclosing the smectite illitization kinetics (Cuadros and Linares, 1996) traces a thermal evolution (Fig.3.10) consistent with a constant geothermal gradient similar to the present day one (38°C/Km), indicating that overpressure did not affect the smectite to illite conversion and giving back a more realistic pattern than that derived from organic maturation kinetics alone.

As smectite illitization depends also on potassium availability (K), the right choice of this variable needs particular attention in order to strengthen and better constrain thermal modelling.

K concentration defined by Cuadros (2006) as the "effective K concentration" represents the concentration of either K or other cations that compete with K for the smectite interlayer site at the time of the smectite to illite conversion. For this reason, together with the intrinsic differences between natural and experimental conditions, values found through modelling are generally very small when compared with values from experimental data.

There is no way to assess the real values of K concentration at the time at which smectite to illite transition occurred, but Cuadros (2006) shows a similitude between the "effective K concentration" used to fit his models and the ratio between the potassium content and the calcium content multiplied by two. This is because Ca is the main competitor for the smectite interlayer site and Ca is twice as effective as K.

In a similar way, to check the validity of our model, we compared K concentration with the ratio between the two principal K and Ca-bearing minerals in the studied succession. The comparison is shown in Figure 3.12 where fluctuations of K approximately follows those of K/Ca ratios, supporting the values of K concentration used in our model.



Figure 3.12 Variation of the $K_{eq}/2Ca_{eq}$ ratio obtained from XRD analyses (a) and effective K concentration used in the models (b).

The evaluation of K concentration can be considered as an insight on the potassium availability during smectite illitization. The low values for K availability found through the model could be also related to the presence of two populations of I-S crystals with different stacking order in the same sample according to McCarty's model (2009).

3.6. Conclusion

Vitrinite reflectance and illite content in mixed layers illite-smectite are generally considered two powerful thermal indicators that can be used to unravel the thermal history of sedimentary basins. Both methods have their own limits that can vary from basin to basin.

In the Lower Congo Basin, we demonstrate that when retardation and/or suppression phenomena in organic matter maturation occur, thermal evolution of sediments can be successfully modelled by an alternative approach based on smectite illitization kinetics.

Hence, thermal models calibrated against vitrinite reflectance in case of suppression/retardation, can be strongly biased and the assessment of hydrocarbon generation/expulsion windows can provide maturation

scenarios that underestimate actual thermal evolution with possible negative influence on prospects assessment.

In particular, a correct evaluation of the organic matter maturation can be provided using kinetic equations (Carr, 1999 and/or Zou et al., 2001) that incorporate pressure data along the whole overpressured section.

For this reason, in geological setting where rapid changes of sediment supply may occur (e.g., fan delta depositional environments) or when kerogen is particularly rich in liptinites, thermal evolution of clastic successions should be calibrated also against inorganic thermal indicators (e.g., mixed layer I-S) using appropriate clay minerals reaction kinetics. In this work, this approach allowed us to better define the thermal evolution of the Malembo Fm and to provide insights on pore fluid chemistry.

Chapter 4

Thermal evolution of Mesozoic-Cenozoic successions of the Carpathian orogenic system (Ukraine)

4.1.Introduction

The Ukranian sector of Carpathians fold and thrust belt constitute the central segment of the chain (Fig. 4.1). In this sector Cretaceous and Paleogene terrigenous flysch sequences with interbedded organic-rich sequences constitutes the outer Carpathians flysch belt (Roure et al., 1993).

The outer Carpathians and the adjacent foreland constitute one of the largest petroleum provinces in Central Europe (Kuśmierek, 1990) and in particular in the Ukrainian Carpathians, the oil exploration in the Boryslav area began as long ago as 1870 (Kotarba and Koltun, 2006). Two significant organic-rich units, both with a basin-scale distribution, occur within the area: the first comprises the Lower Cretaceous Shypot and Spas Formations, the second one the Oligocene-Lower Miocene Menilite Formation (Koltun, 1998).

One of the main issues addressed in hydrocarbon exploration consists of assessing thermal maturity and quality of potential source rocks. Consequently, many authors have widely studied Shypot and Melinite source rocks by means of Rock Eval Pyrolysis (Koltun et al., 1998; Kosakowski et al., 2012; Kotarba, 2012; Kotarba and Koltun, 2006a; Kotarba and Nagao, 2008). Nevertheless in many cases thermal maturity of these units is only approximatively assessed by Tmax values. In addition, due to the lack of well calibrated thermal modelling, it is often difficult to provide reliable constraints to the timing and/or the origin (e.g. sedimentary and/or tectonic loading) of the burial in the thermal evolution of the source rocks.

In this chapter we present the results of Pyrolysis Rock Eval analyses coupled with optical organic petrography analyses on a set of samples collected in the SE sector of the Ukranian Carpathians, close to the border with Romania. Results allow to characterized the hydrocarbon generation potential of the source rocks and to constrain in detail their thermal maturity. In addition we adopted Tmax and vitrinite reflectance data to calibrate thermal models of the sampled main tectonic units. These provided possible reconstructions of the burial- thermal history of this sector of the chain.

4.2.Geological setting

4.2.1 Carpathians Orogenic system and Ukraine Outer Carpathians

The Carpathian orogenic system is a segment of the alpine- himalayan chain which joins the Alps to the west and the Balkans and Rhodopes to the south (Fig.4.1). The Carpathian chain is the result of several



Figure 4.1 Geodynamic setting of the Carpathian-Pannonian region in the general framework of the Europe-Africa-Arabia convergence (modified from Ustaszewski et al., 2008). The box indicates location of Fig. 4.2

orogenic cycles (e.g. Variscan and the Alpine) and is traditionally divided into Inner and Outer Carpathians (Fig. 4.2) separated by the Pieniny Klippen Belt, a narrow zone that was affected by both Late Cretaceous



Figure 4.2 Sketch-map showing the major tectonic units in the Ukrainian Carpathians. B-V = Bilche-Volytsia unit; SA = Sambir Nappe; B-P = Boryslav-Pokuttia Nappe; SK = Skiba Nappe; KR = Krosno Nappe; CH = Chornogora Nappe; DU = Dukla Nappe; PO = Porkulets Nappe; RA = Rakhiv Nappe; MA = Marmarosh Nappe; PE = Pieniny Klippen Belt (redrawn after Koltun et al., 1998)

and Tertiary tectonic phases (Birkenmajer et al., 2008). The Inner Carpathian are made up of continental crust of Variscan age which is overlain by Paleozoic-Mesozoic continental and shallow marine sedimentary successions unconformably covered by Paleocene-Oligocene flysch Lower-Middle Miocene marine and sediments. The Outer Carpathians form a fold-and-thrust belt including Upper Jurassic to Lower Miocene flysch-type sedimentary rocks (Zattin et al., 2011; Andreucci et al., 2013). The External Carpathians comprise a series of tectonic units that from NE (external) to SW (internal) are: the: Boryslav-Pokuttia, Skiba (Skole), Krosno (Silesian), Chornogora, Dukla, Porkulets, Rakhiv and Marmarosh (Kruglov, 1989) (Fig. 4.2). The lithospheric boundary between the European Craton and the Carpathian chain is marked by the Trans European Suture Zone (TESZ). The TESZ is a 2,000 km long complex and long-lived tectonic lineament which extends from the North Sea to the NW to the Black Sea to the SE.

4.3 Sampling and materials

Samples analysed in this work derive from the Ukranian sector of the Outer Carpathians (Fig. 4.2). In detail they were collected from the flysch sequences that composes the outer part of the orogenic belt. Here the flysch sequences are mainly made up of sandstones, siltstones and shales, with interbedded organic-rich Lower Cretaceous and Oligocene – Lower Miocene black shales (Figs. 4.3 and 4.4). The base of the flysch succession forms a major decollement (Roure et al., 1993) whereas in the most external units, the flysch sequences are unconformably overlain by orogenic molasses (Koltun et al., 1998). In detail, my work was focused on the Lower Cretaceous Shypot formation of the Chornogora unit, on the Upper Cretaceous Inoceramian / Strij formation in the Chornogora and Boryslav-Pokuttya units and in the Paleocene-Oligocene (Green shales, Globigerina marls, Melinite cherts) and Oligocene-Miocene (Melinite shales and Krosno beds) successions of the Skiba unit .



Figure 4.3 Geological map of the Ukranian-Romania border. Black dots mark the location ofsampling sites (redrawn from Jankowski L. et al., 2007)



Figure 4.4 Stratigraphic successions for the Flysch Belt in the study area (Ukrainian External Carpathians). Black dots mark the location of sampling sites (modified after Koltun et al., (1998)

Sampling was performed along the Ceremos and Siret Rivers valleys in the southern portion of the Ukranian Carpathians close to the Romanian border (Fig. 4.3 and 4.4) from East to West the: Boryslav-Pokuttya, Skiba and Chornogora tectonic units (Fig. 4.3). The only sample collected in the Boryslav-Pokuttya unit comes from a black shales interval, interbedded in arenaceous beds, belonging to the Upper Cretaceous Inoceramian / Strij formation (PL 98, Fig. 4.3-4.4).

In the external part of the Skiba unit the older sample collected is the PL 102 belonging to a pelitic interval from the Eocene-Oligocene series of the Globigerina Marls, while the Oligocene-Miocene Melinite shales are represented by PL 97, PL 104b samples and PL 103b.

In the internal part of the Skiba unit, PL 100 and PL 94 come from pelitic horizons in sandstones at the transition between the Melinite shales and Krosno Beds, while in the turbiditic successions of the Krosno beds were sampled Miocene pelitic intervals (PL 93.1, PL 93.2) and black shales (PL 95) and the Oligocene part of the Krosno beds is represent by sample PL 101.1.

In the Chornogora unit were sampled Upper Cretaceous (Inoceramian / Strij units and Gray Shales) and Lower Cretaceous (Shypot unit) successions. The Hauterivian-Albian Shypot unit outcrop with alternance of limestones, marls and black shales (PL 103a, PL 103a2 and PL 92a). The Senonian-Paleocene Inoceramian unit comprise thick arenaceous beds with siltitic intercalation (PL 103) that pass gradually to black shales at the top (PL 92, Fig. 4.4).

4.4 Results

4.4.1 Pyrolysis Rock Eval

Results from Pyrolysis Rock Eval and TOC are listed in Table 4.1 and plotted in Figure 4.5, in Peter and Cassa's diagram (1994). As shown in Figure 4.5 samples indicate types II and III with fair to excellent HC potential.



Figure 4.5 Kerogen type and potential of studied samples plotted in Peter and Cassa's graph (1994). Grey areas indicate the kerogen type, dashed line delimitate HI ranges, black lines indicate the HC potential of the source rocks. From the diagram samples with TOC > 3.5% and S2 > 16 mg/g are excluded. They are reported in Table 4.1 and show oil and mixed oil and gas prone type II kerogen with excellent HC potential

In detail, in the Boryslav-Pokuttya unit, PL 98 sample from the Senonian-Paleocene Inoceramia beds shows a fair content in organic carbon (0.58) and poor HC potential, as suggested by low values of S2 and HI indexes that are respectively of 0.25 mg/g and 43. Tmax of 436°C suggests a thermal maturity that falls in the oil window.

For the Skiba unit, sample PL 102 from its external part, shows low TOC (0.58%), S2 (0.91 mg/g) and HI (157) that suggest a gas prone source rocks for the Eocene–Oligocene interval. Oligocene-Miocene samples from Melinite beds in the Skiba tectonic unit (PL 97, PL 103b and PL 104b) show very high TOC (2.92% and 3.37 % respectively), S2 values between 9 and 15 mg/g and with an HI > 300, suggesting a very high HC potential and an oil prone kerogen. Samples from the Krosno beds in the internal part of the Skiba unit indicate differences in HC potential. Samples PL 93a, PL 95a, PL 100, PL 101.1 and PL 101.2 show TOC < 1% or at about 1%, S2 generally below 2.5 mg/g and low HI generally below 100 (except for PL 95a), suggesting a very poor or inconsistent HC potential. On the other hand, samples PL 93.1, PL 93.2 and PL 95 in the same time interval, have very high organic carbon content that can exceed 10% in PL 93.2. S2 for these samples is higher than 10 mg/g and HI always more than 300 indicate excellent oil prone sources.

Finally, in the Chornogora unit, black shales from the Inoceramia beds and Shypot formation show TOC between 1.1 and 3.13%, for PL 92, PL 103, S2 lower than 1mg/g and HI below 100, while for samples PL 92a, PL 103a and PL 103a2 S2 values are between 1 and 9 mg/g and HI values between 118 and 292.

4.4.2 Organic petrography and Vitrinite reflectance

Organic matter observed under incindent light microscope has shown to be highly heterogeneous for almost all samples. In general different families of macerals have been found, each of them showing different average reflectance. Among them only vitrinite reflectance can be considered as a thermal maturity proxy. Vitrinite fragments were recognized, based on morphological features and on distribution of measured reflectance values reported in the frequency histograms.

In the Boryslav-Pokuttya unit, PL 98 from Upper Cretaceous Inoceramia beds, shows three group of macerals: the vitrinite group with an average value of $0.58 \text{ R}_0\%$, a second group with higher values of about



Figure 4.6 Reflectance histograms on all visible macerals (on the left) and vitrinite reflectance histograms (on the right) for Upper and Lower Cretaceous samples in the Boryslav-Pokuttya and Chonogora units (samples PL 98, PL 103a and PL 103)

 $0.7-0.75R_0\%$ and few inertinite fragments with reflectance values higher than 1.2 % (Fig. 4.6).

In the Chornogora unit, on Lower Cretaceous samples (PL 103and PL 103a), reflectance measured on all visible organoclasts shows a high hetereogeneity (at least on PL 103a), whereas mean Ro% ranges between 0.6 and 0.7 % (Fig. 4.6).

In the Skiba unit, in sample PL 102 from Eocene –Oligocene pelitic interval in the Globigerina marls, inertinite fragments were abundant. Mean Ro% is 0.45 %, while a reflectance value of about 0.7 % is probably referred to semi-fusinite (Fig. 4.7). Traces of bituminite were found with a weak brownish fluorescence and reflectance values of about 0.3 % (Fig. 4.8).

In the external part of the Skiba unit, thermal maturity of the Melinite shales (Oligocene-Miocene) come from analyses on PL 97and PL 103b (Fig. 4.7). These two samples show a very heterogeneous composition of the organic matter with an

abundant occurrence of macerals of the inertinite group (fusinite and semi-fusinite macerals similar to those shown in Fig. 4.9) and of bituminite group with lower reflectance values (between about 0.2. and 0.35%) and weak brownish fluorescence. Vitrinite reflectance are respectively 0.44 % and 0.55% (Fig.4.7).


Figure 4.7 Reflectance histograms on all visible macerals (on the left) and vitrinite reflectance histograms (on the right) for Eocene - Oligocene and Oligocene - Miocene samples from the Skiba units (samples PL 102, PL 97 and PL 103b)

From the internal portion of the Skiba Unit, microscopical analyses on Melinite shales (Oligocene-Miocene) were performed on samples PL 93.1 and PL 93.2 . In detail, PL 93.1 is rich in inertinite and the histogram on the other organoclasts show dinstinct modes, in which the one on the left one refers to vitrinite reflectance with a mean value of 0.46 % and the one on the right one refers to semi-fusinite fragments reflectance value at about 0.7% (Fig. 4.10). Similarly sample PL 93.2 shows a great variety of macerals with the most abundant ones belong to the vitrinite group with a mean reflectance value of 0.42 % and the bituminite group with average reflectance value of 0.32%. PL 101.1 (Fig. 4.10) represents the Oligocene interval of the Melinite shales and shows vitrinite reflectance of 0.5%, while the most abundant group of macerals other than vitrinite is bituminite with weak brownish fluorescence.

Finally, PL 95 and PL 94 were collected in the Upper Krosno beds and at the transition between Melinite shales and Krosno beds from the internal portion of the Skiba Unit. They show Ro% of 0.45% and 0.58% respectively (Fig. 4.11).

4.4.3 Thermal modelling

Two thermal models for the Chornogora and Skiba tectonic units were perfomed in order to provide quantitative information regarding the experienced maximum burial in the study area. In the Borislav-Pokuttya unit, thermal modelling was not perfomed because of scarcity of maturity data. Thickness values used for modeling performed according to the pseudo-well method (Nöth et al., 2001; Oncken, 1982) derive from the work by Koltun et al. (1998). Pseudo-well thermal histories were calibrate using original Tmax and R_0 % maturity data summarised in Figure 4.12, using the kinetic equation by Sweeney and Burnham (1990). Tmax data were converted into vitrinite reflectance equivalent data using the conversion table by Robertson et al., (2008).



Figure 4.8 Microphotograph at 50X magnification in oil immersion taken on samples PL 93.1. The photo shows bituminite fragments (indicate by the circle) with brownish fluorescences during UV-light excitation



Figure 4.9 Microphotograph at 50X magnification at incident light in oil immersion taken on samples PL 101.1 showing an inertinite fragment



Figure 4.10 Reflectance histograms on all visible macerals (on the left) and vitrinite reflectance histograms (on the right) for Oligocene - Miocene samples from the Skiba units (samples PL 93.1, PL 93.2 and PL 101.1)

Calibration curve for the Chornogora unit is shown in Figure 4.13 a. In this unit the best fit was attained adopting a constant heat flow of 45 mW/m^2 . This value corresponds to the presentday heat flow value reported by Pospil (2006) and Kutas (1977) in the study area. No significant variations in the heat flow were found by other authors (Kotarba and Koltun, 2006b) up to, at least, Oligocene time and for the sake of simplicity, we adopted a constant value up to Cretaceous times.

Furthermore to fit the model a burial of 1,260m was required. Such a load equals to the minimum thickness of the Eocene to Lower Miocene succession that deposited on top of the Creataceous unit before thusting initiation in Aquitanian times (Koltun et al., 1998). In fact, according to Koltun, thicknesses of Eocene to Lower Miocene succession vary from about 1,200m to 4,000m.

Thus sedimentation started about 130 Ma ago, during Hauterivian times, with the deposition of the Shypot shales and sandstones and went on in

Upper Cretaceous and Cenozoic until Middle Miocene times with no significant changes in the sedimentation rates, except for a slowdown between the end of Cretaceous and the beginning of Eocene times (Fig. 4.13 b). According to the model, the Shypot formation was buried at depths of about 2 km and entered the oil window at the end of Cretaceous times. Finally, exhumation was set at about 5 My ago according to low T thermochronology data (e.g., apatite fission tracks FT and He dating on apatite) and models provided by Andreucci et al. (2015) along trasects located a few tens of km to the NW of the study area.

Calibration curve for the Skiba unit is shown in Figure 4.14 a. The fit between calculated and measured thermal maturity is not as good as in the Chornogora unit as Tmax data for sample PL 97, PL 94 and PL 101.1 tend to overestimate thermal maturity with respect to corresponding vitrinite reflectance data, and R_0 % value for sample PL_102 underestimate the calculated thermal maturity (Fig. 4.14 a). Nevertheless we chose to keep the same heat flow adopted for the Chornogora unit for the sake of simplicity.

Furthermore we cannot exclude that vitrinite reflectance (PL_102) in the Eocene interval is underestimated because of difficulty in discriminating true vitrinite from semifusinite fragments.



Figure 4.11 Reflectance histograms on all visible macerals (on the left) and vitrinite reflectance histograms (on the right) for Oligocene - Miocene samples from the Skiba units (samples PL 94 and PL 95)

A higher thickness of the Melinite shales formation was assumed in the Skiba with respect to the Chornogora unit. It is of 1,500m in agreement with values reported by Andreeva-Grigorovich et al. (1986) and Vialov et al. (1988). Furthermore an additional load, later on eroded of about 1,500 m, was hypothesised in order to fit the calibration curve (Figs. 4.14 a-b). It is interpreted as due to overthrusting (see the "Discussion" paragraph).

Burial and thermal history in Figure 4.14 b indicates a slow sedimentation during the whole

Paleocene and Eocene times and an increase in sedimentation rate in Oligocene and Miocene times due to the sedimentation of the Melinite shales-Krosno Beds and to thrusting since

Aquitanian times. In particular, Figure 4.14 b indicates that the Melinite beds were buried up to almost 3,000m of depth and the bottom of this unit entered in the oil window at about the end of Oligocene times. Finally exhumation was set at about 5 My according to Andreucci et al., (2015).

4.5 Discussion

4.5.1 Implications for HC generation

The area of interest in this study is part of the wider flysch belt of the Ukranian Carpathians, that is one of the oldest petroleum-producing region in the world (Kotarba and Koltun, 2006). In particular, the Melinite shales, buried in the Boryslav-Pokuttya tectnonic unit, act as the main oil-bearing succession in the whole Carpathian region (Kotarba and Koltun, 2006).

Our analyses pointed out the quality of the outcropping source rocks by means of TOC, HI and S2 values carried out by means of Pyrolysis Rock Eval, while the degree of thermal maturity has been assessed by means of organic petrography and Pyrolysis Rock Eval. The combination of both Tmax and vitrinite reflectance was crucial to unravel and correctly interpret data. In fact, as illustrated in the Results paragraph, reflectance on organoclasts often exhibit poli-modal distributions as often semi-fusinite and/or fusinite fragments were difficult to be distinguished from vitrinite ones. Thus, in many cases the comparison of reflectance values with Tmax helped in correctly assessing maturity.

According to the integrated approach, we can state that in the Chornogora Unit, black shales of the Shypot beds act as a good to very good gas and mixed gas and oil prone source rock (Fig. 4.5) and thermal maturity falls at the top of the oil window (Table 4.1). In the same tectonic unit, black shales from the Inoceramia beds

Sample	Coordinates	Tectonic unit	Age	Formation	Rock Type	TOC (%Wt)	S1 (mg/g)	S2 (mg/g)	ні	Tmax (°C)	Type of Kerogen	Ro% (n. of meas.)	stdv
PL 98	N48.16 E25.09122	Boryslav- Pokuttya	Senonian – Paleocene	Inoceramian Beds (Stryi Beds)	Siltite	0.58	0.01	0.25	43	437		0.58 (9)	0.07
PL 92a	N48.012 E24.91361	Chornogora Unit	Haterivian — Albian	Shypot	Black Shale	2.89	0.14	4.25	147	434	III gas- prone	ND	ND
PL 103a	N47.803 E25.15563	Chornogora Unit	Haterivian —Albian	Shypot	Black Shale	3.13	0.43	9.15	292	436	II Mixed Oil and Gas Prone	0.61 (30)	0.07
PL 103a2	N47.80345 E25.156	Chornogora Unit	Haterivian —Albian	Shypot	Black Shale	1.1	0.09	1.31	118	436	III Gas Prone	ND	ND
PL 92	N48.004 E24.90719	Chornogora Unit	Senonian– Paleocene	Inoceramian beds	Black Shale	1.41	0.02	0.83	59	441	III gas- prone	ND	ND
PL 103	N47.826 E25.17931	Chornogora Unit	Senonian– Paleocene	Inoceramian Beds	Siltite	0.18	0.01	0.03	17	ND	-	0.7 (12)	0.04
PL 102	N47.878 E25.22077	SkibaUnit	Eocene – Oligocene	Krosno/Menilite / Gl mrl	Pelite	0.58	0.04	0.91	157	433	III Gas prone	0.45 (32)	0.04
PL 104a	N48.07284 E25.284	Skyba Unit	Oligo – Lower Miocene	Menilite beds	Pelite	3.37	0.16	15.94	473	433	ll Oil Prone	ND	ND
PL 101.1	N47.9107 E25.251883	SkibaUnit	Oligocene - Lower Miocene	Upper Krosno Beds	Pelite	1.25	0.03	1.35	108	439	III Gas Prone	0.51 (50)	0.03
PL 101.2	N47.91073 E25.252	SkibaUnit	Oligocene – Lower Miocene	Upper Krosno Beds	Pelite	0.18	0.01	0.11	61	ND	-	ND	ND
PL 103b	N47.98211 E25.26851	Skyba Unit	Oligocene– Lower Miocene	Menilite beds	Pelite	1.6	0.21	5.64	353	436	ll Oil Prone	0.55 (5)	0.01

To be continued

		Tectonic unit			Rock Type	TOC	61	63		Tmov	Type of Kerogen	Ro%	
Sample	Coordinates		Age	Formation		(%Wt)	51 (mg/g)	52 (mg/g)	HI	(°C)		(n. of meas.)	stdv
PL 100	N47.951 E25.22248	Skiba Unit	Oligocene	Menilite beds / Krosno transition	Pelite	0.32	0.04	0.27	84	441	-	ND	ND
PL 94	N48.079 E24.98634	SkibaUnit	Oligocene - Lower Miocene	Upper Krosno Beds	Siltite	0.39	0.04	0.48	123	436	III Gas prone	0.58 (8)	0.06
PL 97	N48.145 E25.07269	SkibaUnit	Oligocene – Lower Miocene	Menilite beds	Pelite	2.92	0.32	9.54	327	433	ll Oil Prone	0.44 (11)	0.03
PL 93.1	N48.034 E24.92101	SkibaUnit	Oligocene – Lower Miocene	Lower Krosno Beds	Pelite	4,55	0.30	12.18	268	421	ll Mixed Oil and Gas Prone	0.46 (50)	0.03
PL 93.2	N48.034 E24.92101	SkibaUnit	Oligocene - Lower Miocene	Lower Krosno Beds	Pelite	11,29	1.21	41.26	365	422	ll Oil Prone	0.42 (31)	0.03
PL 93a	N48.03397 E24.9206	SkibaUnit	Oligocene -Lower Miocene	Upper Krosno Beds	Pelite	0.15	0.01	0.11	73	ND	-	ND	ND
PL 95	N48.094 E24.98933	SkibaUnit	Oligocene – Lower Miocene	Upper Krosno Beds	Black Shale	6.61	0.52	18.69	283	427	II Mixed oil and gas prone	0.45 (27)	0.05
PL 95a	N48.099 E24.98732	SkibaUnit	Oligocene – Lower Miocene	Menilite beds	Black Shale	1.1	0.10	2.12	193	430	II – III Gas prone	ND	ND

Table 4.1 Pyrolysis Rock Eval data collected in the area. Acronyms: TOC – total organic carbon; HI – hydrogen index; PI – production index; N.D. – not determined.



Figure 4.12 Thermal maturity distribution in map view (a) and in stratigraphic and tectonic order (b) derived from vitrinite reflectance (circles) and Tmax (triangles). Light Blue indicates immature samples, red indicate oil window

indicate a good potential for gas generation (Fig. 4.5), although Tmax values of 441°C is too low to generate gas.

In the internal portion of the Skiba unit, the Krosno beds show an excellent oil prone potential according to pyrolysis data (samples PL 93.1, PL 93.2 and PL 95), whereas PL 101.1 indicates a good gas generation potential. Nevertheless, thermal maturity of PL 93.1, PL93.2 and PL 95 indicate very immature source rocks and PL 101.1 show higher Tmax and R_0 % values, that are suitable for oil generation but not for gas.

In the external part of the Skiba Unit, the Melinite shales (PL 95a, PL 97, PL 103b and PL 104a) show a good, very good or excellent oil potential (Fig. 4.5) except for sample PL 95a that shows mixed good oil and gas potential. Thermal maturity indicators suggest the immature stage of HC generation except for sample PL 103b whose Tmax and R_0 % indicate suitable maturity for oil generation, but not for gas.

Finally in the Boryslav-Pokuttya tectonic unit, PL 98 sample shows a very low HC potential and thermal maturity in the oil window.

According to these results, we can figure out that only a few samples (PL 92a, PL 103 a1 and PL 103a2) in the analysed dataset were able to generate hydrocarbons. Nevertheless the three analysed tectonic units are part of a complex thrust stack where the Cretaceous and Oligocene-Lower Miocene black shales can be buried even at higher depths to those experienced by analysed samples.

As a result, source rocks can occur at different depths with the Melinite shales with the potential to generate oil and gas and the Shypot shales mainly gas.



Figura 4.13 (a) Thermal modelling calibration of Lower and Upper Cretaceous thermal maturity data (Ro% and Tmax) in the Chornogora unit. (b) 1D burial and thermal history of succession of the Chornogora unit. The thermal modeling has been performed using the kinetic EASY %Ro approach by Sweeney and Burnham (1990)

4.5.1 Implication for the tectonic-thermal evolution of the Carpathian fold-and-thrust belt

The thermal model presented in the "Results" paragraph for the Chornogora unit indicates that thermal maturity recorded by the stratigraphic succession was acquired in the undeformed sedimentary basin before thrusting. This interpretation is in agreement with Roure et al. (1993) who stated that no significant tectonic loading is expected in the Chornogora unit. On the other hand, Koltun and Kotarba (2006) underline the important role played by thrusting in the acquisition of the thermal signature for the same tectonic unit. Nevertheless their interpretation is biased by the fact that they calibrated their models only against Tmax data from the Shypot blak shales collected both in outcrops and in boreholes at different depths, but they did not show calibration curves.

In the Skiba unit, thermal maturity distribution is more complex than in the Chornogora one. Furthermore map of Figure 4.12 shows that the Skiba unit is internally stacked in a series of minor thrusts.

In this framework, it can be noted that less mature samples lies at the footwall of the basal thrust of the Chornogora unit, whereas slightly higher maturity values are mainly preserved in minor thrusts of the Skiba unit in more external positions. this evidence suggests that the role of the internal stacking in the Skiba unit must have played a role in tectonically overprinting the thermal signature of the Skiba stratigraphic succession. Our model is an acceptable simplification of this maturity distribution. It shows that a tectonic loading occurred overprinting the central part of the Skiba unit.

This model agrees with the Roure et al.'s restoration, (1993) and is in contrast with Koltun et al. (1998) who interpret the thermal maturity of outcropping Melinite shales in the Skiba unit as acquired before overthrusting.



Figura 4.14 (a) Thermal modelling calibration using Lower and upper Cretaceous thermal maturity data (Ro% and Tmax) in the Skiba unit. (b) 1D burial and thermal history of successions from the Skiba unit. The thermal modeling has been performed using the kinetic EASY %Ro approach of Sweeney and Burnham (1990)

4.6 Conclusion

A set of 21 samples collected on outcrops of three tectonic units in the central sector of the Ukranian outer Carpathians were analysed by means of Pyrolysis Rock Eval and organic petrography, in order to evaluate the HC generation potential of source rocks and to define the magnitude and the origin of the experienced burial.

Results from Pyrolysis analyses indicate good to eccelent quality source rocks, in particular in the Hauterivian-Albian black shales of the Shypot series and in the Oligocene-Lower Miocene Meleinite shales/Krosno beds. Major gas prone intervals are located in the Mesozoic formations, while oil and mixed oil and gas prone source rocks were found in Cenozoic successions. Nevertheless thermal maturity in the Lower Cretaceous just fall in the oil window ($0.6 < R_0\% < 0.7$ and 436 < Tmax < 441) while Oligocene-Lower Miocene samples are immature or very early mature ($0.42 < R_0\% < 0.51$ and $421^{\circ}C < Tmax < 433^{\circ}C$).

Organic petrographic analyses revealed a complex macerals assemblage that could have strongly biased an accurate thermal maturity estimation. Nevertheless integration with Tmax brought to a very good correlation between vitrinite reflectance data and Tmax that helped in a correct thermal maturity assessment. In addition data are in agreement with Tmax values performed on outcrop samples collected in the same area from Kotarba and Koltun (2006) and Koltun (1998).

After careful comparison with previous works, what our analyses point out is that Shypot black shales that outcrop in the Chornogora unit keep their pre-overthrusting thermal maturity signature after a maximum sedimentary burial of about 1,200 m. On the other hand, the Skiba unit must have been overthust by a 1,500m thick tectonic load to reach thermal maturities of its Cenozoic successions. This means that although

thermal maturity in the different tectonic units generally increase from older to younger sediments, local tectonic imprinting due to thrusting can affect the Skiba unit.

Our reconstruction partially differs from the previous interpretation after Kotarba and Koltun (2006) regarding the Chornogora and Skiba units, while are a good agreement with the model of Roure et al., (1993) as well as with the larger scale tectonic and thermal evolution of the Outer Carpathians drawn by Andreucci et al., (2015). In this last work was demonstrated on the basis of AFT data that the central tectonic units in the Polish Carpathians suffered higher tectonic loading during the compressional phases form the Upper Miocene. Even if at a smaller scale, our data indicate that a similar pattern can be observed in this sector of the Ukranian Carpathians.

Chapter 5

Modelling thermal maturity evolution of Paleozoic successions in the Holy Cross Mts (Poland) by means of new and old datasets of indicators of temperature exposure

5.1 Introduction

Reliable assessments of thermal maturity of sedimentary successions is crucial for evaluating hydrocarbons generation/expulsion scenarios. Uncertainties of thermal maturity data can affect decisions on the development of prospects, especially when aimed at exploring shale gas targets. In particular, this happens for lower Paleozoic targets, because of the lack of vitrinite macerals in kerogen. However, marine organoclasts and reflectance measurements can be carried on other kinds of organoclasts (e.g., scolecodonts, chitinozoans and in particularly graptolites; cfr., Bertrand, 1990; Bertrand and Heroux, 1987; Goodarzi and Norford, 1987, 1989; Tricker et al., 1992). In these cases the use of indicators of maximum thermal exposure other than vitrinite need to be correctly addressed especially in areas where studies of thermal maturity have been performed for many years by various generations of organic petrographers.

This is the case of Poland where in the last decade, a great interest in unconventional resources has been developed. Poland, , together with England, is the most perspective country in Europe for exploration in unconventionals. Here the Lower Paleozoic successions preserved in the subsurface in a wide belt (named the Golden belt), extending from the Baltic Sea to the NW, to the Ukraine border to the SE, between the Baltic basin and the Lublin basin, are targets for shale-gas exploration. Holy Cross Mountains (HCM) Paleozoic outcrops in Central Poland, to the W of the Golden Belt, provide a unique opportunity to study successions that can be envisaged as analogues for those preserved along the Golden Belt (Figs 5.1 and 5.2).

The Holy Cross Mountains (HCM) are located to the east of the Trans-European Suture Zone (TESZ) where well preserved outcrops of Cambrian to Permian sedimentary rocks are exposed as a results of the uplift of the area at the end of Mesozoic times.



Figure 5.1 Location of the study area and shale and oil prospectivity areas in north Europe (Dittrick, 2011, http://www.ogj.com)

Many works (Belka, 1990; Marynowski 2001; Narkiewicz, et al.. 2002: Szczepanik, 1997, 2001) have been performed to unravel the complex burial and thermal history of the HCM using different datasets of thermal maturity indicators (e.g., Conodont Alteration Index- CAI; Acritarchs Alteration Index – AAI, Thermal Alteration Index, TAI), but a comprehensive and fully accepted model has not yet elaborated. In particular, major uncertainties derive from the lack of univocal correlation of thermal indicators (e.g., TAI, CAI, maximum AAI) against paleotemperatures that should lead to

contrasting interpretations in the assessment of maturation patterns and timing of hydrocarbon generation of potential Lower Silurian source rocks (Belka, 1990; Marynowski et al., 2001; Narkiewicz, 2002, 2010; Poprawa et al., 2005).

Recently, Silurian source rocks have been studied by organic matter optical analyses and Pyrolysis Rock Eval (Malec et al., 2010; Mustafa et al., 2015; Smolarek et al., 2014) but these data were not employed as constraints for burial and thermal modelling.

In this Chapter available thermal maturity data from literature have been revised and integrated with new thermal maturity data derived from the analyses of the organic (e.g., Tmax from Pyrolysis Rock Eval, and organoclasts reflectance from organic petrography) and inorganic fraction (e.g., illite content in illite-smectite mixed layers) of sediments.

This multi-method approach allowed us to calibrate two thermal and models, for the two tectonostratigraphic blocks in which the geological structure of the HCM is organized: the southern Lysogory and southern Kielce blocks, in order to highlight the burial and thermal evolutionary scenario since Paleozoic times for both sectors.

Furthermore, the integration of different thermal indicators from the organic and inorganic portion of sediments is proposed to reduce the level of uncertainties in thermal maturity assessment and can be successfully applied to similar Paleozoic source rocks successions worldwide.



Figure 5.2 Geological map of the HCM with sampling location. Modified and redrawn after Konon (2007)

5.2 Geological setting

5.2.1 Stratigraphy

The Paleozoic succession of the Holy Cross Mts. is made up of marine sedimentary rocks aged between Cambrian to Permian, which were buried by a thick Permian-Mesozoic sedimentary cover and by Neogene continental deposits, nowdays totally eroded (Kutek and Głazek, 1972).

The HCM are organized into two distinct tectono-stratigraphic blocks: the southern block (Kielce Region) and the northern block (Łysogòry Region), bounded by by a deep regional lineament, known as Holy Cross Fault (HCF, Figs. 5.2, 5.3,5.4) (Dadlez, 2001; Kutek, 2001).

The Paleozoic sedimentary succession, exposed in both blocks, consists of Cambrian siliciclastic rocks deposited along the SW passive margin bordering the Baltic continent (Mizerski, 2004). Cambrian sediments are made up of shales evolving to quartzarenites and sandstones towards the top (Narkiewicz, 2002).

Since the Ordovician up to the Carboniferous, the sedimentation differently evolved in the two blocks leading to considerably differences in facies and thickness distribution. These differences have been related by some authors (Dadlez et al., 1994; Narkiewicz, 2002) to a different paleogeographic positions of the two blocks in the Lower Paleozoic, while, according to Mizerski (2004) and Jaworowski and Sikorska (2006) the



Figure 5.3 Geological section of the NW sector of the Holy Cross Mountain. From Stefano Celano Msc Thesis, AA 2013/2014.

Łysogòry Region



Figure 5.4 Stratigraphy of the Paleozoic succession in the Lysogory (a) and Kielce blocks (b). Modified and redrawn after Kozlowski (2008) and Gągał (2015)

two blocks had a similar paleogoegraphic position and the different evolution could be related to differential vertical movements along the Holy Cross Fault.

In the Kielce region, Ordovician clayey and silty marine deposits lie with a distinct angular unconformity over the Lower to Middle Cambrian rocks (Konon, 2007; Kozłowski, 2008; Kozłowski et al., 2014; Narkiewicz, 2002; Schätz et al., 2006; Urban and Gagol, 2008), (Fig. 5.4).

Ordovician deposits are covered by about 300m of Lower Silurian graptolitic shales (Kozłowski, 2008), 300m of Ludfordian greywackes (Niewachow Beds, Kozłowski et al., 2014) and 400m of the Kielce Beds sandstones. Locally, in the Bardo syncline and in Gruchawa area, the Miedziana Góra Conglomerate occurs (Kozłowski et al., 2014).

Devonian sediments (Pragian-Emsian) are composed of sandstones which unconformably overlie Silurian and/or locally Cambrian rocks(Kowalczewski, 1974), and by shallow marine carbonate facies (Narkiewicz and Narkiewicz, 2010).

Lower Carboniferous marine marly and clay rocks can be observed at the core of the Devonian folds in the northern part of the Kielce block near the HCF (Fig. 5.2).

In the Łysogóry block, no unonformities were found at the base of Ordovician rocks, over which Llandoverian-Wenlockian graptolites shales with thickness between 150 and 300m lie (Kozłowski 2008, 2014 and Narkiewicz 2002). Niewachow Beds of the Kielce block are represented in the Łysogóry block by 500 m-thick lithic arenites and shales of the Trzcianka Formation which are overlaid by 550m of shale-siltstone succession of the Trochowiny Formation (Kozłowski, 2008). Unlike the Kielce region, in the Łysogóry block, the Ludfordian greywackes are covered by a thick succession of clastic sediments representing a continuous Late Ludlovian -Lochkovian succession in composed of the Pridolian Bronkowice/Sarnia, Podchelmie and Rudki Formations and by the Lochovian Bostow formation (fig. 5.4). Middle to late Devonian carbonate deposits cover conformably these clastic formations (Szulczewski et al., 1996).

In both Łysogóry and Kielce regions, the whole Cambrian to Devonian/Carboniferous successions were unconformably covered by a Late Permian–Early Triassic continental clastic succession (Konon, 2004; Kozłowski, 2008).

5.2.2 Tectonic setting

Tectonic setting of the HCM is dominated by the intensive folding of Paleozoic successions and by the multi-phase activity of the WNW–ESE-striking HCF which separates the area into two tectonic blocks (Fig. 5.3). This fault shows a strong overprint related to transpression (Narkiewicz, 2002) probably due to the detach of the southern block along the SW margin of Baltica, according to some authors (Dadlez et al., 1994). This hypothesis can be explained assuming a separate origin of two tectonic blocks along the passive margin of Baltica, but is still under debate.

The role of different orogenetic cycles is still a matter of debate in the HCM.

The primary role played by the Variscan deformation to explain the present day tectonic features is generally recognized (Lamarche et al., 1999 and Mizerski, 2004) with a pre-Late Carboniferous NW-SE compression and polyphase folding associated with a dominant N-S to NNW-SSE shortening (Lamarche et al., 1999).

Furthermore, not all all authors recognize the polyphase Early Caledonian deformation detected by Gągała (2005) in the Lower and Middle Cambrian rocks of the Kielce block and the Late Caledonian movements that caused a shallowing of the marine basin in the Łysogóry block and wide-radius deformations associated with faulting in the Kielce region, as evidenced by Mizerski (2004).

Early Paleozoic deformed successions were unconformably overlain by conglomerates of Upper Permian age and the Mesozoic cover deposited as a result of the reactivation of the HCF as a normal fault associated with the extensional tectonic regime that dominated from Permian until Cretaceous times (Kutek, 1974; Lamarche, 1999 and Mizerski, 2004).

Finally at the Cretaceous– Paleogene boundary, tectonics associated with the Laramide stage caused a positive tectonic inversion with the HCF acting as a reverse fault. This last deformation brought to the exhumation of the Palaeozoic strata (Konon, 2004; Mizerski, 2004).

5.2.3 Previous thermal maturity data

Thermal maturity of Cambrian rocks has been assessed by Thermal Alteration Index of Acritarchs (AAI) (Szczepanik, 1997, 2001), while Conodont Alteration Index (CAI) data were collected from Ordovician and Silurian rocks (Narkiewicz, 2002). A dataset of organic matter reflectance measurements performed on graptolites and other organoclasts is provided by Smolarek et al. (2014) for Silurian rocks, while a large number of vitrinite reflectance and CAI data from Devonian successions, in particular in the Kielce region, are from Marynowski et al. (2001) and Rospondek et al. (2008).

To be compared, the different thermal indicators have been converted into paleotemperatures. CAI data have been converted using correlation tables proposed by Scotti (2005), while R_0 % values by using the most accepted Barker and Pawlewicz's equation (1994). As univocal conversion does not exist for TAI data, we used the paleotemperatures provided by Szczepanik (1997, 2001) in his works.

Data for each selected time interval (Cambrian-Ordovician, Silurian and Devonian) have been interpolated using Kernel Interpolation tool with ArcGis software, in order to produce three different prediction maps of paleotempratures in the HCM (Fig. 5.5). Kernel Interpolation tool was preferred with respect to other available interpolation tools for the possibility to introduce a tectonic discontinuity such as the Holy Cross Fault.

5.2.3.1 Cambrian and Ordovician

CAI and Translucens Index AMOCO (TAI) data come principally from the works of Szczepanik (1997) and Narkiewicz (2002) from samples collected in a series of boreholes, mainly not deeper than 500m.

In the Kielce region CAI values (Narkiewicz, 2002) and TAI performed on acritarchs (Szczepanik, 1997) were analysed in Lower Cambrian (Zareby-2, Ossolin-1, Wrzachow-2 boreholes) and Upper Cambrian

(Ublinek 1-bis borehole) and Tremadocian (Mojcza borehole) rocks (Fig. 5.5 a) according to the trilobite and acritarchs zonation of Żylińska and Szczepanik (2009).

In terms of paleotemperatures these data never exceed 100°C (TAI 5-6 in the Zareby-2 boreholes) and are usually comprised between 50-80°C according to Szczepanik (1997).

In the Łysogóry block, data are from the Upper Cambrian shales of the Wilkow-1 borehole and the Chabowe Doły and Wiśniówka Mała outcrops (Szczepanik, 1997) and from Ordovician rocks collected in the Pobrośzyn borehole (Narkiewicz, 2002).

CAI and TAI values are systematically higher than those observed in the Kielce block, between 3-4 (CAI) and between 6-7 (TAI AMOCO). According to the two authors, maximum paleo-temperatures range between 150 and 300°C.

5.2.3.2 Silurian

Thermal maturity of Silurian graptolites-bearing shales have been assessed by CAI indexes reported in Narkiewicz (2002) and by reflectance measurements performed on vitrinite-like macerals by Smolarek et al., (2014).

Samples are from boreholes and outcrops and correspond to the Llandoverian (Zbrza, Wilkow and Szumsko boreholes and Bardo Stawy outcrops) to Ludlow time interval (Bardo Pragowiec outcrops).

There are only two CAI values from the Kielce region which show low maturity (1.5) in the Bardo syncline and a higher values of 4 close to the HCF (borehole Gruchawka 1, Fig. 5.5b). Values from graptolites reflectance analyses and/or other organoclasts (Smolarek et al., 2015) indicate higher maturities with respect to those found in previous works that generally increase from north to south, from values of about 0.7 in the Zbrza-1 borehole, to values up to 1.9 in the Daromin-1 borehole.

In terms of maximum paleo-temperatures (Fig 5.5 b), the Kielce block mainly experienced maximum values between 100 and 120°C with the exception of one samples close to the fault (Kleczanow and Lenarczyce boreholes) and in the NW sector (Mojcza outcrop and Zagorze-1 borehole) where maximum paleo-temperatures exceeded 150°C. In the Łysogory region, higher temperature were recorded, ranging between 150 and 180°C or exceeding 200°C in the outcrops along the northern limb of the Bodzentyn syncline.

5.2.3.3 Devonian

Organic matter optical analyses on Devonian rocks have been widely performed in the Kielce region where limestones and shales are exposed in several quarries, while in the Lysogory region data are from the Eifelian sandstones and Emsian shales in the northernmost part of the region (Belka 1990).

Thermal maturity generally increases toward the north from about 0.5 to 1.2 in the Kielce block and reaching maximum CAI values of 3.5 in the northern part of the Łysogory region (Fig. 5.5c).

Lower thermal maturities were measured in the south-western part of the Kielce region where Fammenian to Eifelian limestones and dolostones crop out or are reached by drilling. Here vitrinite reflectance values ranges between 0.55 for the Frasnian black shale in the Kowala quarry, to about 0.67 for the Eifelian

Cambrian and Ordovician



Silurian



Devonian



Figure 5.5 Paleothermal maps derived from thermal maturity indicators from: Belka (1990); Marynowski et al. (2001); Narkiewicz (2002); Smolarek et al. (2014); Szczepanik (1997, 2001)

dolostones collected from the Kowala-1 borehole (Marynowski et al., 2001; Rospondek et al., 2008). Moving toward the NE, vitrinite reflectance values range between 0.74 and 0.83 along the Holy Cross Fault, whereas higher values of $1.15-1.2 \text{ R}_0\%$ were observed in the Laskowa Gora where shales and dolostones from the Givetian to Frasnian Komosloty formations crop out.

In the Łysogóry block, Devonian successions are exposed only in the northern part, near the town of Bodzentyn. Thermal maturity of these rocks was assessed by CAI (Marynowski et al. (2001) and Belka (1990), showing values of about 3.5.

Conversion into paleo-temperatures shown in Figure 5.5 c indicate values between about 85 and 110°C in the northern block and between 110 and 220°C reaching maximum values in the northernmost portion of the study area.

5.3 Materials

Samples analyzed in this work are located in map of Figure 5.2 and listed in Tables 5.1. Suitable samples for the X-ray diffraction analyses of fine grained sediments and optical, TOC and pyrolysis analyses of kerogen mainly derive from shaly- silty and organic matter rich beds.

In the Kielce block, HCM 7.1 is the only sample collected from brownish siltstones Cambrian rocks outcropping in the southern Ocieseki anticline.

In the Bardo syncline (Fig. 5.2) Upper Ordovician (Hirnatian) to Lower Ludlow samples were collected (Trela et al., 2012). In the southern limb of the syncline from the outcrop of the Bardo Stawy, sample HCM 5.4 is from the sandy mudstones with subordinate shales and sandstones of the Zalesie Formation (Upper Ordovician). Three samples (HCM 5.1, HCM 5.2, HCM 5.3) are from the black radiolarian cherts of the Zbrza member and from the light brown shales of the Rembów Member (Llandoverian).

Middle-Upper Silurian samples (HCM 4.1, HCM 4.2, HCM 4.3a, HCM 4.3b, HCM 4.4, HCM 4.5) for the Kielce block were collected from the northern limb of the Bardo syncline, in the Prągowiec ravine where Lower Ludlow graptolitic shales and Upper Wenlock graptolitic shales and mudstones crop out.

Sample HCM 19.1 comes from the Llandoverian graptolitic shales cropping out on top of the Ordovician glauconitic sandstones. in the Międzygórze syncline.

Devonian samples in the Kielce region range in age from Givetian to Fammenian. Samples HCM 16.1 and HCM 16.2 were collected from a mudstones and calcareous mudstones of the Szydłowek formation in the Mogiłki quarry. Sample HCM 15.1 comes from a Frasnian shaly interval interbedded in dark limestones of the Kostomłoty formation (Kostomłoty hill. to the south of Kielce). Sample HCM 20.1 represents the shaly intercalation into cherty-rich mudstones at the Frasnian-Fammennian boundary in the Łabędziow anticline.

In the Lysogory region, Cambrian interval was sampled close to the HCF in the northern part of the Miedziana Góra syncline where weakly metamorphosed black shales crop out (HCM 1.1, HCM 1.2, HCM 1.3) interbedded with shaly mudstones and limestones.

For the Silurian interval, Ludfordian graywackes were collected on both limbs of the Bodzentyn syncline. In the southern limb (Fig. 5.2) shaly intervals of the turbiditic successions of the Ludlowian-Pridolian Winnics

Samples	Coordinates (Lat-Long)	Formation	Age	Area	Lithologies
		PALEOZOIC			
HCM 7.1	N50° 36' 24.2", E20° 04' 23.0"	Zbrza	Cambrian inf.	Kielce	Marl
HCM 1.1	N50° 53' 41.2", E20° 47' 24.5"		Cambrian sup.	Lysogory	Laminated shales
HCM 1.2	N50° 53' 43.9", E20° 47' 34.2"		Cambrian sup.	Lysogory	Laminated shales
HCM 6.1	N50° 43' 13.3", E21° 04' 46.2"		Ordovician sup.	Kielce	Laminated shales
HCM 5.4	N50° 43' 27.4", E21° 03' 31.2"		Ordovician sup.	Kielce	Black shales
HCM 19.1	N50° 44' 24.8", E21° 33' 49.9"		Llandoverian	Kielce	Black shales
HCM 5.1	N50° 43' 27.5", E21° 03' 02.5"	Bardo	Llandoverian	Kielce	Silty shales
HCM 5.2	N50° 43' 27.5", E21° 03' 02.5"	Bardo	Llandoverian	Kielce	Silty shales
HCM 5.3	N50° 43' 28.4", E21° 03' 36.6"	Bardo	Llandoverian	Kielce	Silty shales
HCM 4.5	N50° 44' 46.8", E21° 02' 14.6"		Wenlock	Kielce	Silty shales
HCM 4.4	N50° 44' 43.3", E21° 02' 00.3"		Wenlock	Kielce	Marly clay
HCM 4.3b	N50° 44' 49.3", E21° 01' 58.0"		Ludlowian	Kielce	Marly clay
HCM 4.3a	N50° 44' 49.3", E21° 01' 58.0"		Ludlowian	Kielce	Marly clay
HCM 4.2	N50° 44' 49.4", E21° 01' 55.5"		Ludlowian	Kielce	Marly clay
HCM 4.1	N50° 44' 48.9", E21° 01' 50.5"		Ludlowian	Kielce	Silt
HCM 13.1	N50° 50' 34.8", E21° 05' 13.6"	Trzcianka	Ludlowian	Lysogory	Shales
HCM 12.1	N50° 58' 43.5", E21° 00' 11.9"	Trzcianka	Ludlowian	Lysogory	Silty shales
HCM 12.2	N50° 58' 43.5", E21° 00' 11.9"	Trzcianka	Ludlowian	Lysogory	Silty shales
HCM 11.1	N50° 58' 39.6", E21° 00' 46.3"	Trochowiny	Ludlowian	Lysogory	Shales
HCM 11.2	N50° 58' 39.6", E21° 00' 46.3"	Trochowiny	Ludlowian	Lysogory	Silty shales
HCM 10.1	N50° 52' 23.0", E21° 06' 15.7"	Winnica	Ludlowian	Lysogory	Silty shales
HCM 8.1	N50° 53' 41.2", E21° 09' 30.6"		Eifelian	Lysogory	Marly clay
HCM 16.1	N50° 55' 24.5", E20° 34' 48.7"	Szydłówek	Givetian	Kielce	Marly clay
HCM 16.2	N50° 55' 24.5", E20° 34' 48.7"	Szydłówek	Givetian	Kielce	Marly limestones
HCM 9.1	N50° 51' 43.3", E21° 01' 32.1"		Givetian/	Lysogory	Silty shales
HCM 2.1	N50° 54' 30.6", E20° 47' 45.2"		Frasnian	Lysogory	Black shales
HCM 15.1	N50° 53' 11.3", E20° 35' 07.9"	Kostomłoty	Frasnian	Kielce	Marly clay
HCM 20.1	N50° 51' 07.9", E20° 49' 12.9"		Frasnian/	Kielce	Marly limestones
		MESOZOIC			
HCM 14.1	N50° 57' 38.1", E21° 11' 40.9"		Triassic	Lysogory	Arenite
HCM 17.1	N51° 08' 49.7", E20° 39' 41.3"		Hettangian	Lysogory	Arenite
HCM 17.2	N51° 08' 49.7", E20° 39' 41.3"		Hettangian	Lysogory	Black shales
HCM 17.3	N51° 08' 49.7", E20° 39' 41.3"		Hettangian	Lysogory	Shales
HCM 17.4	N51° 08' 49.7", E20° 39' 41.3"		Hettangian	Lysogory	Marly limestones
HCM 17.5	N51° 08' 49.7", E20° 39' 41.3"		Hettangian	Lysogory	Arenite
HCM 18.1	N50° 53' 30.2", E21° 21' 36.3"		Lias	Lysogory	Silty shales

Table 5.1 The table indicate the coordinates, ages, tectonic block and lithology for each sample

formation (HCM 10.1) and of the lower Ludlowian Trzcianka formation (HCM 13.1) were collected. In the southernmost part of the Bronkowice-Wydryszów anticline four shaly intervals were sampled, two belong to the lower Ludlowian Trzcianka formation (HCM 12.1 and HCM 12.2) and two to the upper Ludlowian Trochowing formation (HCM 11.1 and HCM 11.2).

In the core of the Bodzentyn syncline, to the north of Nowa Słupia, sample HCM 8.1 was collected from the Eifelian mudstones. Upper Devonian samples come from Givetian-Frasnian siltstones near Lupianka (HCM 9.1) and from black shales to the north of the Miedziana Gora syncline (HCM 2.1).

Samples from the Mesozoic come from two localities. Sample HCM 14.1 belongs to Triassic red sandstones cropping out in a quarry close to Ostrowice Świętokrzyski locality, whereas samples HCM 17.1, HCM

17.2, HCM 17.3, HCM 17.4, HCM 17.5 and HCM 18.1 come from the Jurassic deposits of the Sołtyków abandoned quarry.

5.4 Results

5.4.1 TOC and Pyrolysis Rock-Eval

TOC measurements and Pyrolysis Rock-Eval are listed in Table 5.2. TOC content in analysed samples is very low, almost always below 1%.

In the Kielce region, the Ordovician-Silurian samples with TOC content higher than 1% are those from Wenlock-Ludlow (HCM 1.3b and HCM 4.4), Llandoverian (HCM 5.1, HCM 5.2, HCM 5.3) and Ordovician (HCM 5.4) intervals collected in the Bardo syncline.

Middle Devonian samples from the Mogiłki quarry (HCM 16.1 and HCM 16.2) show highest TOC values of 4.57 and 9.17% respectively.

Jurassic rocks show very high TOC with a maximum of 5.89 for sample HCM 18.1.

Samples from the Łysogory region generally show very low content of organic carbon with values always below 0.5%.



Figure 5.6 S1+S2 pyrolisys data vs. total organic carbon showing the petroleum source rock potential for Cambrian to Triassic rocks

Results from Pyrolysis Rock-Eval show a general low potential except for sample HCM 16.2 that shows S1 and S2 values indicating a good potential (respectively higher than 1 and 5).

Hydrogen index (HI) values indicate in almost all samples gas prone sources (0 <HI < 150) and only for three samples from the Bardo syncline (HCM 4.3b. HCM 5.1 and HCM 5.2) and for two Jurassic samples (HCM 17.4 and HCM 17.5) gas and oil prone sources (HI > 150).

Samples	TOC (Wt%9	S1 (mg/g)	S2 (mg/g)	HI	Tmax	PI				
PALEOZOIC										
HCM 7.1	0.08	0.01	0.02	25	N.D.	0.33				
HCM 1.1	0.31	0.02	0.02	6	N.D.	0.50				
HCM 1.2	0.60	0.07	0.06	10	N.D.	0.54				
HCM 6.1	0.08	0.01	0.04	50	N.D.	0.20				
HCM 5.4	2.31	0.03	2.92	126	439	0.01				
HCM 19.1	0.82	0.02	0.53	65	442	0.04				
HCM 5.1	2.01	0.09	4.36	217	439	0.02				
HCM 5.2	2.04	0.10	4.28	210	437	0.02				
HCM 5.3	1.88	0.09	2.81	149	440	0.03				
HCM 4.5	0.81	0.09	0.84	104	441	0.10				
HCM 4.4	1.16	0.16	1.72	148	442	0.09				
HCM 4.3b	1.18	0.28	2.36	200	441	0.11				
HCM 4.3a	0.93	0.15	1.35	145	441	0.10				
HCM 4.2	0.72	0.10	0.79	110	439	0.11				
HCM 4.1	0.50	0.10	0.41	82	441	0.20				
HCM 13.1	0.2	0.02	0.05	25	N.D.	0.29				
HCM 12.1	0.09	0.02	0.02	22	N.D.	0.50				
HCM 12.2	0.09	0.04	0.03	33	N.D.	0.57				
HCM 11.1	0.11	0.01	0.04	36	N.D.	0.20				
HCM 11.2	0.10	0.02	0.04	40	N.D.	0.33				
HCM 10.1	0.13	0.01	0.01	8	N.D.	0.50				
HCM 8.1	0.23	0.01	0.05	22	N.D.	0.17				
HCM 16.1	4.57	0.10	0.41	9	530	0.20				
HCM 16.2	9.17	1.27	5.52	70	476	0.17				
HCM 9.1	0.11	0.01	0.03	27	N.D.	0.25				
HCM 2.1	0.32	0.06	0.05	16	N.D.	0.55				
HCM 15.1	0.30	0.01	0.10	33	N.D.	0.09				
HCM 20.1	0.49	0.03	0.35	71	441	0.08				
		M	ESOZOIC							
HCM 14.1	0.03	0.02	0.02	67	N.D.	0.50				
HCM 17.1	0.39	0.01	0.13	33	N.D.	0.07				
HCM 17.2	4.72	0.01	1.50	32	439	0.01				
HCM 17.3	0.87	0.01	0.52	60	439	0.02				
HCM 17.4	1.33	0.01	2.36	177	438	0.00				
HCM 17.5	1.66	0.02	2.87	173	437	0.01				
HCM 18.1	5.89	0.04	2.25	38	433	0.02				

Table 5.2 Pyrolysis Rock Eval data collected in the area. Acronyms: TOC – total organic carbon; HI – hydrogen index; PI – production index; N.D. – not determined.

Tmax values were defined for 19 samples, mainly in the Silurian rocks outcropping in the Bardo syncline (HCM 4.1, HCM 4.2, HCM 4.3a, HCM 4.3b, HCM 4.4, HCM 4.5, HCM 5.1, HCM 5.2, HCM 5.3 and HCM 5.4), and in HCM 19.1, in Givetian rocks outcropping in the Mogiłki quarry (HCM 16.1 and HCM 16.2) and HCM 20.1 and in the Jurassic samples (HCM 17.1, HCM 17.2, HCM 17.3, HCM 17.4, HCM 17.5 and HCM 18.1). Tmax values are between 437 and 441°C in Ordovician-Silurian of the Bardo syncline, indicating the oil window, whereas the gas window was achieved in samples HCM 16.1 and HCM 16.2 (Tmax > 470°C) and the immature stage to the onset of the oil window (433 < Tmax < 439) for the Jurassic samples. Samples HCM 19.1 and HCM 20.1 show Tmax values of 442 and 441°C respectively.

Figures 5.6 and 5.7 summarized the HC generation potential of analysed samples. In particular, Figure 5.6 indicate that mainly Silurian, Jurassic and in minor account Devonian kerogen shows values indicative of source rocks with fair to good HC generation.

Figure 5.7 indicates that kerogen for almost all samples show affinities with a type III kerogen and that sources are mainly gas prone.



Figure 5.7 Diagram of S2 vs TOC for kerogen classification and source rocks potential according to Langfor and Blac-Valleron (1999)

5.4.2 Clay mineralogy data

X-ray diffraction results for the whole-rock composition and the $< 2 \mu m$ grain-size fraction of Cambrian to Jurassic samples of both tectonic blocks are shown in Table 5.3 and plotted in Figure 5.8.

Randomly oriented whole-rock powder patterns of Cambrian samples are composed mainly of phyllosilicates (73-76%) and quartz (18-23%) with subordinate amounts of plagioclase (3-4%) and k-feldspar (1-2%, Table 2). The <2 μ m grain-size fraction contains illite (91%) as major mineral and subordinate amounts of rectorite, kaolinite, chlorite and pyrophyllite.

The whole-rock mineralogical assemblage of Cambrian sample HCM 7.1, collected in the Kielce area, is made up of phyllosilicates (76%), quartz (13%), plagioclase (10%) and minor amounts of hematite (1%). The $<2\mu$ m grain size fraction shows illite as the principal component (72%), and subordinately mixed layers illite-smectite (10%), chlorite-smectite (17%) and low amounts of chlorite (1%). Mixed layers illite-smectite are composed of two populations of illite-smectite crystals characterized by short-range and long-range structures with low expandability (R1-R3 I-S with an illite content of 77%).

Ordovician samples were collected from the Bardo syncline, in the Kielce block. They are mainly characterized by phyllosilicates and quartz, which constitute 96%-97% of the overall composition. Plagioclase, hematite (HCM 6.1) and k-feldspar (HCM 5.4) occur as minor phases. Illite, mixed layers I-S

Samples	Whole-rock composition	<2µm grain size fraction	%l in I-S (R)	%C in C-S					
PALEOZOIC									
HCM 7.1	Qtz ₁₃ Pl ₁₀ Ph ₇₆ Hem ₁	I ₇₂ I-S ₁₀ C-S ₁₇ Chl ₁	77 (R1-R3)	55					
HCM 1.1	Qtz ₁₈ Kfs ₂ Pl ₄ Ph ₇₆	I ₉₁ Rec ₅ Chl ₃ Prl ₁	N.D.	N.D.					
HCM 1.2	Qtz ₂₃ Kfs ₁ Pl ₃ Ph ₇₃	I ₉₀ Rec ₃ KIn ₆ PrI ₁	N.D.	N.D.					
HCM 6.1	Qtz ₂₃ Pl ₂ Ph ₇₃ Hem ₂	I ₆₉ I-S ₁₁ KIn ₂₀	83 (R3)	N.D.					
HCM 5.4	Qtz ₃₃ Kfs ₁ Pl ₂ Ph ₆₄	I ₅₉ I-S ₂₀ KIn ₂₁	83 (R3)	N.D.					
HCM 19.1	Qtz ₁₇ Pl ₃ Ph ₇₄ Gt ₆	I ₈₇ I-S ₇ KIn ₅ ChI ₁	83 (R3)	N.D.					
HCM 5.1	Qtz ₄₀ Kfs ₁ Pl ₃ Ph ₅₆	I72 I-S15 ChI13	77 (R1)	N.D.					
HCM 5.2	Qtz ₃₁ Kfs ₁ Pl ₆ Ph ₆₂	I ₇₄ I-S ₁₅ ChI ₁₁	77 (R1)	N.D.					
HCM 5.3	Qtz ₁₄ Pl ₇ Ph ₇₉	I_{85} I-S ₁ C-S ₉ KIn ₁ ChI ₄	83 (R1-R3)	60					
HCM 4.5	Qtz ₁₇ Kfs ₁ Pl ₇ Ph ₇₅	I ₆₉ I-S ₇ C-S ₁₇ KIn ₃ ChI ₄	83 (R3)	60					
HCM 4.4	Qtz ₁₄ Cal ₄ Kfs ₁ Pl ₈ Ph ₆₉ Py ₂ Dol ₂	I67 I-S2 C-S10 KIn4 ChI17	81 (R3)	80					
HCM 4.3b	Qtz ₁₇ Cal ₅ Kfs ₁ Pl ₉ Ph ₆₇ Dol ₁	I ₆₅ I-S ₂ C-S ₈ KIn ₃ ChI ₂₂	80 (R3)	80					
HCM 4.3a	Qtz ₁₇ Cal ₆ Kfs ₁ Pl ₁₂ Ph ₆₂ Py ₁ Dol ₁	I ₆₆ I-S ₆ C-S ₉ KIn ₅ ChI ₁₄	82 (R3)	80					
HCM 4.2	Qtz ₁₃ Cal ₂ Kfs ₁ Pl ₁₀ Ph ₇₄	I ₅₅ I-S ₁₂ C-S ₁₂ KIn ₄ ChI ₁₇	83 (R3)	80					
HCM 4.1	Qtz ₁₂ Kfs ₁ Pl ₈ Ph ₇₉	I ₆₄ I-S ₁₉ C-S ₁₄ KIn ₁ ChI ₂	80 (R1-R3)	60					
HCM 13.1	Qtz ₉ Pl ₂ Ph ₈₉	Sm ₄₃ I ₅₀ I-S ₂ ChI ₅	88 (R3)	N.D.					
HCM 12.1	Qtz ₁₆ Pl ₆ Ph ₇₈	I ₆₂ I-S ₄ ChI ₃₄	86 (R3)	N.D.					
HCM 12.2	Qtz ₁₅ Pl ₆ Ph ₇₉	$I_{62} I-S_8 C-S_{11} KIn_4 ChI_{15}$	86 (R3)	54					
HCM 11.1	Qtz ₅ Pl ₄ Ph ₈₈ Hem ₃	I_{83} I-S ₅ KIn ₁₀ ChI ₂	85 (R3)	N.D.					
HCM 11.2	Qtz ₁₅ Pl ₄ Ph ₈₀ Hem ₁	I_{79} I-S ₁₂ KIn ₄ ChI ₅	85 (R3)	N.D.					
HCM 10.1	Qtz ₁₅ Pl ₆ Ph ₇₉	I ₅₈ I-S ₂₄ C-S ₁₀ KIn ₇ ChI ₁	85 (R3)	78					
HCM 8.1	Qtz ₂ Cal ₂₅ Ank ₁ Ph ₇₂	I ₇₆ I-S ₁₆ KIn ₈	83 (R3)	N.D.					
HCM 16.1	Qtz ₇ Cal ₂₅ Kfs ₁ Pl ₂ Ph ₆₅	I ₇₉ I-S ₇ ChI ₁₄	82 (R3)	N.D.					
HCM 16.2	$Qtz_5 Cal_{52} Kfs_1 Pl_1 Ank_5 Ph_{35} Py_1$	N.D.	N.D.	N.D.					
HCM 9.1	Qtz ₉ Pl ₂ Ph ₈₇ Hem ₂	I ₅₉ I-S ₆ KIn ₂₇ ChI ₈	82 (R3)	N.D.					
HCM 2.1	Qtz ₁₀ Pl ₄ Ph ₈₆	I ₉₅ I-S₁ C-S₃ KIn₁	84 (R3)	50					
HCM 15.1	Qtz ₆ Cal ₄₈ Pl ₁ Ph ₄₅	I ₈₅ I-S ₁₅	85 (R3)	N.D.					
HCM 20.1	Qtz ₂ Cal ₇₅ Ph ₂₃	I ₈₀ I-S ₁₂ ChI ₈	80 (R1-R3)	N.D.					
	ME	ESOZOIC							
HCM 14.1	Qtz ₃₄ Pl ₂ Ph ₅₈ Hem ₆	I ₇₈ I-S ₅ KIn ₁₄ ChI ₃	80 (R3)	N.D.					
HCM 17.1	Qtz ₈₆ Ph ₁₄	N.D.	N.D.	N.D.					
HCM 17.2	Qtz ₂ Pl ₁ Ph ₉₇	N.D.	N.D.	N.D.					
HCM 17.3	Qtz ₁₅ Pl ₁ Ph ₈₄	I ₃₈ I-S ₂₆ KIn ₂₅ ChI ₁₁	65 (R1)	N.D.					
HCM 17.4	Qtz ₆₉ Ph ₃₁	N.D.	N.D.	N.D.					
HCM 17.5	Qtz ₇₂ Kfs ₁ Ph ₂₇	N.D.	N.D.	N.D.					
HCM 18.1	Qtz ₁₀ Kfs ₁ Pl ₄ Ph ₈₄ Sd ₁	I15 I-S3 KIn68 ChI14	75 (R1-R3)	N.D.					

Table 5.3 Clay mineralogy data collected in the area. Acronyms: % I in I-S— percentage of mixed layer illite-smectite; R parameter— mixed layer illite-smectite stacking order; C-S - mixed layers chlorite-smectite; Rec - rectorite; I— illite; I-S - mixed-layer illite-smectite; K— kaolinite; Ch— chlorite; Qtz— quartz; Cal— calcite;Dol - dolomite; Kfs— K feldspar; Plg— plagioclase; Ph— phyllosilicates; Sid— siderite; Pyr— pyrite; Hem – hematite; Ank - ankerite; Gt - goethite; Prl – pyrophyllite; N.D. – not determined.. Subscript numbers correspond to mineral weight percentage

and kaolinite are the occurring minerals in the <2 μ m grain-size fraction. Non-clay minerals such as quartz and k-feldspar are also observed in this fraction. Mixed layers illite-smectite are composed of long-range structures (R3) with an illite content of 83%.

Llandovery shales are mainly composed of phyllosilicates (56-79%), quartz (17-40%) and minor amounts of plagioclase (3-7%). Locally, goethite and k-feldspar occur in the sediments. Among the phyllosilicates in the

 $<2 \mu m$ grain-size fraction, illite, mixed layers illite-smectite and chlorite occur (Table 5.3). Small amounts of kaolinite and mixed layers chlorite-smectite have been identified in sample HCM 5.3. Mixed-layered clay minerals consist of short range ordered structures (R1) with an illite content of 77% or long range ordered (R3) with an illite content of 83%.

Ludlow-Wenlock samples in the Kielce block display a whole-rock composition made of phyllosilicates (62-79%), quartz (12-17%), plagioclase (7-12%) and low amounts of calcite (<6%) and k-feldspar (1%). Occasionally, small amounts of dolomite and pyrite (<2%) occur. The <2 μ m grain size fraction is mostly composed of illite (55-69%) and subordinate amounts of chlorite (2-22%), , mixed layers I-S (2-19%) and C-S(8-17%) and kaolinite (<5%). Mixed-layered clay minerals generally consist of long-range ordered I-S with an illite content between 80% and 83% and mixed layer C-S with a chlorite content ranging from 60% to 80%.

Ludlow silty shales in the Lysogory block are characterized by phyllosilicates (78-89%) quartz (5-16%) and albite (2-6%). Low amounts of hematite (1-3%) occasionally occur. Oriented mounts of the <2 μ m grain size fraction display mostly illite rich assemblages, which constitute at least 58% of the overall composition, and subordinate amounts of chlorite, kaolinite and mixed-layered minerals (Table 5.3). Discrete smectite has been detected in sample HCM 13.1 as result of retrograde diagenesis (Nieto et al., 2005). Mixed layers I-S are long-range ordered (R3) structures with an illite content between 85 and 88%. Mixed layers chlorite-smectite show a chlorite content ranging between 54 and 78%.

Samples from Givetian to Famennian (HCM 15.1, HMC 16.1, HCM 16.2 and HCM 20.1) collected in the Kielce block are composed of high amounts of carbonate group minerals (calcite, dolomite and ankerite) and phyllosilicates, and subordinate amounts of quartz (2-7%) and albite (1-2%). Occasionally,k-feldspar and pyrite occur (Table. 5.3). Oriented mounts show an illite-rich assemblage (79-85%) with subordinate amounts of chlorite (8-14%) and mixed layers I-S(7-15%). Observed I-S corresponds to low expandability R3 or R1-R3 (in sample HCM 20.1) structures where the illite component is dominant (80-85%). In the Eifelian-Frasnian samples (HCM 8.1, HCM 9.1, HCM 2.1) from the Lysogory block, phyllosilicates constitute at least 72% of the overall composition, followed by quartz (2-10%) and occasionally by calcite, ankerite and albite. Among clay minerals, illite (59-95%) prevails on kaolinite (1-27%) and mixed layer I-S (1%-16%). The I-S corresponds to R3 structures with an illite content of 82-84%.

Samples from the Jurassic successions are mainly composed of quartz and phyllosilicates and low amounts of k-feldspar and plagioclase that never exceed 4%. In the $<2\mu$ m grain size fraction illite and kaolinite are the most abundant minerals followed by mixed layers I-S and chlorite (Tab. 5.3). Mixed layers I-S are R1 structures with 65% of illitic layers or R1-R3 structures with an illite content of 75%.

5.4.3 Analysis on the Organic matter: Raman spectroscopy and Graptolites and vitrinite Reflectance data As shown in Table 5.2, samples from the Cambrian rocks are poor in organic carbon (TOC < 1%). Optical analyses on organic matter dispersed in the bulk rock were not reliable because the scarse fragments found



Figure 5.8 Distribution of vitrinite reflectance and illite content in mixed layers I-S data





Figure 5.9 Microphotographs from polished section HCM 1.1

were generally oxidised. Optical analyses on the concentrated organic matter on samples HCM 1.1, HCM 1.2 and HCM 1.3 show that kerogen is composed by fragments with reflectance values that range between about 2 and 5% and rare fragments with even higher reflectance ($R_0\% > 10$) that correspond to the anthracite to graphite stages (Fig. 5.9 a-b). Thus Raman spectroscopy analyses were performed on bulk kerogen of these samples. Raman spectrum shown in Figure 5.10 is representative of organic matter dispersed in Cambrian samples in the Lysogory region (HCM 1.1, HCM 1.2, HCM 1.3). It indicates the presence suggests highly ordered material that suffered transformation under temperatures of at least 200°C (Beyssac et al, 2003 and Lahfid et al., 2010). Figure 5.10 b shows Raman spectrum of the organic matter found in the Cambrian rocks of the Kielce region (HCM 7.1) indicating lower thermal maturity. In addition, optical analyses on samples HCM 7.1 show greatly

Samples	es R₀% 1σ		Nr. Measures	R₀% eq.						
	PALEO	ZOIC								
HCM 7.1	1.06	0.2	8	1.03						
HCM 1.1	N.D.	N.D.	N.D.	N.D.						
HCM 1.2	N.D.	N.D.	N.D.	N.D.						
HCM 6.1	0.86	N.D.	1	0.84						
HCM 5.4	1.07	0.05	45	1.04						
HCM 19.1	0.7	0.09	25	0.69						
HCM 5.1	1.04	0.17	46	1.01						
HCM 5.2	0.96	0.11	53	0.93						
HCM 5.3	0.89	0.12	21	0.87						
HCM 4.5	0.88	0.12	16	0.86						
HCM 4.4	0.92	0.1	86	0.89						
HCM 4.3b	0.95	0.14	89	0.92						
HCM 4.3a	0.82	0.09	83	0.8						
HCM 4.2	0.8	0.09	50	0.78						
HCM 4.1	0.69	0.07	17	0.68						
HCM 13.1	1.55	0.08	13	1.48						
HCM 12.1	1.6	0.008	3	1.53						
HCM 12.2	N.D.	N.D.	N.D.	N.D.						
HCM 11.1	N.D.	N.D.	N.D.	N.D.						
HCM 11.2	1.62	0.08	7	1.55						
HCM 10.1	1.68	0.17	45	1.63						
HCM 8.1	0.84	0.14	54	0.82						
HCM 16.1	1.7	0.16	18	1.62						
HCM 16.2	1.95	0.09	4	1.86						
HCM 9.1	1.08	0.11	7	1.04						
HCM 2.1	0.92	0.04	18	0.88						
HCM 15.1	1.12	0.016	2	1.08						
HCM 20.1	0.8	N.D.	1	0.78						
	MESOZOIC									
HCM 14.1	N.D.	N.D.	N.D.	N.D.						
HCM 17.1	0.51	0.03	23	N.D.						
HCM 17.2	N.D.	N.D.	N.D.	N.D.						
HCM 17.3	0.57	0.07	9	N.D.						
HCM 17.4	N.D.	N.D.	N.D.	N.D.						
HCM 17.5	N.D.	N.D.	N.D.	N.D.						
HCM 18.1	0.57	0.06	47	N.D.						

Table 5.4 Organic petrography collected in the area. Acronyms: Ro%— reflectance; Ro% eq. – vitrinite reflectance equivalent according to the Betrand and Malo (1990) conversion; 1σ – standard deviation; N.D. – not determined

oxidized organic matter with a mean reflectance value of about 1 R_0 % eq.

Ordovician samples collected from the Bardo syncline (HCM 5.4, HCM 6.1), in the southern block, are very poor in organic matter content. The more reliable result for optical analysis comes from the concentrated kerogen on samples HCM 5.4 that indicate a mean value of about 1 R_0 % eq. Pyrite in small globular aggregates locally occur along the rims of graptolites.



Figure 5.10 Raman spectra of organic matter dispersed in Cambrian rocks. (a) sample HCM 1.1, (b) sample HCM 7.1

Samples from Silurian rocks are very rich in organic matter, thus analyses in reflected light provided highly reliable R_0 %eq data with generally tens of analyzed fragments per sample (Table 5.4) and a Gaussian distribution of measurements, representing the indigenous population of marine organoclasts. Identified graptolite fragments occur as gray elongated thin fragments with non-granular texture (Fig. 5.11).



Figure 5.11 Microphotograph of a graptolite at 50X in oil immersion

Llandovery samples come from the southern block (HCM 5.1, HCM 5.2, HCM 5.3, HCM 19.1) and indicate a R_0 %eq mean value between about 0.9 and 1% (Fig. 5.12).

In the Wenlock interval, the $R_0\%$ eq mean values in the southern region are of 0.92%±0.10 (HCM 4.4) and 0.89% ± 0.12 (HCM 4.5), whereas in the northern block $R_0\%$ eq show a value of 1.55% ± 0.08 (HCM 13.1).

In the Ludlow interval, samples of the southern block (HCM 4.1, HCM 4.2, HCM 4.3a and HCM 4.b) show increasing reflectance values from $0.67\% \pm 0.07$ for the youngest sample to 0.95 ± 0.14 for the oldest one, whereas in the Łysogory region samples (HCM 10.1, HCM 11.1 and HCM 11.2) show values of about 1.6 R₀% eq.

Devonian samples in the Kielce region near the HCF show very high reflectance values (1.7 and 1.95 R_0 % eq for HCM

16.1 and HCM 16.2 respectively), whereas sample HCM 20.1 shows a value at about 0.8%.

In the northern block, Devonian samples show a value of 0.82% (HCM 8.1) for Eifelian rocks and 1.08% and 0.92% for Givetian/Frasnian successions (HCM 9.1 and HCM 2.1 respectively).

Jurassic Ro% in samples HCM 17.1, HCM 17.3 and HCM 18.1 show respectively values of 0.51, 0.50 and 0.57 $R_{\rm o}\%$.



Figura 5.12 Organoclasts reflectance for the Silurian successions in Kielce and Lysogory regions. Stratigraphic columns are form Kozlowski (2008)

5.4.4 Burial and Thermal modeling

Thermal model in the northern block (Fig. 5.13 c) was calibrated against thermal indicators obtained from Silurian and Devonian samples collected in both limbs and in the core of the Bodzentyn syncline.

Two major burial events associated with two main uplift phases were recognized in this model. The older burial phase produced a deep basin between the Late Devonian and the Carboniferous during which were deposited 4,700 m of sediments. Uplift during the Permian removed that 4,7 km thick succession as suggested by the unconformity recognized in the HCM at the base of the Permian-Triassic successions.

A second burial event was attained at the end of Mesozoic times. In the model, about 1,500m of Cretaceous rocks were firstly deposited and then removed by the Laramide uplift and exhumation recognized by He closure temperature on apatite of samples PL 107 and PL 112 dated at 57-58 My (M. Zattin, personal communication).

Figure 5.13 c shows a calibration curve fitting thermal maturity data with a very steep slope. In this case the best fit was attained using a constant heat flow (HF) of 35 mW/m² during Ordovician to Carboniferous time, followed by a peak in heat flow of 55 mW/m² between the end of



Figure 5.13 (a) 1D burial and thermal history of the Paleozoic successions from the Lysogory region. (b) heat flow distribution through time. (c) Present-day maturity data for Silurian and Devonian rocks plotted against calculated maturity curve. The thermal modeling has been performed using the kinetic EASY %Ro approach of Sweeney and Burnham (1990)

Carboniferous and Permian times, and a heat flow that increased from 35 mW/m² in Triassic times to 40 mWm², similar to the present day value (Fig. 5.13 b).

Such an increase is widely recognize in nearby areas (e.g. Lublin basin, Podolia region and correspond to the last phases of the Variscan orogenesis (Carrozzo et al., 2012; Poprawa et al., 2005) (Andreucci et al., 2015, Carrozzo et al., 2012, Poprawa et al., 2005).

Figure 5.14 shows the evolution of thermal maturity through time attained by the Jurassic successions that fall between the immature stage and the early mature stages of HC generation according to our vitrinite reflectance and mineralogical data.

Kielce region, on the other hand, according to our models, were reached in Mesozoic times (Fig. 5.15 a).

Burial related to the Variscan orogenesis is limited and only 400 m of Carboniferous sediments (actual thickness of Carboniferous measured in well Gałęzice G-5) were deposited and eroded during Permian time. On the other hand 1500m of Cretaceous sediments were deposited and eroded in the Laramide events whose uplift is marked by He closure temperature on apatite of samples PL 105 dated at 56 My. Figure 5.16



Figure 5.14 Maturity evolution of the Jurassic succession in the Lysogory region. The lower line indicate the top and the upper bottom of Jurassic sediments

shows the evolution of thermal maturity through time attained by the Permo-Triassic successions according to our model that are in agreement to those measured in the Kowala well by Marynowsky et al., 2001 (Zechstein in Gałęzice $R_0\% = 0.56$).

5.5 Discussion

Paleozoic rocks and in particular Silurian sequences are major gas and petroleum source rocks in a wide range of geological contexts (Hasany and Khan, 2003). However, the assessment of thermal maturity for lower Paleozoic rocks by vitrinite reflectance is limited due to the lack of organic fragments derived from the degradation of the lignin-cellulose part of upper plants. . The use of organoclasts reflectance for Paleozoic rocks revealed to be a successfully alternative (Poprawa 2010, Petersen et al. 2013, Smolarek et al., 2014, Suárez-Ruiz et al. 2012). Neverthless, the greater the number of thermal indicators adopted, the more reliable the burial/thermal reconstruction of the sedimentary succession, especially if each has its own kinetically controlled response to the burial history. When paleothermal data from different techniques are considered in the same geological context, more realistic and accurate simulations of the basin history are generated. In this work, we coupled organic matter optical analyses with Pyrolysis Rock Eval data, Raman spectroscopy performed on kerogen and X-ray diffraction of clay minerals. Furthermore, the integration of different thermal indicators from the organic and inorganic portion of sediments revealed to be an efficient tool for reducing the level of uncertainties in thermal maturity assessment.



Figure 5.15 (a) 1D burial and thermal history of the Paleozoic successions from the Kielce region. (b) heat flow distribution through time. (c) Present-day maturity data for Silurian rocks plotted against calculated maturity curve. The thermal modeling has been performed using the kinetic EASY %Ro approach of Sweeney and Burnham (1990)



Figura 5.16 Maturity evolution of the Permian-Triassic successions in the Kielce region. The two lines indicate the top and the bottom of the Permian-Triassic sediments

5.5.1 Source rocks evaluation by Pyrolysis Rock Eval

TOC and Pyrolysis Rock Eval data in the HCM are not always consistent among different authors.

According to Smolarek et al. (2014) andMalec et al. (2010b), Llandoverian samples from Kielce region sampled in Zbrza 1, Szumsko Kol.2, Wilków 1 and Zalesie 1 boreholes show an excellent HC potential with high values of S1+S2 (between 12 and 100) and a very high organic content (TOC > 4%). According to the same authors, Wenlock, Carboniferous and Permian samples indicate fair to good potential in both Kielce and Łysogory regions . On the other hand, a recent work of Mustafa et al. (2015) indicate a very low TOC for kerogen from black shales sampled at the Ordovician-Silurian boundary that outcrops near Bardo Stawy. Our data indicate fair to good potential for Silurian and Jurassic samples and a very good potential for sample HCM 16.2 (Fig. 5.6), whereas Ordovician, Silurian, Devonian and Jurassic samples have a fair to very good potential according to the classification propose by Langford and Blanc-Valleron (1990)(Fig. 5.7). On the other hand, all authors agree considering Ordovician up to Devonian kerogen a type II of marine origin (Malec et al., 2010, Marynowsky et al., 2002, 2010, Mustafa et al., 2015, Smolarek et al., 2014) while our data suggest a type III gas prone kerogen for the same stratigraphic intervals (Fig. 5.7).

Nevertheless, most of our samples lies at the boundary between type II and type III kerogen and lowered of TOC and HI values have to be taken into account when working with samples coming from outcrops that could have suffered weathering effects (Clayton and King, 1987; Copard et al., 2002; Lo and Cardott, 1995; Marynowski et al., 2011; Wildman et al., 2004).

5.5.2 Thermal maturity assessment

Thermal maturity indicators derived from the organic and inorganic fraction of sediments indicate differences in thermal maturity for the Paleozoic successions exposed in the Kielce and Lysogory blocks. In general, our data suggest, in term of HC exploration, thermal maturities associated with gas generation in the Lysogory block and thermal maturities which may be related with oil generation in the Kielce block, except for the north-western sector. A similar pattern can also be observed by previous works plotted together in figure 5.5 a-b-c, but with some differences.

In detail, in the Kielce block, data from the Lower Cambrian samples (HCM 7.1) is difficult to be interpreted because reflectance was measured on only 8 vitrinite-like fragments that show a high standard deviation (Table 5.4) and mixed layers I-S show R1 structures with an illite content of 77%. Both these indicators could indicated maximum paleotemperatures of at least 130-140°C (Table 5.3).

Compared with existing data performed on Cambrian samples (Fig. 5.5 a), it can be seen that CAI and TAI values from Sczepanicz (1997,2001) and Narkiewicz (2002) probably underestimate thermal maturity .

Our Ordovician to Upper Silurian samples from the Bardo syncline, on the other hand, are well constrained by different indicators. Tmax values suggest that samples are in the oil window of HC generation stages, while reflectance data performed on Paleozoic organoclasts, in particular graptolites, indicate samples in the mid-mature stage of HC generation ($0.7 < R_0\% < 1$). It is worthy to note the increasing trend of reflectance values found from Upper to Lower Silurian-Ordovician. Such a similar trend was not found in I% values, nevertheless mineralogical data show the diffuse presence of R1, R1-R3 and R3 ordering with Illite percentage values varying between 77 and 83% indicating paleotemperatures between 130-140°C according to Merryman and Frey (1999) and Aldega et al. (2007). Their values are systematically lower than Silurian samples collected in the Lysogory block.

Samples from outcrops near Bardo Stawy were also analysed in other works using different methods. Our Tmax and reflectance data agree with those from Smolarek et al. (2014) and with data from Pyrolysis and biomarker parameters provided by Mustafa et al. (2015) (Fig. 5.5 b).

Devonian samples in the NW sector of the Kielce block show high thermal maturity according to Tmax, Ro%eq and I% in I-S data. These data indicate higher maturities than those found by Rospondek et al. (2008), Marynowski et al. (2001) and Narkiewicz et al. (2002) which are anyway unusually higher with respect the rest of the Kielce block. According to Narkiewicz et al. (2002) this area is a part of the Łysogory block rather than the Kielce. What we observed in the field (in particular in the Mogiłki quarry near Kielce) is that this sector is characterized by an intense tectonics evidenced by giant reverse folds and probably thrust that can be guess by the presence of repeated strata in the stratigraphy of the Zawada 1 and Piekosow 1 well in the area. Thus, although an hypothesis is that, the anomaly in thermal maturity could be due to a tectonic loading that developed locally in this area.

Upper to Lower Silurian and Upper Ordovician reflectance values measured from samples collected in the Bardo outcrops were used as constraints to model the burial history of this region. They were chosen because the Bardo Stawy stratigraphic section has a detailed stratigraphical definition.

Our data as shown in Figure 5.15 c, show a good fitting obtained using a HF of 35° C/Km during time with a peak at Carboniferous-Permian times. Model shows that the oil generation was firstly reached during Paleozoic, but that a higher burial was attained at the end of Cretaceous when maximum paletemperatures of about 140°C were reached by Lower Silurian and Ordovician strata. In addition our model, calibrated only with R_o%eq data from Upper and Lower Silurian agree with Devonian Ro% data provided by Rospondek et al. (2008) and Marynowski et al. (2001) plotted in Figure 5.5 c in the Kielce region.

In the Łysogory region thermal maturity indicators all indicate higher thermal maturity than that observed in the Kielce region. This is evidenced first by reflectance data and also by low expandability mixed layers I-S. In detail, the poor reflectance values measured in Cambrian samples (R_0 % eq always > 2.5) are not suitable to assess thermal maturity. On the other hand, the presence of pyrophyllite in samples HCM 1.1 and HCM 1.2 and Raman spectra of dispersed organic matter very similar to that of anthracite, suggest paleotemperature above 200°C, that partially are in agreement with the TAI data provided by Scepanicz (1997).

Upper Silurian data from Winnica, Trochowiny and Trzciaka formations outcropping in both limbs of the Bodzentyn syncline suggest thermal maturity within the gas window of HC generation. The low TOC content does not make the Silurian interval suitable for shale gas exploration, while temperatures carried out from our model suggest that the Wenlockian shales buried in the Bodzentyn syncline could act as good source rocks according to Smolarek et al. results (2014).

The Tertiary burial is constrained also by Jurassic thermal maturity indicators as shown in Fig.5.14.

One important results of our model is that it constrain the gas generation during Paleozoic times in both blocks, differing from previous modellings that set the beginning of HC generation during the Mesozoic(Belka, 1990; Narkiewicz 2002, Narkiewicz et al., 2010).

5.5.3 Paleogeographical implications

The geological and paleogeographical evolution of the two tectonic blocks during Paleozoic times has been widely discussed and is still today a matter of debate.

According to Narkiewicz (2002) and Dadlez (1994), the two blocks were divided during the Cambrian and until the Devonian and welded together as a result of movements along the TTZ of the Malopolska block during late Pragian-early Emsian times. On the contrary, paleomagnetic data of Schätz et al., (2006) indicate that no large scale tectonic movements were recognized after Middle Ordovician.

On the other hand, the amount of sedimentary loading in the Łysogory region during the Upper Devonian-Carboniferous indicate a burial history completely different with respect to that observed in the Kielce region.

In our opinion no differences in paleogeography between the two blocks can be invoked and a simply explanation could be related to the movements of the HCF that could act as a normal fault from Silurian to Carboniferous creating greater accomodation space for sediments accumulation in the northern region.

At the end of the Carboniferous compressional movements related to the Variscan orogenesis could have produced an inversion of the kinematic of the fault leading to an uplift marked by the Permian unconformity in both tectonic blocks.

Mesozoic sediments sutured the fault and Senonian to Paleocene uplift brought to the outcrop of the entire region.

5.6. Conclusion

The Holy Cross mountains are one of the few place in Europe that offer the opportunity to observe in the outcrop a preserved sedimentary cover that span in age from the Lower to the Upper Paleozoic.

Because of their uniqueness they have been widely studied in the past years for both paleontological and paleogeographical porpoise and also because of their economic relevance as they host an optimum analogue of the main gas-shale sources found in the northern Europe (e.g. Llandoverian graptolitic shales).

Many work have been dealing with the thermal maturity assessment of these Paleozoic succession but still lacks a comprehensive model of the thermal and burial evolution of the entire area.

In order to unravel the source rock potential and a detailed thermal maturity evolution of these rocks, in this work we provide new thermal maturity constraints carried out from organic petrography, Pyrolysis Rock Eval, clay mineralogy and Raman spectroscopy and we compare them with thermal maturity indicators collected from previous works (TAI,CAI, R_0 % and R_0 % eq.). Finally we use organic petrography data to calibrate two thermal modeling in the area.
Our results indicate that significant differences exist in the thermal maturities experienced by the two blocks, confirming what already assessed by previous works (Belka, 1990; Malec et al., 2010a; Marynowski et al., 2001; Mustafa et al., 2015; Narkiewicz, 2002; Poprawa et al., 2005; Smolarek et al., 2014; Szczepanik, 1997, 2001). Nevertheless we found that an integrated approach could better constraints thermal maturity. In particular we demonstrated that organoclasts reflectance is a more reliable tool rather than TAI and CAI alone that are not suitable tools because of their great margin of error. In addition clay mineralogy helped us when organic matter was really scarce of totally absent while Raman spectroscopy reveal to be very useful in Cambrian rocks.

Our results from Pyrolysis Rock Eval allow us to characterized the HC potential of the rocks in the area indicating that only some Silurian rocks from the Bardo syncline, Devonian rocks from the Gruchawa area and Jurassic rocks could act as fair to good source rocks.

Considering the thermal maturity indicators found at different stratigraphic ages and using them as constraints for the calibration curves, we proposed two thermal modeling, defining concisely the burial and thermal history of the two blocks. In particular for the first time, we focused our model on the evolution of the Silurian black shale that represent the main source rocks in the area.

Our models indicate that a main burial occurred in the Lysogory region during Paleozoic in the Kielce region and during Mesozoic times. In terms of HC exploration, gas generation by Silurian source rocks was attained at the end of Carboniferous in the northern block, while in the southern block Silurian successions enter in the oil window during Paleozoic, but they reach temperature required for gas generation only at the end of Mesozoic.

In conlusion we want to stress the effectiveness of our approach to unravel the burial history in a complicate Paleozoic setting such as that of the HCM reminding that Paleozoic source rocks represent at the present day a promising frontier in the unconventional HC exploration.

Chapter 6

Burial and exhumation of the western border of the Ukrainian Shield

6.1 Introduction

The Podolia region (Southern Ukraine) is located to the east of the Trans European Suture Zone (TESZ), a suture between the weaker and younger Western European lithosphere, and the thicker and stronger Eastern European Craton (e.g., Drygant, 2000; Skompski et al., 2008; Małkowski et al., 2009; Fig. 6.1), in the so-called Peri-Tornquist margin (i.e. western margin of the Eastern European Craton). Between the Early Paleozoic and the Neogene, this area has been part of the epicontinental basin system extended along the Peri-Tornquist Margin (e.g., Wrona and Lis, 2012, and references therein). The outcropping sedimentary succession is characterized by two major angular unconformities: the first is located between the Upper Ordovician/Upper Lower Devonian and the Middle-Upper Jurassic/Lower Cretaceous strata, the second between the Middle-Upper Cretaceous and the Miocene deposits (Figs. 6.2 and 6.3). A third minor unconformity separates the Ordovician units from the Lower Silurian deposits (e.g., Wrona and Lis, 2012).

The Lower Paleozoic shales deposited along the margin of the East European Craton are currently among the major hydrocarbon exploration targets of eastern Europe.

One of the main issues addressed in hydrocarbon exploration consists of assessing thermal maturity of potential source rocks. Consequently, this area has been extensively investigated in the last few years with studies on its diagenetic evolution (e.g. Środoń et al., 2013), with particular focus on the succession outcropping along the Dniester River (Huff et al., 2000). However, no univocal result has been reached on timing and extent of burial and exhumation, and different hypotheses have been proposed for their driving forces (e.g. Środoń et al., 2013, Świdrowska et al., 2008). In this work, we combine X-ray diffraction and organic matter optical analysis of the inorganic and organic fraction of sediments, with apatite fission-track ($T_c\approx110^{\circ}C$) and U-Th/He ($T_c\approx60^{\circ}C$) analysis on Silurian bentonite layers in order to trace the burial and exhumation history of the Dniester River succession. The reconstruction of burial and exhumation events allowed us to unravel the tectonic evolution of this part of the margin of the East European Craton (EEC) and to evaluate the response on the border of the EEC to the orogenic cycles succeeding along the plate margin. This work finally allows to verify how keen is an epicontinental basin located along a cratonic margin to preserve in its burial-exhumation history a record of the orogenic episodes involving the margin itself.



Figure 6.1 (a) Simplified tectonic sketch map of the margin of the East European Craton (EEC). TESZ: Trans European Suture Zone; WEP: West European Platform. (b) Geological map of the pre-Neogene succession

6.2 Geological setting

The Ordovician-Silurian succession in Podolia is mainly characterized by shelf facies, consisting of lagoonal, reef and open shelf deposits, with distal facies extending to the west moving toward the TESZ. During the late Silurian and the Early Devonian, slope and basin facies tend progressively to prevail on shelf facies, whereas at the end of Early Devonian the continental margin progrades westward and continental "Old Red Sandstones" sedimentary environment establishes throughout the Peri-Tornquist margin. Younger Paleozoic deposits occur farther to the NW (Fig. 6.2).

Fig. 6.2 and Fig. 6.3 show how the Paleozoic-Mesozoic stratigraphic gap tapers off towards the TESZ (i.e. westwards), as a result of the westward increase of the Paleozoic

sedimentary thickness and the progressive onlap of Mesozoic sediments on the SW-ward gently tilted Paleozoic strata of the Peri-Tornquist margin to the east (e.g., Kurovets et al., 2012). The older Mesozoic sediments onlapping against the Lower Devonian deposits consisting of Middle Jurassic terrestrial conglomerates passing upward to Upper Jurassic to Cenomanian lagoonal and open shelf sediments. Middle-Upper Miocene marine sediments onlap against the Mesozoic sediments of the Peri-Tornquist margin. Isolated remnants of Upper Eocene quartz-glauconitic sands occur in the easternmost portion of the Podolia region, indicating that major erosion of the Paleogene deposits occurred in Oligocene-Early Miocene times. Continental conditions established during the Pliocene-Quaternary period.



Figure 6.2 Geologic map of the study area with sampling location

6.3 Materials

Eighteen samples for X-ray diffraction and organic matter optical analyses were collected from black shales and siltstones cropping out along the Dniester river.

Starting from the oldest sampled outcrop to the east, the first two samples (PO7, PO8) belong to the Ordovician Molodovo Formation composed of sandstones and dark grey clayey sandstones. The Molodovo Formation is separated by the lowermost Silurian Kytayhorod Formation by a regional unconformity.

Middle and Upper Silurian carbonates and shales are divided into four stratigraphic units: the Kytayhorod, Bahovytsya, Malynivtsi and Skala Formations. The most suitable samples for mineralogical analyses (10) come from siltites and pelites layers that are alternated with marls, limestones and dolomites. Samples from the Devonian units are from:

- pelitic and marly horizons in the Lower Devonian Borshchiv Formation (1);
- Lochkovian pelites and marly cherts in the Ivanie Formation (4);
- Old Red Sandstones at the base of the Dniester Formation (1).

As the investigated sedimentary succession is composed mainly by calcareous lithologies with interbedded shales, samples suitable for thermochronology are exclusively from Silurian bentonite layers and finegrained Devonian sandstones. Silurian apatites are all euhedral crystals, as expected from a volcanogenic source, whereas Devonian grains are smaller and rounded, therefore not suitable for apatite (U-Th/He) dating.



Figure 6.3 Top left: panoramic view of the Silurian succession; Top right: chronostratigraphy of the sedimentary succession exposed along the Dniester River; Bottom: simplified cross-section across the L'viv Depression

6.4 Results

6.4.1 Clay mineralogy

Randomly oriented whole-rock powders for Devonian rocks show a mineralogical assemblage composed of phyllosilicates in the range of 79-85%, quartz (9-13%), plagioclase (5-8%) and subordinate amounts of calcite, siderite and ankerite minerals (1-6%; see Table 2). Only sample PO21 from the oldest formation of the Devonian rocks shows higher amounts of carbonates minerals such as calcite (21%), ankerite (11%) and dolomite (6%) and lower amounts of phyllosilicates (48%). Minor contents of K-feldspars (1%) occasionally occur.

Comple	A = 0	$R_0\% \pm sd$		XRD analisys					
Sample	Age	(n. meas.)	%I IN I-S	<2µm	Whole rock				
Po24	Lower Devonian	-	86	$I_{81}I\text{-}S_4Ch_{15}$	$Qtz_9Plg_5Ph_{85}Sid_1$				
Po15	Lower Devonian	-	86	$I_{54}I$ - $S_{20}K_4Ch_{22}$	$Qtz_{11}Cal_1Plg_5Ph_{82}Sid_1$				
Po16	Lower Devonian	-	85	$I_{62}I-S_{14}K_7Ch_{17}$	$Qtz_9Cal_5Plg_5Ph_{80}Ank_1$				
Po13	Lower Devonian	-	86	$I_{59}I-S_7K_5Ch_{29}$	$Qtz_{11}Plg_8Ph_{80}Sid_1$				
Po12	Lower Devonian	-	86	$I_{56}I$ - $S_{10}K_5Ch_{29}$	Qtz ₁₃ Plg ₈ Ph ₇₉				
Po23	Lower Devonian	0.87 ± 0.08 (5)	89	$I_{56}I\text{-}S_{15}K_{12}Ch_{17}$	$Qtz_{10}Cal_2Plg_5Ph_{82}Sid_1$				
Po20	Upper Pridoli	-	85	$I_{73}I-S_5K_6Ch_{16}$	$Qtz_6Cal_{23}Kfs_1Plg_4Ph_{57}Dol_5Ank_4$				
Po17	Pridoli	-	90	$I_{73}I-S_8K_4Ch_{14}$	$Qtz_6Kfs_1Plg_3Ph_{75}Dol_{15}$				
Po10	Ludlowian	-	90	$I_{46}I$ - $S_4K_{25}Ch_{25}$	$Qtz_{18}Cal_{23}Kfs_2Plg_8Ph_{43}Sid_1Dol_1Ank_4$				
Po11	Ludlowian	0.65 ± 0.07 (4)	90	$I_{65}I-S_7K_8Ch_{20}$	$Qtz_{10}Cal_1Kfs_2Plg_8Ph_{69}Sid_1Dol_3Ank_6$				
Po19	Ludlowian	-	89	$I_{65}I-S_{16}Ch_{19}$	$Qtz_{10}Cal_{15}Kfs_2Plg_5Ph_{56}Sid_1Dol_{11}$				
Po18	Ludlowian	-	89	$I_{62}I-S_{17}C-S_7K_4Ch_{10}$	$Qtz_9Kfs_1Plg_6Ph_{74}Sid_1Dol_9$				
Po4	Wenlockian	-	85	$I_{55}I-S_{31}C-S_3K_4Ch_7$	$Qtz_6Cal_{48}Plg_2Ph_{42}Dol_2$				
Po3	Llandoverian- Wenlockian?	0.75 ± 0.12 (5)	88	$I_{52}I$ - $S_{25}K_{12}Ch_{11}$	Qtz ₂₇ Kfs ₃ Plg ₇ Ph ₆₃				
Po2	Llandoverian	0.77 ± 0.08 (3)	85	$I_{52}I-S_{30}C-S_{10}K_4Ch_4$	Qtz ₁₃ Kfs ₁ Plg ₇ Ph ₇₉				
Po1	Llandoverian	-	85	$I_{42}I$ - $S_{25}C$ - $S_{13}K_7Ch_{13}$	Qtz ₁₉ Kfs ₁ Plg ₉ Ph ₇₁				
Po7	Ordovician	-	84	$I_{26}I-S_{17}Ch_{57}$	$Qtz_{16}Kfs_1Plg_{19}Ph_{64}$				
Po8	Ordovician	-	82	$I_{34}I\text{-}S_{35}K_{14}Ch_{17}$	$Qtz_{13}Kfs_2Plg_{12}Ph_{73}$				

Table 6.1 The table summarized for each analized sample: the age of the sample, the measured mean value of organoclast and/or vitrinite reflectance, the Illite percentage values in mixed layers Illite-Smectite and the mineralogical content measured on both $<2\mu$ m grain size fraction and the whole rock content.

Acronyms: I = illite; I-S = mixed layers illite-smectite; K = kaolinite; Ch = chlorite; C-S = mixed layers chlorite-smectite; Qtz = quartz; Cal = calcite; Ph = phyllosilicates; Plg = Na-plagioclase; Kfs = K-feldspar; Dol = dolomite; Sid = siderite; Ank=ankerite

The <2 μ m grain size fraction is constituted by illite (56-81%), mixed layers illite-smectite (1-20%), chlorite (15-34%) and kaolinite (0-12%). Mixed layers illite-smectite are long-range ordered structures with an illite content ranging between 85-95%.

Silurian rocks, Pridoli and Ludlowian in age, are characterized by phyllosilicates (34-74%), quartz (6-18%), plagioclase (2-8%), K-feldspar (1-2%) and higher amounts of carbonate minerals than the Devonian counterpart. Calcite ranges between 15 and 53%, dolomite between 1 and 15% and ankerite never exceed 6%. Siderite is a minor component of the carbonate fraction with contents of about 1%.

The Llandoverian-Wenlockian portion of the succession does not show carbonate minerals and is mainly constituted by phyllosilicates and quartz and subordinate amounts of plagioclase and K-feldspar.

X-ray diffraction analysis of the $<2 \mu m$ grain-size fraction for the Silurian rocks displays illite (42-75%), long-range ordered mixed layer illite-smectite (2-31%), kaolinite (0-25%), and chlorite (4-32%) in almost all samples (Tab.2). In a few samples (PO1, PO2, PO4, PO18) mixed layers chlorite-smectite with a chlorite content of 70-80% were detected. Mixed layered clay minerals are low expandable illite-smectite with an illite content ranging between 85 and 96%.

Ordovician rocks are composed of phyllosilicates (64-73%), plagioclase (12-19%), quartz (13-16%) and low amounts of K-feldspar (1-2%, see Table 6.1). Among minerals of the $<2 \mu m$ grain size fraction, chlorite, illite and mixed layer illite-smectite were identified (Tab.6.1). Mixed layered clay minerals are long-range ordered Illite-smectite with an illite content of 82-84%.

6.4.2 Organic matter reflectance data

Samples are very poor in organic matter content (Table 6.1). Reflectance was measured on fragments of vitrinite like and graptolites in the Silurian-Devonian stratigraphic interval. After measurement, organoclasts reflectance data were converted in vitrinite reflectance data equivalent using Bertrand and Malo's equation (2012).

In pelites of Landoverian-Wenlockian age, two samples (PO2, PO3) provided reliable R_0 % org with a mean value of about 0.76%. Slightly lower values (mean of 0.66%) have been obtained on two samples (PO9, PO11) from marly mudstones of Ludlowian age. Finally, in the Lochkovian interval, a R_0 % org value of 0.87% was measured (sample PO24).

6.4.3 Thermochronology

As a whole, AFT data are quite consistent as they all indicate: a) maximum burial at temperatures exceeding the total reset temperature (as all the single grain ages are younger than the stratigraphic age) and b) a Late Triassic-Early Jurassic cooling phase.

In details, up to twenty grains per sample have been analyzed and chi-square test indicates a low spread of single grain ages (Fig.6.4). Measurement of track lengths was possible only on Silurian samples although only in a couple of them the number of lengths was high enough to be considered representative of the track length distribution.

AHe ages for Silurian samples are more difficult to be interpreted. We have analyzed five grains per sample but a large age dispersion is nearly everywhere present. In fact, samples M2, M6 and C3 show up to 400 m.y. of difference among ages from crystals of the same sample. Age spread is somehow limited for sample C6, in which age ranges between 162 and 242 Ma. Actually this age range comprises the youngest grains detected on the other samples and is consistent with the AFT central ages, which are, as expected, systematically older. Therefore, we consider only youngest ages to be representative of a cooling event and



Figure 6.4 Radial plots of apatite fission-track data. n: number of analyzed grains; $P(\chi 2)$: probability of obtaining $\chi 2$ -value for v degrees of freedom (where v=number of crystals-1); a probability >5% is indicative of an homogenous population; Dpar: length of the of the etch pit figure

keep them for following discussion. The source of errors for the remaining grains is not clear but its evaluation is not among the aims of this work.

AFT and AHe ages have been then modelled using the HeFTy software (Ketcham, 2005). The only geological constraint here used was the depositional age of the analyzed sample. The results of thermal modelling indicate that the thermochronometric dataset is compatible with a major cooling event in the Late Triassic-Early Jurassic, following a period of heating (Fig. 6.5) and possible retention to temperatures higher than ca. 120°C (AFT total reset temperature). As the results of thermal modelling are fully reliable only for the temperature intervals corresponding to the partial retention zones of the thermochronometers applied, i.e. 40-120°C, our thermochronological modelling is not able to detail the thermal path for temperatures higher than 120°C and lower than 40°C. However, we assume some sedimentation to have taken place after the Early Jurassic but the total amount of sediments being less than 2 km as this heating stage did not affect the AHe system (which closure temperature is of ca. 60°C).

6.4.4 Burial modelling

Thermal maturity data plotted on a simplified map of the area and the thickness and location of the paseudowells used to model the burial history of the successions are shown in Figure 6.6 a-b. These data and the



Figure 6.5 Thermal evolution of analyzed samples derived by thermal modelling with HeFTy (Ketcham, 2005) which generates possible T–t paths using a Monte Carlo algorithm. Shaded areas mark envelopes of statistically acceptable (light grey, goodness-of-fit [GOF]: 0.05-0.5) and good (dark grey, GOF>0.5) fit. Thick lines correspond to the average thermal history with good fit. On the right, track length histograms

thermochronological data were used to perform the simplified reconstructions of the burial and exhumation history of the sedimentary successions outcropping along the Dniestr river that are shown in Figures 6.7,6.8,6.9.

The burial history of the succession of pseudo-well 1 begins with the deposition of 50m-thick siltstones in the Ordovician since about 460 My. At that time the basin was characterized by low or null sedimentation rates as suggested by the paraconformity between Ordovician and Llandoverian units.

During the Silurian, shallow water conditions environments developed, with the deposition of about 220 m thick shallow water carbonates. nodular limestones and dolostones. Since the Upper Silurian and trough the lower Devonian, sedimentation of 530 m of siltstones took place in deeper water marine environments. In the Pragian, the sector evolved to inshore lagoon to fluvial estuarine environments (Wrona and Lis, 2012) with the deposition of the Old Red Sandstones (Dniestr formation). The basin deepened during the Carboniferous as a result of subsidence related to a large infill of sediments (about 3,700 m) until about 300 My ago. At that time, the succession experienced maximum burial at about 4,700 m (Fig. 6.7a) and maximum temperatures at about 220 My (Fig. 6.10). After nearly 100 m.y. of scarce to null sedimentation since maximum burial occurred, a Late Triassic-



Figure 6.6 (a) Geological map of the study area and thermal indicators estimated by clay mineralogy and vitrinite reflectance data for each sampling location. (b) Stratigraphy of the three pseudo wells used to model the area

Early Jurassic exhumation event brought the Paleozoic rocks close to surface eroding the Carboniferous infill. From Middle Jurassic onwards, a few hundred meters of carbonates sedimented, as reported by Gutowski et al, 2005 and up to the end of Eocene sedimentation continues until a new phase of exhumation recorded by the Miocene unconformity occurs.

The type of evolution outlined allows an acceptable calibration against measured data, as shown by the resulting maturity curve of Figure 6.7 b.

The burial reconstructions of pseudo-wells 2 and 3 differ from pseudo-well 1 for the thickness of the Carboniferous infill and the amount of exhumation since Triassic time. The amount of eroded thickness carried out from the numerical models decreases moving toward the EEC and is about 3600 m for pseudo-well 2 and 3,100 m for pseudo-well 3 (Fig. 6.8,6.9). These differences affect the maximum temperatures the



Figure 6.7 (a) 1D burial and thermal history of Devonian successions (pseudo well 1). (b) Thermal model is calibrated by Silurian illite content in mixed-layer I–S and reflectance data. The thermal modeling has been performed using the kinetic EASY %Ro approach of Sweeney and Burnham (1990)



Figure 6.8 (a) 1D burial and thermal history of Upper Silurian successions (pseudo well 2). (b) Thermal model is calibrated by Silurian illite content in mixed-layer I–S and reflectance data. The thermal modeling has been performed using the kinetic EASY %Ro approach of Sweeney and Burnham (1990)

successions underwent that are about 120°in pseudo–well 3 (Fig. 6.10 c) and 140°C in pseudo-well 2(Fig. 6.10 b).

During the Triassic a rapid cooling occurred and a new temperature increase highlights the last phase of burial during Jurassic and Cretaceous times. A gentle temperature decrease is recorded by the pre-Devonian successions (Fig. 6.10) between 70 and 40 My as a result of quicker rates of isotherm depression in comparison

to burial rates. Eventually a Tertiary to present day cooling corresponds to the youngest exhumation in the study area interrupted by a slight heating of isothermal evolution in correspondence of Miocene deposition.



Figure 6.9 (a) 1D burial and thermal history of Ordovician and Lower Silurian successions (pseudo well 3). (b) Thermal model is calibrated by Silurian illite content in mixed-layer I–S and reflectance data. The thermal modeling has been performed using the kinetic EASY %Ro approach of Sweeney and Burnham (1990)



Figure 6.10 Temperature-time diagrams of the best fit models for: (a) Devonian (pseudo well 1), (b) Upper Silurian (pseudo well 2) and (c) Ordovician-Lower Silurian successions (pseudo well 3)

6.5 Discussion

6.5.1 Maximum Burial estimate

Considering that the Mesozoic regional unconformity covers progressively younger and thicker Paleozoic successions moving from the EEC to the West, we summarized the burial history of the Podolia basin with three representative pseudo-wells (Fig. 6.6 b) that were calibrated against organic and inorganic thermal indicators.

Paleothermal data from Devonian, Upper, Middle and Lower Silurian intervals indicate the mid-mature stage of HC generation (about 0.7-1 R_0 % and 82-90% illite content in mixed layers I-S) highlighting lateral variations of thermal maturity through time.

Assuming changes in the heat flow values similar to those found in nearby areas (e.g.,Lublin basin) according to Botor, (2002), Poprawa et al.,(2005) and Carrozzo et al.,(2012), time-temperature diagrams for pseudo-well 1 and 2 indicate maximum palaeotemperatures for the Silurian and Devonian successions between 110° and 150°C (Fig. 6.10 a b) consistent with AFT total reset temperature (120°C). On the other hand , the time–temperatures diagram of Middle and Lower Silurian rocks in pseudo-well 3 (Fig. 6.10 c) shows lower palaeotemperatures according to clay minerals and organic petrography data.

As matter of fact a number of studies on thermal evolution of sediments, based mainly on conodont alteration index (CAI), clay minerals and vitrinite reflectance have been performed along the Peri Tornquist margin (Drygant, 1993; Nehring-Lefeld et al., 1997; Środoń et al., 2009, 2013).

Our thermal maturity data are consistent with those derived from Drygant's zonation (1993) based on Conodont Alteration Index (CAI). In this paper, Silurian and Devonian successions of the Podolia Basin can be grouped in the 2-3 zone corresponding to 110°C-140°C according to Epstein et al., (1977) and Marshall (1999).

Furthermore these temperature estimates have been recently reviewed by Środoń et al. (2013). The authors observed an illite content in mixed layers illite-smectite between 81 and 99% indicating deep diagenetic conditions, maximum burial of 5-10 Km and related maximum paleotemperatures of about 200°C that are higher than our palaeotemperatures (110-150°C) and burial depths (3.5 to 4.7 km). Geological evidence (Nikishin et al. 1996) are in favor of moderate burial (4-5 Km) reached during the Paleozoic, hardly supporting higher amounts of sedimentation (5-10 Km).

Furthermore, the numerical models performed in this work allow us to outline the Podolia basin as an asymmetric Paleozoic basin where sediments accommodation space became thinner moving toward the European Craton, instead of considering a uniform burial throughout the basin (Srodon et al., 2013).

This alternative burial and thermal scenario depends on the choose of a variable heat flow through time. The heat flow was set at 50 mW/m2 during the Paleozoic and Mesozoic with a peak of about 65 mw/m2 in Carboniferous times (Botor, 2002; Poprawa et al.,2005 and Carrozzo et al.,2012), and decreased constantly up to 30 mw/m2 during the Cenozoic. On the contrary, Srodon et al., 2013 adopted a constant thermal model assuming a geothermal gradient of 20-40 °C/Km.

6.5.2 The Late Triassic-Early Jurassic exhumation

Thermochronometric ages indicate that Paleozoic sediments were exhumed close to surface in the Late Triassic-Early Jurassic (Fig. 6.5). These data match well with the age of the oldest sediments overlapping the widespread unconformity occurring along the margin of the craton. However, AFT ages differ significantly from those obtained by Środoń et al. (2013). As a matter of fact Środoń et al. (2013) report ages spanning from 63 to 107 Ma, in a couple of cases with a large spread among grains of the same sample. Also track

lengths differ from our measurements as all of theirs are shorter than our means and with a larger standard deviation. As a consequence, Środoń et al. (2013) indicate an exhumation event during the Cretaceous followed by a heating event to temperatures of about 100°C. We have no tools to explain these differences but there are some arguments that make us confident on the reliability of our dataset. First of all, there is an internal consistency among our AFT samples, with very similar central ages (taking into account the analytical error) and between AFT ages and AHe ages. Then the cooling event depicted by our modelling is fully compatible with the widespread unconformity, above which Jurassic sediments were deposited. On the other hand, the model presented by Środoń et al. (2013) implies about 3 km of burial during the Late Cretaceous which does not find any geological evidence in the study region. This 3 km-thick succession would have to be eroded sometime in the Miocene but, again, there are no clues of a relevant uplift phase after the Cretaceous. Finally, AHe analysis displayed Middle Jurassic ages ruling out a post-Cretaceous heating event to ca. 100°C, which should have caused the total reset of the He system.





Accepting the hypothesis of a Late Triassic-Early Jurassic cooling event, a major question would arise about its geological meaning. In fact, such a cooling implies vertical displacements that have to be related to some tectonic activity. All the single grain ages (both AFT and AHe) have been plotted in Figure 6.11. Most of them fit well with the age of Cimmerian orogeny whereas both older (Variscan) and younger (Alpine) orogenesis are far to be expressed by thermochronological data. Around the Triassic-Jurassic boundary, in the central Tethys area, several blocks collided with the Eurasian margin in the so-called Eo-Cimmerian orogeny (Şengör, 1984; Şengör and Natalin, 1996). This collision brought to the uplift of large regions along the block margins (Golonka, 2000; Golonka et al., 2003). In the circum-Carpathian area, the Eo-Cimmerian orogeny is marked by the uplift of the Inner Carpathian Plate, testified by the lack of Upper Triassic-Lower

Jurassic deposits (Golonka et al., 2003). Our study area is immediately north of the Scythian Platform whose basement is exposed in the Pre-Dobrogea depression in a highly tectonized area about 100 km wide (Seghedi, 2012). Here deformation is associated to Eo-Cimmerian tectonics, similarly to what better expressed in the nearby North Dobrogea (Seghedi, 2001; Seghedi, 2012). Farther to the east, it has been argued that the left-lateral transpressional regime observed in the Donbas fold-and-thrust belt, although poorly constrained in age, could be a record of the Triassic-Jurassic Eo-Cimmerian tectonics (Saintot et al., 2003). In this work, we suggest that the exhumation event detected by thermochronological ages could be related to far-field tectonic effects related to the Cimmerian collision (Fig. 6.12). Spatial and temporal strength variations of the lithosphere control the far-field tectonic stresses that can be induced at distances > 1500 km from the collisional front (Ziegler et al., 1995; Dickerson, 2003). Examples can be found in the deformation at the northern margin of the Tibetan Plateau which was synchronous with the early stage of India–Asia collision (e.g. Yin et al. 2008; Clark et al. 2010) and in the southeastern Black Sea region, where Neogene deformation is related to far-field effects of the Arabia-Eurasia indentation (Albino et al., 2014). As alternative, the small angular unconformity observed in our study area between the Paleozoic and Mesozoic sediments could reflect a relative sea-level fall in combination with differential post-rift subsidence rates from the basin margin to its axis (Stephenson et al., 2001, 2006). However, the amount of cooling and uplift recorded by our data cannot be justified by a sea-level fall process alone.



Figure 6.12 Paleogeographic sketch of the entire area for the Late Triassic

Conclusions

Paleothermal indicators, thermochronological data and burial modeling allowed us to unravel the burial and exhumation history of the Paleozoic succession exposed along the western border of the Ukrainian Shield and to infer valuable information about the tectonic history of this area. Firstly, we defined the extent and

amount of maximum burial experienced by the Paleozoic succession(3.5-4.7 Km) proposing an asymmetric basin during the Carboniferous.

Secondly, we dated a well-defined cooling event through the 120-40°C temperature range in the Late Triassic-Early Jurassic. The recognition of this exhumation event is surprising as it is far in time from either the Variscan or Alpine orogenesis. In particular, it is noteworthy that no major effect on burial and exhumation of this region was induced by the Alpine cycle, which collisional front is less than 100 Km East of it. On the other hand, our temporal constraints fit well with the Cimmerian collision, although the margin of the East European Craton is some hundreds of km away from its collisional front. Therefore, we argue that the Mesozoic exhumation in Podolia occurred as a response to a far field effect of the Cimmerian Collision.

Chapter 7

Characterization of dispersed organic matter in Oligocene to Upper Miocene drilled successions in the Lower Congo Basin (offshore Angola)

7.1 Introduction

Fourier Transform infrared spectroscopy (FTIR) Infrared spectroscopy is commonly utilized for characterizing the chemical structures of maceral in coals and kerogen in source rocks (Guo and Bustin, 1998; Ibarra et al., 1996; Kister et al., 1990; Lin and Ritz, 1993; Mastalerz and Bustin, 1996) or has also been used to investigate maturation level and kerogen types (Benshan et al., 1983; Ganz et al., 1990; Lis et al., 2005; Mastalerz and Bustin, 1993).

In particular, FTIR studies assigning specific bands to chemical bonds in complex kerogen molecules (Baruah, 1986; Painter et al., 1981; Painter et al., 1983), proved to be diagnostic for determining the degree of thermal maturity of marine source rocks lacking in vitrinite macerals (Chen et al., 1998; Chen et al., 2012; Christy et al., 1989; Ganz and Kalkreuth, 1987; Kister et al., 1990; Lin and Ritz, 1993; Lis et al., 2005).

Thus, in successions where organic matter has marine origin like amorphous organic matter (AOM) and/or phytoplankton, such as those studied in Chapter 3, FTIR studies could be a viable alternative when traditional optical analyses cannot provide reliable thermal maturity assessment because of scarcity of data and/or phenomena of retardation/suppression of reflectance.

In the well drilled in the Lower Congo Basin (Chapter 3), thermal maturity trend, according to mineralogical analyses perfomed along the whole well, evolved following a single geothermal gradient of 37-38 C°/Km during Oligocene and Miocene time. Analyses on the organic fraction (e.g. vitrinite and bitumen reflectance) were restricted to a little number of samples (11) on which suitable vitrinite or bitumen fragment were found for reflectance measurement. Moreover was found that in the Lower Miocene interval vitrinite reflectance results are affected by retardation and/ or suppression phenomena.

To evaluate the thermal evolution of the organic matter along the whole depth of the well, in this work we used different parameters from FTIR spectroscopy in order to define the changes in aromaticity or aliphaticity (Lis et al., 2005) and obtained information on the thermal evolution of the organic matter.

7.2 Results

7.2.1 KBr-FTIR analyses on bulk kerogen from the Lower Congo Basin

The evolution along the well of the AOM cannot be derived by classic optical parameters (reflectance or palynomorph fluorescence), but according to several authors (Chen et al., 2012; Ganz and Kalkreuth, 1991; Ibarra et al., 1996; Iglesias et al., 1995; Lis et al., 2005a; Petersen et al., 2008) an insight on the short-order



Figure 7.1 FTIR spectrum of concentrated kerogen of LIRA well samples at different depth. Measured band areas and peaks and related assignation to functional groups according to Chen et al. (2012), Christy et al., (1989), Ganz et al., (1990), Ibarra et al. (1996) and Lis et al. (2005) are reported

interpretation of the spectra at these wavenumbers.

during maturation can be performed using Fourier Transform Infrared Spectroscopy (FTIR) on the bulk kerogen.

range chemical processes that occur

In Fig. 7.1 are shown the aromatic absorption between 3000-3100 cm⁻¹, and 700-900 cm⁻¹, the aliphatic absorption between 2800-3000 cm⁻¹ and 1370-1450 cm⁻¹. The region of the oxygenated groups is between 1600-1700 cm⁻¹ while the ether group (C-O-C) that link the aliphatic chains absorbed between 1500 and 1000 cm⁻¹. As shown in Figure 7.1, the aliphatic absorption decreases with the increasing depth, in the oxygenated group region the peak at 1600 cm⁻¹ became more prominent with respect to that at about 1700 cm⁻¹ and the aromatic absorption at 700-900 cm⁻¹ became detectable only in the lower part of the well. Below 1500 cm-1 the presence of mineral matter caused а strong absorption that difficult the make

FTIR parameters of thermal maturity derived from the area ratio of specific absorption bands are plotted versus depth of the LIRA well (Fig.7.2).

According to Chen et al. (2012) and Lis et al. (2005) we use only the more intense and stable peaks and related ratio to perform a chemical characterization of our samples. The ratio used are listed in Table 7.1.

In two band regions (2800-3000 and 1600-1800) peaks area was measured after performing a Fourier deconvolution, respectively with fivepeaks, the CH_2 and CH_3 in the region 2800-3000, according to Ibarra et

al., (1996) and with five peaks in the oxygenated group region (1600-1700 cm⁻¹) according to Petersen et al. (2008).

An increase of the aromaticity parameters has been found against the increasing depth (Fig.7.2). In particular, the Ar1 parameters show values that range between less than 0.001 at the top of the well, to about 0.05 for lower depth. The Ar2 increase in a range of values between 0.1 and 0.4, the Ar3 show an almost linear trend passing

Semi-quantitative index	Index calculation	Band region					
Aromaticity Ar1	CH _{ar stretching} / CH _{al stretching}	(3000-3100)/(2800-3000)					
Aromaticity Ar2	CHar stretching / CHal bending	(3000-3100)/(1450)					
Aromaticity Ar3		(3000-3100)/(1370)					
Aromaticity Ar4	$CH_{ar out of plane deformation}$ / $CH_{al stretching}$	(700-900)/(1370)					
Degree of condensation DOC1	CH _{ar stretching} / C=C stretching	(3000-3100)/(1600)					
		(700.000) /(1.000)					
Degree of condensation DOC2	CH _{ar out of plane deformation} / C=C stretching	(700-900)/(1600)					
Aliphatic chain lenght	CH ₂ /CH ₃	(2900-2940)/(2940-3000)					
'A' factor	CH _{al stretching} /(CH _{al stretching} + C=C)	(2800-3000)/[(2800-3000)+1600]					
'C' factor	C=O / C=O + C=C	(1650–1800)/ [(1650–1800)+1600]					

Table 7.1 FTIR band assignment of the main functional groups

from values of about 0.5 at the top to about 2.5 at the bottom of the well and finally the Ar4 parameters show a scattered trend across the well, that is probably influenced by the high interference from mineral matter in this region (Fig.7.1), and his values range between 0.5 and 7.



Figure 7.2 Trend against depth of the aromaticity parametrs calculated according to Lis et al., (2005): (a) Ar1, (b) Ar2, (c)Ar3 and (d) Ar4

The degree of condensation of the aromatic rings during increasing of rank is well expressed by the DOC1 and DOC2 parameters (Fig.7.3), firstly used by Ibarra et al. (1996) and Iglesias et al. (1995) and recently by Chen et al. (2012). DOC1 parameters in this set of samples show a linear correlation in the first 4000m depth and more scattered values in the deeper samples, with values between 0.01 and 0.25, while the DOC2 parameter doesn't show any significant trend with depth, probably because is related the absorption between 700-900 that is very



Figure 7.3 Trend against depth of DOC1(a) and DOC2 (b) parameters calculated according to Chen et al., (2012)



Figure 7.4 Trend against depth of the CH2/CH3 aliphaticity parameter calculated according to Lis et al., (2005)

difficult to measure with precision.

The methylene/methyl ratio measured by integrating the peaks of asymmetric stretching vibrations in the 2,900-3,000 cm⁻¹ region (CH₂/CH₃) reflects the length of aliphatic chains (Lin and Ritz, 1993; Pradier et al., 1992) and is strongly dependent on maceral type, being higher in the liptinite and lower in the vitrinite group macerals(Mastalerz and Bustin, 1996) . This ratio was calculated according to Chen et al. (2012) integrating the area of the two peaks in the region between 2900 and 3000 cm⁻¹. The values obtained are very high with respect to those found in literature, indicating the presence of very long aliphatic chains in these materials. Nevertheless the trend show in Fig.7.4 indicate a rapid decrease with values from about 6 to about 3.5 up to 4000m followed by a scattered values after this depth with values ranges around 4. An interesting trend is that of the C=O/C=C parameter that show an initial



Figure 7.5 Trend against depth of the A factor (a) and C factor (b) calculated according to Chen et al., (2012)

decrease followed by an increase for depth lower than 4000m about and with values ranging between 0.5 and 1.5 (Fig. 7.5). Finally, the A factor and the C factor have been widely used for describing kerogen type and maturation level (Ganz and Kalkreuth, 1991). In particular, according to Chen et al., 2012 and Iglesias et al., 1995, high values of A factor in the high-volatiles bituminous rank indicate a strong hydrocarbon generating potential while, a C factor increase reflects the maturation level. Our samples indicate a high HC generating potential as indicated by the high values of the A' factor with values of about 0.9 at the bottom of the well. The C factor show a very similar trend with respect to that observed for the C=O/C=C parameter and his values range from about 0.6 to about 0.4 (Fig.7.5).

Other parameters don't shown significant changes with depth, suggesting that their utility as thermal maturity indicators is not relevant for this set of samples.

7.3 Discussion

FTIR analyses permit us to obtain information about the chemical composition of the OM extracted from cuttings along the depth of the well through the analyses of the absorption band area in the FTIR spectra.

Although differences can exist in the FTIR spectra obtained for different kind of kerogen and/or different macerals, according to Chen et al. (2012) the overall evolutionary trends of functional group abundances in vitrinite and liptinite were similar to each other and also similar to those in bulk coal samples, and followed those described previously in the literature. Thus was possible to carry out information from the analyses of the bulk kerogen although it is composed by different materials in the upper part with respect to the lower part of the well.

An universally accepted correlation between thermal maturity and FTIR parameters doesn't exists and parameter can be scattered along a trend due to uncertainties in spectra analysis, so is not possible to obtain direct detailed information about thermal maturity. In this work we want to study the evolution of the amorphous rich organic matter, present along the well, with thermal maturity by means of FTIR derived maturity parameters. In addition we compare the maturity trends obtained in this study with those found in literature for a similar kerogen.

In this Chapter we compare the trend of FTIR parameters with those calculated assuming that maturation occurs following a constant geothermal gradient similar to the actual as suggested by temperature measurement along the well and illitization patter (Chapter 3).

In the same Chapter we demonstrate that vitrinite reflectance suffer suppressions phenomena probably due to development of overpressure at least from the Lower Miocene interval. Nevertheless we suggest that amorphous organic matter thermal maturation is not affected by retardation phenomena according to the following statements:

- 1) No apparent reduction of aromaticity parameter were observed with respect to the overall trend from the interval in overpressure (Lower Miocene to Oligocene);
- 2) The gas isotopic signature measured in the source rocks at the bottom of the well (ENI's personal communication) indicate temperature of generation similar to the present day ones s and to the paleotemperatures carried out from smectite illitization model (Chaper 3);
- 3) According to (Fang et al., 2004) different component of the OM evolved through different reactions that have different activation energy, different rates of product concentration variation, and different volume expansion effects, and therefore have different responses to overpressure. In particular we speculate that the early gas generation from vitrinite rich intervals could have more significant effects on the pore pressure conditions with respect to the AOM rich intervals.

Aromaticity parameters express the increase of the aromatic structures against the loss of the aliphatic chains. They usually are calculated from the ratio between the aromatic and the aliphatic absorption. The aromatic parameters that show the stronger correlation against calculated R_0 % are the ratio between the aromatic absorption band (3000-3100 cm⁻¹) and the aliphatic absorption bands between 2800-3000, at 1450 and 1370 cm⁻¹ (Fig.7.6). Their values are in the order of magnitude of those found by Lis et al., (2005) and Chen et al. (2012) in a thermal maturity range between 0.3 and 1.5 Ro%



 CH_2/CH_3 ratio show similar exponential trend (Fig. 7.7) to that described by Lis et al., (2005), but with higher values. This could be related to difference in material and in particular our samples are probably hydrogen richer with respect to those of Lis et al., 2005. According to Guo et al., (1998) similar high values could be related to a high alginite content in the liptinitic fraction.





Parameters related to the presence of oxygen are the C=O/C=C parameter and the C factor (Fig.7.8). These show a very uniform decrease until values of about 1.0 R_0 %, that can be related to a very uniform thermal maturity increase. The evolution of this region in the immature stage of HC generation has been widely discussed by Petersen et al. (2008) that recognized a decrease of the carbonyl (C=O) related band with increase thermal maturity at the immature stages of HC generation. The strong absorption between 1500 and 1000 cm⁻¹ depth (Figure 7.1) up to 1600m depth is due, according to Petersen et al., (2008), to the presence of ether group (C-O-C) absorption that link the aliphatic chains. This is also a typical features of alginite. Unfortunately the same frequency are characterized by a strong mineral matter absorption that at higher depth do not permit to observed the evolution of ether groups with depth.

In the oxygenated group region (1600-1700) a new increase of the absorption at 1700 was observed that led to the increase of the C=O/C=C value for values of R_0 % higher than 1.0.

A similar trend was found by Lis et al (2005) in a type II kerogen in the Exshaw Formation and in the samples heated with hydrous pyrolysis (Fig.7.8). The later increase of the C=O/C=C value has been interpreted as due to the oxidation of alcohols that would increase the absorption of the carbonyl/carboxyl group at 1700 cm⁻¹. The presence of pyrobitumen (from asphaltene to bitumen) that are easily more readily oxidized than kerogen can contribute to the increase of the C=O/C=C value. The presence of bitumen, found in traces in all samples from 3,900m depth could be the explanation for the anomalous trend of the C=O/C=C and C factor parameter that are known to be strongly related to the thermal maturity increase (Chen et al., 2012; Ibarra et al., 1996; Lis et al., 2005a; Petersen et al., 2008). These could explain also the irregular trend for the deeper sample of the DOC1 parameter, also related to the aromatic absorption at 1600 cm⁻¹ and 1700 cm⁻¹.



Figure 7.8 - Trend against calculated Ro% of C=O/C=C (a) and C factor (b) parameters and C=O/C=C parameter for the samples of Lis et al., (2005)

7.4 Conclusions

FTIR analyses of the dispersed organic matter extracted from the cuttings along the depth of the LIRA well allow to assess that:

- Aromaticity parameters (Fig. 3) show a linear increase with depth and values that according to other works (Lis et al., 2005 and Chen et al., 2012) indicate a thermal maturity range between 0.3 and 1.5 R_o%;
- CH2/CH3 ratio parameter show a similar trend to that of Lis et al., (2005) but higher values, that, according to Guo et al., (1998) could be associate to high alginite contribution in the liptinitic fraction.
 Presence of high alginit content is further confirm by the diffuse presence of ether bonds between 1500 and 1200 cm⁻¹ at shallow depth;
- Parameters related to the oxygen content (C=O/C=C and DOC1) show a very constant decrease up to about 3000 m with values that according to Lis et al., (2005) and Chen et al., (2012) are related to an increase in thermal maturity up to about a value of 1 R_o%. The subsequent decrease and increase indicate also the oxidation of alkenes to alcohols and a subsequent oxidation of alcohols that would appear for maturity higher than about 1.1 R_o% or could be related to the presence of pyrobitumen.

In conclusion, looking at the trend and values of parameters related to both aromaticity and aliphaticity and compared them with existing values, the retard in maturation registered by the anomalous low values of vitrinite reflectance, was not found in the maturation of the bulk kerogen.

These results thus further confirm through a direct analyses on the dispersed organic fraction in the sediments, the thermal maturity evolution of the LIRA well presented in Chapter 3.

Chapter 8

Raman spectrosopy characterization of dispersed organic matter at low diagenetic stages

8.1 Introduction

Recently Raman spectroscopy has been identified as a potential powerful no-destructive tool able to evaluate thermal maturities of organic matter in a quantitative matter.

Specifically, two bands on the Raman spectra, called G (graphitic) and D (disordered), have been related to the growth of the ordered with respect to the amorphous organic matter. Parameters linked - either directly or indirectly - to D and G bands have been used to describe the temperature paths of metamorphic rocks (Aoya et al., 2010; Beyssac et al., 2002; Endo et al., 2012; Lahfid et al., 2010a; Wopenka and Pasteris, 1993) with reliable correlations between Raman parameters and palaeotemperatures between 320°C and 200°C.

Other authors (Jehlička et al., 2003; Kelemen and Fang, 2001; Liu et al., 2012; Quirico et al., 2005) applied this methods to derive information about the thermal maturity of coals and dispersed organic matter on bulk samples in the mature stage of HC generation, while Guedes et al. (2010a) used micro-Raman to perform punctual analyses on the different classes of macerals on coal samples.

All these works provide correlations between Raman parameters and thermal reflectance measured on vitrinite (R_0 %) in a range of thermal maturities approximately between 1 and about 5-6 R_0 %. However, very little work has been performed on the low diagenetic stage (0.4-1.2 R_0 %), which represents a fundamental window for basin analysis studies and HC exploration. To date, only one study by Wilkins et al. (2014) has been performed. In their work, the authors propose an empirical equation to derive thermal maturity values by correlating Raman parameter to both vitrinite and inertinite data in the low reflectance and diagenetic range (0.4-1.2 R_0 %).

In general, despite the great amount of work on this subject, a general parameterization of the thermal maturity of organic matter through Raman indicators is still lacking, due to differences in experimental setup, fitting procedure, material analyzed.

In particular, a systematic analysis of samples at the immature and middle mature stages of hydrocarbon (HC) generation, of particular relevance for basin analysis studies and HC exploration is missing.

Given this, we decided in this work to extend the applicability of Raman spectroscopy as thermal indicator by systematically investigate the immature and middle mature stages of hydrocarbon generation. We present a robust dataset of Raman and micro-Raman parameters based on the analyses on the first order Raman spectra on Cenozoic and Paleozoic dispersed organic matter measured in two different laboratories and using different preparation techniques.

Different case histories were chosen in order to explore a large range of vitrinite reflectance (about 0.3 to about 1.5 R_0 %) and macerals variability (Table 8.1).

Well-offshore Angola	Carpathian fold and thrust belt	Holy Cross Mountains	Podolia
LIRA 1290	PL 93.1	HCM_4_1	PO_2
LIRA1390	PL 93.2	HCM_4_2	PO_3
LIRA1500	PL 95	HCM_4_3_A	PO_23
LIRA1600	PL 97	HCM_5_1	
LIRA1700	PL 101.1	HCM_5_2	
LIRA1800	PL 102	HCM_5_3	
LIRA1950	PL 103	HCM_5_4	
LIRA2120		HCM_8_1	
LIRA2260			
LIRA2460			
LIRA2600			
LIRA2790			
LIRA2930			
LIRA3070			
LIRA3190			
LIRA3370			
LIRA3610			
LIRA3710			
LIRA3830			
LIRA3910			
LIRA4020			
LIRA4110			
LIRA4220			
LIRA4270			
LIRA4380			
LIRA4510			
LIRA4570			
LIRA4600			
LIRA4680			
LIRA4780			
LIRA4810			
LIRA4880			
LIRA4950			

Table 8.1 Samples analysed using Raman spectroscopy for the four case histories studied in this work

Mesozoic and Cenozoic samples were collected in a well drilled in the offshore Angola and in outcrops in the Carpathians fold and thrust belt. Raman analyses were performed on bulk kerogen (type II and type III) and on individual vitrinite fragments.

Paleozoic samples were collected in the Holy Cross Mountains (Poland) and in the Podolia foreland in Ukraine and the analyses on the organic matter were performed both on bulk kerogen and directly on graptolites fragments, the latter very common in shaly lithologies.

Raman parameters were correlated against vitrinite or vitrinite equivalent data derived from thermal modeling, based on a multi-methods approach using both organic and inorganic indicators.

8.2 Materials and methods

8.2.1 Source rocks and kerogen

The first set of analyses presented in this work was performed on 33 samples originated from cuttings from a 5,000 meters thick section drilled in offshore Angola (Malembo Formation – Lower Congo Basin) (LIRA well hereafter). The succession ranges from the Upper Miocene to Oligocene in age and is composed mainly by organic rich shale interbedded by near shore to deep water sandstones.

Fragments with different origins, measured by optical analyses, were found in the upper well (1,290-3,360m) where wooden fragments (CWF) and herbaceous fragments (CHF) of continental origin are present together with amorphous organic matter (AOM) and marine phytoplankton (MPH), while the lower part (3,600-4,950 m) is composed mainly by amorphous organic matter with some traces of bitumen (Table 8.2).

Samples from the Carpathian fold and thrust belt (PL hereafter) come from the SW sector of the chain. In the area, the outer fold-and-thrust belt is made up of three NW-SE striking thrust sheets dated between early Cretaceous and early Miocene and composed of sandstones, siltstones and shales. In detail, organic matter rich samples were collected in stratigraphic levels characterized by three anoxic events that favoured the deposition of organic-matter rich black shales of the Shypot formation (Cretaceous) and the Melinite shales (Oligo-Miocene). The organic matter in this samples is highly heterogenous as indicate by organic petrography analyses in Chapter 4.

Finally, Paleozoic samples were collected in the Carpathian foreland of the Podolia region (Ukraine) (PO) and in the Paleozoic core in the Holy Cross Mountains in Poland (HCM).

In the Podolia region were sampled the Ordovician to Devonian shale and siltstones that outcrop along the Dniestr river while the Holy Cross Mountain are characterized by Cambrian to Permian outcrops exhumed after the Variscan orogenesis.

In these samples organic matter is derived essentially from algae and bacteria in Cambrian and Ordovician rocks while lipids from marine organisms such as trilobite, graptolites and chitinozoas are the source for the Silurian and Devonian OM.

Raman analyses were performed on different starting materials and/or differently prepared specimen (Table 8.1):

- i) powder of isolated bulk kerogen of 33 samples from LIRA well drilled in the offshore of Angola, of 7 surface samples from Carpathians fold and thrust belt (PL) and 11 surface samples from Holy Cross Mountains (HCM). This kind of analysis has the advantage of being rapid and does not need any specific and time-consuming preparation;
- polished sections containing isolated bulk kerogen of samples from Carpathians fold and thrust belt (PL) or finely crushed bulk rock of samples from the Podolia region in Ukraine (PO), previously used for optical analysis of kerogen in reflected light (see Chapters 4-6);
- iii) polished sections of fragments of graptolites cut parallel to the original bedding and then mounted in epoxy resin for samples from Holy Cross Mountains (HCM), previously used for optical analysis of kerogen in reflected light (see Chapters 5).

Kerogen concentration was done by means of the traditional HF–HCl method described by Robl and Davis (1993) and Schimmelmann et al. (1999).

8.2.2 Curve fitting

Working on highly disordered carbon materials, Raman spectra are affected by interference due to high fluorescence caused by the diffuse presence of hydrogen or by the residual mineral matters.

The first step to analyze the spectra is therefore the removal of the high fluorescence background by a proper baseline subtraction procedure. Of course, once that the best procedure has been, this has to be used for the entire set of sample.

Spectra collected in this work were fitted using a third order polynomial curve. We used a polynomial curve because it best follow the real trend of the fluorescence in the most immature samples with higher fluorescence background.

After having removed the background, the spectra need to be deconvoluted and the appropriate band profile needs to be chosen.

There are several fitting procedures available in literature, starting from Voigt profile used by Beyssac et la., (2002; 2003), (Aoya et al., 2010), (Endo et al., 2012), to a mixed Lorentzian and Gaussian profile for more disordered material (Guedes et al., 2010; Lahfid et al., 2010; Quirico et al., 2005; Sadezky et al., 2005). Some authors propose the use of pure Lorentzian (Schopf et al., 2005) or pure Gaussian (Li, 2007) while according to Ferrari and Robertson (2000) the Breit-Wigner-Fano (BWF) line in an excellent mean to fit Raman spectra of all carbons.

For this set of samples, we uses a mixed Gaussian–Lorentzian curve-fitting procedure performed with a Labspec program of Horiba, as it best described the spectral features for our samples.

A six peaks deconvolution was chosen as it obtained best fitting results using the minimum number of parameters. Because of the similarity in the bands positions and for the sake of simplicity we decided

to refer to Rebelo et al., 2015 for band nomenclature, without considering, for the moment, the chemical or structural assignment of the bands. . Position and bands names are shown in Figure 8.1.

Best fit results were achieved considering S, Dl and Dr as purely Gaussian while D, G adn Gl as more mixed Gaussian-Lorentzian component.



Figure 8.1 Example of the bands and bands position obtained by Raman analysis on dispersed organic matter. The solid black line is the original curve, the dashed line is the curve for each band and the solid grey line is the sum of the fitting curves

8.2.3 Raman thermal maturity parameters

Despite many literature studies, debate still exists on which Raman parameters better correlate with the carbonization and/or graphitization ranks. In general, the first discovery that permitted the use of Raman spectroscopy as a tool to study carbon materials thermal evolution was the Tuinstra Koenig (TK) relation (Tuinstra & Koenig, 1970): $ID/IG = C(\nu L)/La$.

Here ID/IG is the ratio between the intensities of the D and G peaks, La is the lateral dimension (parallel to the graphene planes) of the nanocrystal and $C(\nu L)$ is a constant which depends on the laser frequency. Taking IG is a reference value, which is not expected to depend on the size of the crystal (Cancado et al., 2008), TK relation found an inverse relation between the intensities of the D band and the crystal dimensions. Following the TK correlation, Wopenka & Pasteris (1993) first correlated some Raman parameters with the metamorphic zone assessed by the mineral assemblage.

Subsequently Yui et al. (1996) demonstrated the high sensitivity of some Raman parameters to the metamorphic grade from low-grade metamorphism to greenschist facies, while Beyssac et al., (2004) develop the so called RSCM geothermometer for Raman Spectroscopy of Carbonaceous Material. RSCM expressed a relationship between the Raman parameter R2 (R2 = D/([G + D + D']) area ratio) and the metamorphic temperature and was initially calibrated in a range between 330-640°C, but was also extended to contact- metamorphic rocks (Aoya et al., 2010) and low-grade metamorphism (Lahfid et al., 2010, RA1 and RA2 parameters). In addition, other changes in Raman spectra features were observed by the authors such as : a decrease in intensity of the D1 and D2 bands relatively to the G band; a decrease in width of the G band and a shift of the G band position to lower wavenumber.

All the spectral features variations were easily correlated to the graphitization process at high temperature.

Considering the low temperature interval pertaining to the subituminous coal to the anthracite ranks, correlation between spectral features variations and carbonification is not so clearly defined. In general, FWHM, G band position and D/G intensity and area ratio are the most sensible parameters to the maturation increase (Guedes et al., 2010b; Jehlicka et al., 2009; Marques et al., 2009; Sadezky et al., 2005; Zhou et al., 2014). Romero-Sarmiento et al. (2014) suggest that the FWHM of the G band shows the best correlation against Tmax values (temperature of the S2 peak in pyrolysis) in a set of samples from the Barnett shales and finally Liu et al. (2012) determine thermal maturity by using the the D-G distance in matured to highly matured carbonized samples of solid organics.

In this work most of the parameters used in literature were compared for our different sets of samples in order to find those that better correlate against thermal maturity in diagenesis.

In particular, we determined the following parameters: D and G position, width at half height of the D and G bands (FWHM), D-G distance and D/G intensity and area ratio. Moreover, we redefined the parameters RA1 and RA2 (following the work of Lahfid et al., 2010) and tested the D and G full width at half height ratio, calculated as follows:

- 1) RA1 = area (S+Dl+D) / area (S+Dl+D+Dr+Gl+G);
- 2) RA2 = area (S+Dl+D) / area (Dr+Gl+G).
- 3) wD/wG = width at half height of D band and G band ratio

8.3 Raman analyses results for differents materials and case histories

8.3.1 Raman analyses on powder of bulk kerogen

8.3.1.1 Malembo Formation – Lower Congo Basin (age: Tertiary)(LIRA)

Previously acquired data on LIRA samples (FTIR spectroscopy on kerogen in Chapter 6, XRD investigation on clay mineralogy in Chapter 3) and thermal modelling (Chapter 3) indicated that thermal maturity along the well range between about 0.35 and 1.50 R_0 %.



Figure 8.2 Examples of Raman spectra measured from organic matter extracted from cuttings at different stratigraphic depth

Furthermore optical analysis in reflected light on kerogen (Chapter 3) showed that, when organic matter of continental origin is present, it is essentially represented by vitrinite group macerals, whereas inertinite group macerals are totally absent. On the other hand, optical observations by Raman apparatus on powder of isolated kerogen do not allow to distinguish vitrinite from inertinite group macerals (Fig.8.3).





Figure 8.3 Microphotographs showing some grains on which Raman analyses were performed. Images obtained using the x 50 air objectives lens mounted on the Raman spectrometer

Raman spectra and derived parameters will be described as a function of depth and related calculated R_0 % values. Fig. 8.2 shows the evolution of Raman spectra as a function of depth and thermal maturity. Some typical features can be recognized from a qualitative assessment of the spectra.

First of all, the fluorescence signal, and the width of the G bands both decrease regularly with increasing depth. The decrease in the width of the G band is still clearly recognizable after the background subtraction procedure and therefore is not an artefact of the fluorescence signal (Fig. 8.4 and 8.5).



Figure 8.4 Example of the bands and bands position obtained by Raman analysis on dispersed organic matter for samples collected: (a) at the top and (b) at the bottom of the well

In Fig. 8.4, deconvolution of two spectra collected respectively at the top and at the bottom of the well are presented. With increasing depth, the area underneath the G band decreases due to both a decrease in the width at half height of peak G and a decrease in the area of the Gl band.

This latter evidence produces the definition of a progressively deep "valley" between the D and G bands (Figs. 8.4b).



Figure 8.5 Example of different Raman spectra colleted between 1000m and 5000m of depths put (a) into perspective and (b) from a front point of viewed

The same spectra evolution can be seen in a 3D plot shown in Figure 8.5a, whereas Figure 8.5b shows the shift of the G band for different depth.

Using the six peaks deconvolution approach described in the Methods and Materials section, it is possible to quantify the major changes in the Raman spectra as observed in Figures 8.4 and 8.5.

The parameters, calculated as average values of about ten spectra measured for each depth, are listed in Table 8.2.

Figures 8.6, 8.7, 8.8 show the trends of the parameters against depth.

The G band position seems to be independent from depth, ranging between 1,590 and 1,600 cm⁻¹, while the D band position decreases slightly with depth from about 1,380cm⁻¹ to 1,360 cm⁻¹ for samples collected at the well bottom (Fig. 6 a-b). As a consequence, the D-G distance slightly increases with depth from about 220 to 240 cm⁻¹ (Fig 8.6c).

The full width at half maximum (FWHM) of the G band decreases from about 90 cm⁻¹ to 55 cm⁻¹, while the full width at half maximum (FWHM) of the D band increases non linearly from 90 cm⁻¹ to 110 cm⁻¹ with anomalously high values in the first 2,000 m of depth (Fig.8.7 a-b).

The intensity ratio between the D and G band does not show any clear correlation with depth, while the D/G area ratio shows a trend of increasing values with depth, ranging from about 0.5 to 1.0 (Fig. 8.8a-b).

The two final parameters presented in Figure 8.8 (c-d) are RA1 and RA2 which take into account the area ratio among all the peaks forming the spectra.

Depth (m)	Kerogen composition	D position	σ D position	G position	σ G position	FWHM D	$\sigmaFWHM\text{-}D$	FWHM G	σ FWHM-G
1290	AOM ₁₀ CHF ₂₅ CWF ₆₅	1378.71	4.14	1595.58	3.48	96.96	9.15	89.82	4.60
1390	AOM ₅ MPH ₅ CHF ₃₀ CWF ₆₀	1376.38	2.98	1596.75	4.34	93.57	8.84	85.07	6.48
1500	AOM ₈₀ CHF ₁₅ CWF ₅	1376.70	4.01	1596.85	6.73	94.29	13.22	87.63	7.18
1600	AOM ₇₀ CHF ₂₀ CWF ₁₀	1372.34	3.54	1593.79	3.02	96.48	6.85	86.00	7.53
1700	AOM ₇₀ CHF ₂₅ CWF ₅	1376.55	3.18	1601.14	2.69	92.35	8.66	83.61	7.78
1800	AOM ₁₀ MPH ₅ CHF ₂₅ CWF ₆₀	1372.48	2.30	1595.36	2.84	98.37	4.65	84.37	5.02
1950	AOM ₂₀ MPH ₁₀ CHF ₂₅ CWF ₄₅	1371.25	2.86	1594.40	4.04	95.80	7.94	81.72	4.94
2120	AOM ₆₀ CHF ₁₅ CWF ₂₅	1375.91	5.47	1599.96	3.45	97.02	4.85	84.76	3.96
2260	$AOM_{10}MPH_{10}CHF_{15}CWF_{65}$	1375.04	2.46	1600.35	4.29	90.29	10.81	82.33	4.64
2460	AOM ₈₀ MPH ₅ CHF ₁₀ CWF ₅	1370.33	3.32	1598.46	3.35	92.54	7.64	79.28	5.55
2600	AOM ₉₀ CHF ₅ CWF ₅	1366.90	3.43	1594.10	4.40	94.35	8.88	84.44	5.47
2790	AOM ₈₀ MPH ₅ CHF ₁₀ CWF ₅	1375.53	1.91	1603.05	1.77	99.12	3.40	78.84	2.74
2930	AOM ₄₀ CHF ₂₀ CWF ₄₀	1366.95	5.75	1597.50	2.11	96.04	4.82	75.14	8.42
3070	AOM ₉₀ CHF ₅ CWF ₅	1363.48	4.10	1592.56	1.22	97.53	4.27	80.53	3.08
3190	AOM ₂₅ CHF ₃₅ CWF ₄₀	1363.32	3.49	1592.70	3.16	97.67	4.59	71.74	8.87
3370	AOM ₃₅ CHF ₁₅ CWF ₅₀	1360.63	3.21	1588.77	2.49	100.04	0.22	83.77	2.79
3610	AOM ₆₀ CHF ₂₅ CWF ₁₅	1366.95	1.90	1600.68	1.36	99.86	1.82	69.37	3.38
3710	$AOM_{80}MPH_{10}CHF_5CWF_5$	1361.53	2.21	1595.32	1.81	100.16	1.92	69.61	4.50
3830	AOM ₉₀ CHF ₅ CWF ₅	1358.91	1.88	1595.29	2.12	100.73	1.30	66.94	3.78
3910	AOM ₁₀ CHF ₂₀ BIT ₇₀	1366.58	1.40	1599.71	2.42	101.30	2.85	68.79	5.61
4020	AOM ₈₅ CHF ₁₅	1358.27	2.97	1597.20	2.98	104.89	7.01	67.39	7.39
4110	AOM ₁₀₀	1358.07	1.45	1594.67	1.03	105.18	4.00	66.98	4.80
4220	N.D	1360.34	4.27	1596.89	3.67	106.20	6.79	65.71	6.30
4270	AOM ₁₀₀	1358.01	3.29	1596.61	2.79	104.93	4.76	67.08	6.99
4380	AOM ₁₀₀	1354.77	2.79	1594.43	1.80	105.20	1.46	64.73	4.39
4510	N.D	1361.91	2.62	1601.08	2.19	104.07	3.91	60.87	3.16
4570	AOM ₁₀₀	1362.64	2.82	1601.82	1.34	106.27	3.26	60.23	3.49
4600	AOM ₁₀₀	1361.13	4.60	1596.56	4.35	104.32	4.98	64.14	6.32
4680	AOM ₁₀₀	1354.64	1.28	1593.58	2.16	107.15	3.44	59.84	3.93
4780	N.D	1360.10	2.41	1598.16	1.82	111.75	3.88	63.13	4.61
4810	AOM ₁₀₀	1359.13	3.08	1593.22	2.84	116.39	8.92	66.81	4.19
4880	AOM ₁₀₀	1354.58	3.09	1595.37	2.83	106.33	5.39	60.04	4.63
4950	N.D	1359.74	1.64	1600.23	2.97	105.69	5.64	57.38	3.90

To be continued

Depth (m)	Kerogen composition	D-G	σ D-G	ID/IG	σ ID/IG	aD/aG	σ aD/aG	RA1	σ RA1	RA2	σ RA2	wD/wG	σ wD/wG
1290	AOM ₁₀ CHF ₂₅ CWF ₆₅	1378.33	4.97	0.57	0.08	0.63	0.27	0.38	0.05	0.62	0.12	1.08	0.11
1390	AOM ₅ MPH ₅ CHF ₃₀ CWF ₆₀	1376.02	3.91	0.54	0.07	0.58	0.16	0.37	0.02	0.58	0.05	1.10	0.10
1500	AOM ₈₀ CHF ₁₅ CWF ₅	1376.35	5.08	0.58	0.06	0.61	0.17	0.35	0.03	0.55	0.07	1.08	0.16
1600	AOM ₇₀ CHF ₂₀ CWF ₁₀	1371.98	4.79	0.60	0.06	0.68	0.21	0.37	0.02	0.58	0.05	1.12	0.13
1700	AOM ₇₀ CHF ₂₅ CWF ₅	1376.17	4.23	0.62	0.05	0.71	0.25	0.38	0.03	0.61	0.07	1.10	0.14
1800	$AOM_{10}MPH_5CHF_{25}CWF_{60}$	1372.09	3.34	0.61	0.05	0.77	0.14	0.38	0.01	0.62	0.03	1.17	0.09
1950	$AOM_{20}MPH_{10}CHF_{25}CWF_{45}$	1370.87	3.28	0.62	0.06	0.72	0.14	0.37	0.02	0.59	0.05	1.17	0.13
2120	AOM ₆₀ CHF ₁₅ CWF ₂₅	1375.53	4.05	0.59	0.06	0.67	0.13	0.38	0.02	0.62	0.04	1.14	0.06
2260	$AOM_{10}MPH_{10}CHF_{15}CWF_{65}$	1374.66	3.36	0.59	0.07	0.67	0.20	0.38	0.02	0.61	0.05	1.10	0.16
2460	$AOM_{80}MPH_5CHF_{10}CWF_5$	1369.95	5.25	0.61	0.05	0.81	0.16	0.38	0.02	0.62	0.05	1.17	0.13
2600	AOM ₉₀ CHF ₅ CWF ₅	1366.51	4.76	0.61	0.06	0.71	0.13	0.38	0.02	0.63	0.06	1.12	0.12
2790	$AOM_{80}MPH_5CHF_{10}CWF_5$	1375.13	2.75	0.64	0.03	0.78	0.12	0.40	0.01	0.68	0.04	1.26	0.06
2930	AOM ₄₀ CHF ₂₀ CWF ₄₀	1366.54	6.47	0.61	0.02	0.76	0.10	0.41	0.01	0.71	0.03	1.28	0.15
3070	AOM ₉₀ CHF ₅ CWF ₅	1363.08	4.33	0.64	0.03	0.70	0.16	0.41	0.01	0.68	0.03	1.21	0.07
3190	AOM ₂₅ CHF ₃₅ CWF ₄₀	1362.90	4.75	0.63	0.04	0.83	0.16	0.42	0.01	0.74	0.04	1.36	0.15
3370	AOM ₃₅ CHF ₁₅ CWF ₅₀	1360.20	3.71	0.64	0.04	0.61	0.03	0.43	0.01	0.74	0.02	1.19	0.04
3610	AOM ₆₀ CHF ₂₅ CWF ₁₅	1366.50	1.99	0.63	0.01	0.84	0.15	0.45	0.02	0.82	0.07	1.44	0.09
3710	$AOM_{80}MPH_{10}CHF_5CWF_5$	1361.07	2.06	0.62	0.03	0.86	0.21	0.46	0.02	0.85	0.09	1.44	0.10
3830	AOM ₉₀ CHF ₅ CWF ₅	1358.45	2.07	0.61	0.02	0.87	0.07	0.46	0.01	0.87	0.05	1.50	0.08
3910	AOM ₁₀ CHF ₂₀ BIT ₇₀	1366.11	1.57	0.62	0.01	0.89	0.19	0.47	0.02	0.90	0.08	1.47	0.12
4020	AOM ₈₅ CHF ₁₅	1357.80	1.73	0.59	0.02	0.89	0.15	0.47	0.01	0.88	0.05	1.56	0.15
4110	AOM ₁₀₀	1357.59	1.39	0.62	0.03	0.94	0.11	0.48	0.02	0.93	0.06	1.57	0.10
4220	N.D	1359.85	2.43	0.62	0.04	1.00	0.21	0.49	0.03	0.97	0.12	1.62	0.12
4270	AOM ₁₀₀	1357.52	2.28	0.61	0.03	1.00	0.16	0.49	0.02	0.97	0.09	1.56	0.14
4380	AOM ₁₀₀	1354.29	3.47	0.59	0.01	0.95	0.08	0.48	0.02	0.92	0.08	1.63	0.10
4510	N.D	1361.42	2.37	0.60	0.03	0.98	0.06	0.49	0.01	0.96	0.03	1.71	0.12
4570	AOM ₁₀₀	1362.14	3.10	0.61	0.02	1.02	0.08	0.50	0.02	1.02	0.06	1.76	0.12
4600	AOM ₁₀₀	1360.66	3.18	0.63	0.14	1.06	0.35	0.48	0.01	0.91	0.03	1.63	0.16
4680	AOM ₁₀₀	1354.14	1.49	0.60	0.02	1.02	0.08	0.50	0.02	1.00	0.07	1.79	0.09
4780	N.D	1359.60	2.61	0.61	0.03	1.03	0.08	0.50	0.02	1.00	0.07	1.77	0.13
4810	AOM ₁₀₀	1358.63	3.87	0.62	0.02	1.02	0.12	0.49	0.02	0.98	0.09	1.74	0.16
4880	AOM ₁₀₀	1354.06	3.46	0.59	0.02	1.06	0.27	0.52	0.04	1.10	0.06	1.77	0.15
4950	N.D	1359.24	3.75	0.57	0.02	1.01	0.06	0.50	0.01	1.01	0.05	1.84	0.10
Table 8.2 Table shows the OM composition for samples collected at each depth and measured Raman parameters with standard deviations. Acronyms: AOM - amorphous organic matter; MPH - marine phytoplankton; CHF - continental herbaceous fragments; CWF - continetal wooden fragments; D position – position of the D band; G position of the G band; FWHM D – full width at maximum height of the D band; FWHM G – full width at maximum height of the G band; D-G - distance between and G bands; ID/IG – intensity ratio of the D and G bands; aD/aG – area ratio between the D and G bands; RA1 - area (S+DI+D) / area (S+DI+D+Dr+GI+G); RA2 - area (S+DI+D) / area (Dr+GI+G); wD/wG full width at maximum height of the D and G bands; σ – standard deviation; N.D – not determined



Figure 8.6 Trends with depth of: (a) position of the D band, (b) position of the G band and (c) difference between G band and D band positions. Red dots indicate terrestrial derived organic matter rich kerogen, black dots amorphous organic matter rich kerogen. Bars indicate standard deviation for each samples

Both RA1 and RA2 show an almost linear increase with depth, with RA1 ranging from 0.35 to 0.50 and the RA2 parameter ranging from about 0.55 to 1.10 (Fig. 8.8, c-d).

From the observed trends it is clear that the area ratio parameters show a better correlation than the intensity ratio parameters.



Figure 8.7 Trends with depth of: (a) width at half height of the D band and (b) width at half height of the G band. Red dots indicate terrestrial derived organic matter rich kerogen, black dots amorphous organic matter rich kerogen. Bars indicate standard deviation for each samples



Figure 8.8 Trends with depth of: (a) intensities ration between D and G bands; (b) area ration between D and G bands; (c) RA1 parameter and (d) RA2 parameter. Red dots indicate terrestrial derived organic matter rich kerogen, amorphous organic matter rich kerogen. Bars indicate standard deviation for each samples

In addition, a new parameter was also tested based on the full width half maximum ratio (FWHM) of D and G bands.

This additional parameter is plotted against R₀% in Fig. 8.10c.

Among all parameters considered in Fig. 8.6-8.7-8.8, best correlations with depth are provided by the D-G distance(Fig. 8.6), the FWHM of peak G(Fig. 8.7), the D/G area ratio (Fig. 8.8), the RA2 parameter (Fig. 8.8) and the FWHM ratio of D and G band (Fig. 8.10).

We plotted these parameters against calculated thermal maturity expressed in R_0 % in Fig. 8.9 and Fig. 8.10. A power equation was used to fit the D/G area ($R^2 = 0.93$), RA2 ($R^2 = 0.95$), D/G width ($R^2 = 0.96$) parameters (Fig.8.10 a-b-c), while FWHM-G parameter ($R^2 = 0.91$) and the D-G distance ($R^2 = 0.94$) were fitted according to a second order polynomial equation (Fig. 8.10).



Figure 8.9 Correlation between Ro% eq. calculated based on clay mineralogy and FTIR analyses and (a) distance between D and G band and (b) width at half height of the G band

The high correlation between Raman parameters and thermal maturity suggests that the Raman spectroscopy can be successfully used at the low thermal maturities investigated in this study.



Figure 8.10 Correlation between Ro% eq. calculated based on clay mineralogy and FTIR analyses and (a) area ratio between D and G bands; (b) RA2 parameter and (c) width ratio between D and G ratio

Furthermore their regular trends with depth suggest that:

1) Raman parameters of thermal maturity, tested in this work, are not affected by retardation or suppression phenomena of thermal alteration that, on the contrary, have been invoked for vitrinite reflectance in the case of LIRA well. This evidence is in agreement with recent statements presented by Wilkins et al. (2014) in the analyses of perhydrous vitrinite.

2) Raman signal and the derived quantitative parameters do not show significant differences from the type of organic matter investigated, as they show continuous trends as a function of depth. In detail these parameters do not show any shift or jump when moving from AOM rich samples to vitrinite rich samples indicating a regular increase of maturity with depth. This piece of evidences resembles the distribution with depth of aromatic parameters derived from FTIR spectroscopy described in Chapter 6. This is in agreement with Chen et al.'s work (2012) in which the authors found that differences in perameters derived from micro-FT-IR analyses on vitrinite and liptinite macerals can be negligible.

8.3.1.2 Carpathians fold and thrust belt (Age: Mesozoic and Cenozoic)(PL)

We performed Raman spectroscopy measurements on powder of isolated bulk kerogen of six samples (PL_93.1, PL_93.2, L_95, PL_97, PL_101.1, PL_102) whose thermal maturities range between 0.42 and 0.61 R_0 %.



Figure 8.11 Raman spectra of two fragments found in samples PL 95

Most of the acquired spectra show very high fluorescence background related to their low thermal maturities except for some spectra with really unusual low fluorescence and features typical of higher

Samples	Kerogen	D position	σ D position	G position	σ G position	FWHM D	σ FWHM D	FWHM G	σ FWHM G
PL 93.1	II	1367.19	2.52	1593.81	2.33	100.00	0.00	0.66	4.94
PL 93.2	П	1368.56	4.67	1595.54	4.17	100.00	0.00	0.72	11.24
PL 95	П	1374.26	1.63	1598.48	2.02	100.00	0.00	0.67	4.28
PL 97	П	1373.69	2.67	1597.94	2.51	99.52	1.18	0.76	8.35
PL 101.1	111	1370.51	4.22	1596.37	4.66	99.61	1.22	0.74	12.02
PL 102	111	1367.95	4.98	1595.88	3.44	97.92	3.98	0.57	5.57
PL 103	П	1370.66	1.88	1598.67	2.10	100.00	0.00	0.87	5.67

To be continued

Samples	Kerogen	D-G	σ D-G	ID/IG	σ ID/IG	aD/aG	σ aD/aG	RA1	σ RA1	RA2	σ RA2	wD/wG	σ wD/wG
PL 93.1	П	226.62	2.35	0.66	0.08	0.59	0.07	0.39	0.01	0.65	0.04	1.19	0.07
PL 93.2	П	226.98	4.28	0.72	0.11	0.84	0.53	0.42	0.02	0.72	0.07	1.28	0.22
PL 95	П	224.22	1.33	0.67	0.06	0.62	0.07	0.41	0.02	0.69	0.05	1.26	0.07
PL 97	П	224.25	2.85	0.76	0.09	0.89	0.37	0.43	0.02	0.75	0.08	1.37	0.14
PL 101.1	Ш	225.85	4.97	0.74	0.11	0.88	0.34	0.41	0.03	0.70	0.08	1.42	0.27
PL 102	Ш	227.93	3.69	0.57	0.03	0.62	0.16	0.39	0.02	0.64	0.06	1.18	0.10
PL 103	Ш	228.01	2.94	0.87	0.13	1.07	0.30	0.47	0.02	0.89	0.06	1.64	0.16

Table 8.3 Kerogen classification according to Peter and Cassa's (1990) and Raman parameters for samples PL. Acronyms: D position – position of the D band; G position of the G band; FWHM D – full width at maximum height of the D band; FWHM G – full width at maximum height of the G band; D-G - distance between and G bands; ID/IG – intensity ratio of the D and G bands; aD/aG – area ratio between the D and G bands; RA1 - area (S+DI+D) / area (S+DI+D+Dr+GI+G); RA2 - area (S+DI+D) / area (Dr+GI+G); wD/wG full width at maximum height of the D and Gbands; σ – standard deviation

maturity ranks. Figure 8.11 shows two spectra acquired from the same samples ($R_0\% = 0.45$) with very different features.

Raman analyses on the bulk kerogen are listed in Table 8.3. In Figure 8.12 and 8.13 we correlated Raman parameters against vitrinite reflectance.



Figure 8.12 Trends with increase R_0 % of: (a) distance between D and G bands (b) FWHM of the G band for the bulk kerogen in samples PL

Unlike the previously described samples set from LIRA well, this set of sample does not show any clear correlation between Raman indicators and vitrinite reflectance.

In particular, the D-G distance does not present any apparent increase with vitrinite reflectance showing almost a constant values of 225 cm⁻¹, the FWHM of the G band vary not linearly between 70 and 80 cm⁻¹ with a minimum value of about 60 cm⁻¹ for the sample PL_103 (Fig.8.12 b).

The D/G area ratio show highly scattered values comprised between 0.5 and 1.0, a very wide range compared to the LIRA well samples (Fig. 8.13a). The RA2 ratio varies between 0.6 and 0.8 in a range of R_0 % between 0.41 and 0.5 without any clear trend (Fig 13b). Finally the D/G width ratio shows values grouping between 1.2 and 1.4 with a maximum value of 1.6 with poor correlation to vitrinite reflectance values.

The scarce correlation between Raman parameters and R_0 % probably reflects the high heterogeneity of the dispersed organic matter and in particular the abundance of macerals of the inertinite group which could have altered the average values of Raman parameters calculated for each sample.

Guedes et al. (2010) demonstrated in their study that Raman spectra could vary as a function of the different classes of materials analyzed and they recognized that for coals samples only variations of Raman parameters measured on collotelinite could be related to the coalification ranks. For this reason

we performed further micro-Raman analyses on these samples focusing only on vitrinite fragments (see paragraph 3.2.1).



Figure 8.13 Trends with increase Ro% of: (a) area ratio between D and G bands; (b) RA2 parameter and (c) width ratio between D and G ratio for the bulk kerogen in samples PL

8.3.1.3 Holy Cross Mts.(HCM) and Podolia region (PO) (age: Paleozoic)

Paleozoic kerogen derived from Holy Cross Mts. and Podolia region is devoid of vitrinite for all samples older that Devonian. Raman analyses were therefore performed only on vitrinite-like fragments, avoiding graptolite fragments whose specific micro-Raman analyses will be discussed in paragraph 8.4.2.2.

As shown in Figure 8.14, spectra from samples are all characterized by very high fluorescence background regardless of the thermal maturity.



Figure 8.14 Raman spectra of samples at different thermal maturity for HCM samples

Figures 8.15 and 8.16 and Table 8.4 present Raman parameters calculated from the fitting of the spectra versus organoclasts reflectance data expressed in vitrinite reflectance equivalent (R_0 %eq.) according to Bertrand and Malo's equation (2012) (see Chapter 6).

Correlation between Raman indicators and R_0 %eq is hampered by the high standard deviation of both reflectance and Raman data.

In general, from Figure 8.15 it can be observed that D-G distance parameter does not correlate with reflectance, showing values ranging from 230 and 250 cm^{-1} .

FWHM of peak G show values ranging between 75 and 65 cm⁻¹ that decrease irregularly with increase of the reflectance average values (Fig. 15 b). D/G area ratio, D/G width ratio and RA2 parameter shown in Fig 16 a-b-c suggest a correlation with R_0 % with D/G area ratio increasing from 0.7 to 1.5, RA2 increasing from 0.6 to 10 and the D/G width ratio increasing from 1.3 to 1.6.

Samples	Analysis	D Position	σ D position	G Position	σ G position	FWHM-D	σ FWHM-D	FWHM-G	σ FWHM-G
HCM_4_1	Bulk kerogen	1360.20	3.31	1607.09	1.25	91.97	7.73	66.24	3.16
HCM_4_2	Bulk kerogen	1362.29	1.60	1607.57	1.99	93.41	8.59	66.43	3.16
HCM_4_3_A	Bulk kerogen	1362.64	3.06	1606.57	1.67	95.86	4.19	66.52	3.36
HCM_5_1	Bulk kerogen	1363.41	3.73	1608.46	2.52	94.54	6.86	68.43	5.85
HCM_5_2	Bulk kerogen	1373.25	2.98	1604.68	1.23	104.21	5.16	68.25	2.55
HCM_5_3	Bulk kerogen	1375.09	4.49	1606.33	3.70	97.13	5.59	65.77	3.40
HCM_5_4	Bulk kerogen	1372.89	2.42	1605.38	2.49	100.82	3.63	66.84	1.47
HCM_8_1	Bulk kerogen	1368.72	2.94	1602.55	1.66	98.79	3.72	65.62	2.82
PO_2	Bulk kerogen	1373.44	3.08	1604.91	2.09	104.07	8.06	70.34	2.39
PO_3	Bulk kerogen	1372.61	4.50	1604.68	1.90	95.78	6.84	73.21	3.56
PO_23	Bulk kerogen	1360.74	7.12	1600.07	2.34	99.92	3.22	63.71	4.34

To be continued

Samples	Analysis	D-G	σ D-G	ID/IG	σ ID/IG	aD/aG	σ aD/aG	RA2	σ RA2	wD/wG	σ wD/wG
HCM_4_1	Bulk kerogen	246.89	4.01	0.40	0.04	0.66	0.19	0.66	0.10	1.39	0.14
HCM_4_2	Bulk kerogen	245.28	1.94	0.41	0.04	0.70	0.11	0.70	0.08	1.41	0.13
HCM_4_3_A	Bulk kerogen	243.93	3.60	0.43	0.05	0.76	0.16	0.76	0.07	1.45	0.11
HCM_5_1	Bulk kerogen	245.05	4.96	0.40	0.04	0.66	0.08	0.66	0.05	1.38	0.08
HCM_5_2	Bulk kerogen	231.42	2.34	0.45	0.07	0.84	0.20	0.84	0.06	1.53	0.10
HCM_5_3	Bulk kerogen	231.24	4.53	0.44	0.10	0.80	0.19	0.80	0.11	1.48	0.12
HCM_5_4	Bulk kerogen	232.50	3.85	0.49	0.07	0.96	0.18	0.96	0.09	1.51	0.06
HCM_8_1	Bulk kerogen	233.84	3.17	0.46	0.05	0.86	0.10	0.86	0.04	1.51	0.07
PO_2	Bulk kerogen	231.46	2.26	0.46	0.04	0.85	0.08	0.85	0.04	1.48	0.13
PO_3	Bulk kerogen	232.07	3.46	0.44	0.04	0.81	0.17	0.81	0.15	1.31	0.10
PO 23	Bulk kerogen	239.33	6.85	0.48	0.09	0.94	0.16	0.94	0.08	1.57	0.10

Table 8.4 Raman parameters for analyses on the bulk rock of samples HCM. Acronyms: D position – position of the D band; G position of the G band; FWHM D – full width at maximum height of the D band; FWHM G – full width at maximum height of the G band; D-G - distance between and G bands; ID/IG – intensity ratio of the D and G bands; aD/aG – area ratio between the D and G bands; RA1 - area (S+DI+D) / area (S+DI+D+Dr+GI+G); RA2 - area (S+DI+D) / area (Dr+GI+G); wD/wG full width at maximum height of the D and G bands; σ – standard deviation



Figure 8.15 Trends with increase Ro% of: (a) distance between D and G bands (b) FWHM of the G band for the bulk kerogen in samples HCM



Figure 8.16 Trends with increase Ro% of: (a) area ratio between D and G bands; (b) RA2 parameter and (c) width ratio between D and G ratio for the bulk kerogen in samples HCM

Among all parameters investigated, the D-G distance show the highest scatter among the data and the poorest correlation with vitrinite reflectance.

8.3.2 Micro-Raman on polished sections on different kinds of macerals

8.3.2.1 Micro-Raman on vitrinite in Carpathians fold and thrust belt (Age: Mesozoic and Cenozoic)

Organic matter from Carpathians fold and thrust belt show a high heterogeneity in macerals components (Fig. 8.17) as previously discuss in Chapter 4 . For this reason, we decided to identify the different maceral components by optical inspection on plugs of concentrated organic matter prepared according to ICCP standard. Macerals in the dispersed organic matter were identified in polished sections using the incident light microscope coupled with the Raman spectrometer, on the basis of their optical properties and morphology according to the ICCP classification and redefinition (Hower et al., 2009; Sýkorová et al., 2005). Figure 8.17 show an example of optical microphotograph of different macerals.

Parameters measured on vitrinite fragments selected through optical inspection are listed in Table 8.5. As shown in Figure 8.18, spectra show high fluorescence background and very similar features with increasing thermal



Figure 8.17 Microphotograph showing the appearance of inertinite and vitrinite fragments seen by the optical microscope connected with Raman spectrometer

width ratio with values ranging from 1.1 and 1.4 and $R^2 = 0.93$.

maturity (as indicated by the R_o % associated to the spectra). The only distinct trend appear to be related to a slight decrease in FWHM of peak G.

To better visualize spectral features and their variation with thermal maturity, also for this set of spectra we present in Fig 8.19 and 8.20 correlations between Raman indicators and vitrinite reflectance.

Correlations between D-G distance, FWHM of peak G and D/G area ratio versus R_0 % are poor (Fig. 8.19a,b and Fig. 8.20a)

Better trends are observed for RA2 parameter with values ranging from 0.6 to 0.7 and $R^2\, of$ 0.82 and D/G

These results leads to an important consideration on the importance of optical support. In fact a good correlation between Raman parameters and R_0 % is best assessed when comparing results from this set of samples with those presented on bulk kerogen of the same set of samples (Fig. 8.13 b-c and paragraph 8.3.1.2)

Samples	Maceral	D position	σ D position	G position	σ G position	FWHM D	σFWHMD	FWHM G	σ FWHM G
PL_93.1	vitrinite	1366.72	3.29	1608.31	1.12	92.92	8.69	78.22	3.19
PL_93.2	vitrinite	1363.69	5.52	1609.51	3.34	86.48	6.29	74.15	5.48
PL_95	vitrinite	1361.98	2.30	1610.48	1.64	86.44	9.18	69.61	3.21
PL_97	vitrinite	1364.66	5.09	1609.08	2.82	79.60	10.41	69.09	4.42
PL_101.1	vitrinite	1359.22	2.51	1601.44	2.25	95.64	9.47	75.07	4.55
PL_102	vitrnite	1356.96	3.63	1605.85	1.98	81.45	9.68	69.17	8.13
PL_103a	vitrinite	1356.53	4.60	1603.49	1.18	93.41	9.32	67.47	7.67

To be continued

Samples	Maceral	D-G	σ D-G	ID/IG	σ ID/IG	aD/aG	σ aD/aG	RA1	σ RA1	RA2	σ RA2	wD/wG	σ wD/wG
PL_93.1	vitrinite	241.28	3.76	0.58	0.04	0.70	0.10	0.40	0.03	0.67	0.09	1.19	0.13
PL_93.2	vitrinite	245.82	5.18	0.49	0.04	0.63	0.07	0.37	0.05	0.59	0.11	1.17	0.12
PL_95	vitrinite	248.50	3.27	0.51	0.03	0.61	0.09	0.38	0.04	0.63	0.10	1.24	0.13
PL_97	vitrinite	213.87	3.27	0.48	0.20	0.50	0.23	0.33	0.14	0.57	0.09	1.15	0.13
PL_101.1	vitrinite	242.22	3.17	0.55	0.05	0.83	0.19	0.41	0.03	0.69	0.09	1.27	0.15
PL_102	vitrnite	248.89	3.67	0.53	0.05	0.64	0.28	0.38	0.06	0.62	0.14	1.18	0.17
PL_103a	vitrinite	246.97	4.79	0.56	0.08	0.75	0.26	0.42	0.04	0.74	0.11	1.38	0.19

Table 8.5 Raman parameters for analyses on vitrinite fragments on samples PL. Acronyms: D position – position of the D band; G position of the G band; FWHM D – full width at maximum height of the G band; D-G - distance between and G bands; ID/IG – intensity ratio of the D and G bands; aD/aG – area ratio between the D and G bands; RA1 - area (S+DI+D) / area (S+DI+D+Dr+GI+G); RA2 - area (S+DI+D) / area (Dr+GI+G); wD/wG full width at maximum height of the D and G bands; σ – standard deviation



Figure 8.18 Raman spectra of samples at different thermal maturity for vitrinite fragments analysed in PL samples



Figure 8.19 Trends with increase Ro% of: (a) distance between D and G bands (b) FWHM of the G band for in vitrinite fragments analysed in PL samples



Figure 8.20 Trends with increase Ro% of: (a) area ratio between D and G bands; (b) RA2 parameter and (c) width ratio between D and G ratio for vitrinite fragments analysed in PL samples

8.3.2.2 Micro-Raman analyses on polished sections on Paleozoic graptolites from Holy Cross Mountains (age: Paleozoic)

Graptolites periderm is known to show strong optical anisotropy (Bertrand, 1990). In particular, according to, maximum and intermediate reflectance axes are found lying parallel to the sedimentary bedding. To evaluate the influence of anisotropy on both graptolite reflectance and Raman signals, we choose 7 samples collected in the Holy Cross Mountains (HCM 4.2. HCM 4.3A, HCM 4.3_B, HCM 4.4, HCM 4.5, HCM 5.2 and HCM 5.3) and we measured reflectance directly on graptolites lying parallel to the sedimentary bedding (R_{max} and R_{int}).

Micro-Raman analyses were performed on the same spots to verify the sensitivity of Raman parameters to anisotropy.

Figures 8.21 and 8.22 show graptolites fragments, parallel to the bedding, in both oil immersion (Fig. 8.21) for optical analyses and in air immersion (Fig. 8.22) for Raman analyses.



Figure 8.21 Microphotograph showing the appearance of graptolites fragments seen at 50X magnification at oil immersion with optical microscope



Figure 8.22 Microphotograph showing the appearance of graptolites fragments seen at 50X magnification at oil immersion with optical microscope connected to Raman spectrometer

Samples	Organoclast	D Position	σ D Position	G Position	σ G position	FWHM-D	σ FWHM-D	FWHM-G	σ FWHM-G
HCM_4_2	Graptolites	1365.10	3.35	1610.22	2.29	83.61	6.07	53.76	3.28
HCM_4_3_A	Graptolites	1365.51	0.52	1608.56	1.62	74.74	4.19	52.68	3.65
HCM_4_3_B	Graptolites	1364.11	0.84	1607.90	1.52	87.26	5.20	54.92	1.83
HCM_4_4	Graptolites	1363.29	1.54	1607.15	2.07	84.23	6.94	55.45	3.65
HCM_4_5	Graptolites	1361.36	1.77	1609.57	2.27	88.10	4.19	54.85	3.97
HCM_5_2	Graptolites	1362.32	1.39	1609.59	1.02	90.44	4.85	56.60	2.22
HCM_5_3	Graptolites	1362.35	1.93	1610.88	0.82	85.96	5.85	54.78	1.57

To be continued

Samples	Organoclast	D-G	σ D-G	ID/IG	σ ID/IG	aD/aG	σ aD/aG	RA1	σ RA1	RA2	σ RA2	wD/wG	σ wD/wG
HCM_4_2	Graptolites	245.12	2.99	0.73	0.08	1.30	0.17	0.48	0.05	0.93	0.09	1.56	0.10
HCM_4_3_A	Graptolites	243.06	1.53	0.68	0.03	1.09	0.11	0.46	0.01	0.85	0.05	1.42	0.11
HCM_4_3_B	Graptolites	243.80	1.79	0.77	0.04	1.67	0.19	0.50	0.03	1.01	0.13	1.59	0.08
HCM_4_4	Graptolites	243.86	2.04	0.74	0.04	1.37	0.18	0.48	0.03	0.93	0.11	1.52	0.10
HCM_4_5	Graptolites	248.21	3.49	0.74	0.05	1.18	0.19	0.43	0.04	0.77	0.13	1.61	0.07
HCM_5_2	Graptolites	247.26	1.71	0.89	0.02	1.33	0.10	0.43	0.01	0.77	0.04	1.60	0.08
HCM_5_3	Graptolites	248.53	2.13	0.77	0.02	1.24	0.09	0.46	0.02	0.85	0.06	1.57	0.09

Table 8.6 Raman parameters for analyses on vitrinite fragments on samples PL. Acronyms: D position – position of the D band; G position of the G band; FWHM D – full width at maximum height of the G band; D-G - distance between and G bands; ID/IG – intensity ratio of the D and G bands; aD/aG – area ratio between the D and G bands; RA1 - area (S+DI+D) / area (S+DI+D+Dr+GI+G); RA2 - area (S+DI+D) / area (Dr+GI+G); wD/wG full width at maximum height of the D and G bands; σ – standard deviation

As already discussed in Chapter 5, graptolite reflectance show higher values for these oriented samples compared to the measurements performed on randomly oriented specimen.

Raman spectra are also sensibly different with respect to those collected on bulk kerogen.

Fluorescence appears to be high even for the more mature samples ((about 1.0 R_0 % eq.), but the most anomalous feature is the very high FWHM of the G band (Table 8.6 and Fig. 8.23), compared to previous measurements. Thermal maturity parameters that show better correlation with average reflectance are the D/ G area ratio and the RA2, with high standard deviation for both Raman and optical indicators (Fig. 8.24 a-b). D/G area ratio ranges between 1 and 1.3 with an R² of 0.78, whereas RA2 ratio values vary between 0.81 and 1.09 and correlate against R_0 % eq with an R² of 0.83.



Figure 8.23 Six peaks curve fitting used to deconvolute Raman signal measured on graptolites



Figure 8.24 Trends with increase Ro% of: (a) D/G area ratio and (b) RA2 ratio for graptolites from HCM samples

8.3.3 Final correlation against Raman parameters and R_0 % or R_0 % equivalent

Results from our analyses show that measurements on bulk kerogen may be effective in some cases but may fail in others. For LIRA samples and in paleozoic HCM and PO samples, bulk kerogen measurements result in very high correlation of spectral indicator against thermal maturity while scarce correlation was found for PL samples. We attribute this different behaviour to the high heterogeneities in macerals composition of the organic matter for this latter case. For this case, measurements on single macerals, selected from optical inspection, were necessary.

Micro-analyses on single macerals provided excellent correlation between D/G area and width ratio and RA2 and R_0 % or R_0 % equivalent (Figs. 8.20-8.24)

Other parameters have proven to be less successfull in predicting thermal maturity.

D-G distance show good correlation with reflectance only in LIRA well, while when dealing with more heterogeneous material or different laser powers, results are highly scattered (Fig. 8.25). Also FWHM-G trends are scattered when considering all samples together (Fig 8.26 a). Best results are obtained when only considering with bulk kerogen (Fig. 8.26 b). In this case, the FWHM-G decreases according to a power equation of the form :

FWHM-G = $0.1702 * R_0\%$ eq.^{4.764} + 66.83* $R_0\%$ eq.^{-0.2732} (R² of 0.8146) Eq.1





Figure 8.25 Trends with increase Ro% of: D-G distance for all set of samples



Figure 8.26 Trends with increase Ro% of: (a) FWHM for all set of samples and (b)FHWM only for analyses perfomed on bulk kerogen

Even though D/G area ratio show good correlation against R_0 % for each single set of samples, parameterizations are different in each case, as it can be seen from Fig.8.27, and, if considered all samples as a whole, a general correlation cannot be found.

Best thermal indicators appear to be the RA2 and the D/G FWHM. When considering all dataset together, RA2 correlates very successfully with thermal maturity (Fig. 8.28) according to the following equation:

$$RA2 = 0.4415 + 0.4343 R_0\%$$
 eq. $(R^2 = 0.82)$ Eq. 2



Figure 8.27 Trends with increase Ro% of: D/G area ratio for all set of samples



Figure 8.28 Trends with increase Ro% of: RA2 ratio for all set of samples

In Fig 8.29 a D/G FWHM for all samples against reflectance is shown. Except for the graptolites samples, which present an anomalous high FWHM-G, the correlation is satisfactory. In Fig 29b, we have discarded the graptolite dataset and we parameterized D/G width at half height ratio versus R% according to the following linear equation:

D/G width =
$$0.89 + 0.6275 R_0\%$$
 eq. ($R^2 = 0.96$) Eq.3



Figure 8.29 Trends with increase Ro% of: (a) D/G width ratio for all set of samples and (b) D/G width ratio for all samples excluded analyses on graptolites

8.4 Discussions on Raman parameters variations

Vast literature exists on Raman spectroscopy applied to study ordered and disordered graphite, carbon materials(e.g. carbon nanotubes, graphene) (Castiglioni et al., 2004; Ferrari and Robertson, 2000; Ferrari and Robertson, 2004; Li et al., 2006; Reich and Thomsen, 2004). Many works also deal with the correlation of coals and OM Raman parameters with vitrinite reflectance (Guedes et al., 2010a; Jehlička et al., 2003; Kelemen and Fang, 2001; Li et al., 2006; Liu et al., 2012; Quirico et al., 2005; Wilkins et al., 2014; Zhou et al., 2014).

Despite the great amount of work on this subject, a general parameterization of the thermal maturity of organic matter through Raman indicators is still lacking, due to differences in experimental setup, fitting procedure and material analysed.

For instance in his review, Quirico et al. (2005) suggest that Raman parameters carried out using a four component fitting procedure LBWF (Lorentzian-Breit–Wigner–Fano) are insensitive to maturity for $R_o < 1\%$ as a result of the perturbation of Raman signal by the intense fluorescence background.

An ingenious solution to the fluorescence background problem was recently proposed by Wilkins et al. (2014) that provided an equation for calculating a vitrinite reflectance equivalent from Raman parameters obtained from the dip of the fluorescence for low thermal maturities $(0.4 < R_o\% < 1.2)$.

Even though this parameterization may be effective for specific set of samples, it cannot be of universal value as we observed that the fluorescence background is not only related to thermal maturity but also to maceral composition, as well as to other mineral matters that can be found in not-completely demineralized organic matter.

Moreover, even though the range of thermal maturity assessed in literature work is quite wide (from 1 to about 7-8 R_0 %), only one work (Wilkins et al., 2014) investigated in detail the low diagenetic stage (0.4-1.2 Ro%) and therefore a systematic analysis of samples at the immature and middle mature stages of hydrocarbon generation is missing.

Given this, we decided in this work to extend the applicability of Raman spectroscopy as thermal indicator by sistematically investigate the immature and middle mature stages of hydrocarbon generation.

We analyzed four case histories, two from Mesozoic and Cenozoic and two from Paleozoic successions performing Raman analyses on:

- 1. bulk kerogen obtained concentrating the organic matter using acid attack;
- 2. vitrinite fragments dispersed in the bulk kerogen;
- 3. dispersed Paleozoic organic matter in the bulk rock;
- 4. graptolites fragments dispersed in the bulk rock.

Using a six peaks deconvolution, we identified several parameters that show regular variations with increasing thermal maturity. However, most of them are sensible to differences in material analysed (macerals) and therefore, even if applicable to selected cases, are not valid for a general parameterization. Here below the parameters investigated are discusses.

The first parameter tested is the D-G distance.

The shift in position of these two bands is related to different processes that can occur at different graphitization/carbonization ranks.

As far as the G peak is concerned, according to Ferrari and Robertson (2000, 2004) shift in its position is generally controlled by: bond disorder, clustering of the sp^2 phases, presence of sp^2 on chains rather than rings and sp^2/sp^3 ratio (Fig. 8.30). Increasing bond disorder tends to shift the G peak toward lower wavenumbers while clustering of the sp^2 phases and the increase of sp^2 on chains with respect to rings tends to have the opposite offect of shifting the position toward higher wavenumber. Finally the increase in sp^3 content (sp^2/sp^3 ratio) can act both way as it yields both an increase in bond disorder and an increase of clustering and sp^2 on chain.



Figure 8.30 Factor affecting the intensity of the D band and the position of the G band. Dotted line indicate the indirect effect related to the increase of sp3 sites (redrawn after Ferrari and Robertson, 2000)

For this, in the Ferrari and Robertson work (2000) the variations of the G peak position can be described in three steps: a first shift upwards due to the clustering of the sp^2 phase passing from ordered graphite to nanocrystalline graphite, a subsequent shift toward lower wavenumbers due to the increase of bond disorder passing from nanocrystalline graphite to amorphous carbon and a final further upwards shift with the increase of the sp^3 phases passing from amorphous carbon to tetrahedral amorphous carbon as the sp^2 sites change gradually from rings to chain.

With the increase of P-T condition in metamorphism, Beyssac et al., (2002) Lahfid et al., (2010) observed a decrease in the G band position from about 1600 cm-1 to 1580 cm-1 the latter corresponding to the triperiodic graphite position.

However, working on coal from bituminous to anthracite ranks Kelemen and Fang (2001), Nestler et al. (2003), Guedes et al., (2010), Liu et al., (2012) and Quirico et al. (2005) did not observe any appreciable shift of the G band peak position whereas a shift of the position of the D band toward lower wavenumber was widely recognized. According to Ferrari Robertson, (2000), the D band shift toward lower wavenumbers is attributable to the increase of larger aromatic clusters passing from disordere to more ordered materials.

Our data indicate that the increase of the D-G distance with thermal maturity in the LIRA well is mainly driven by the shift of the D position toward lower wavenumbers (Fig. 8.6 a). No apparent trend is shown by the G position in Figure 8.6 b. This could be due to the specific amorphization range as described by Ferrari and Robertson (2000) where the effect of chains to rings variation is counteracted by the increase in structural ordering. Alternatively, the effect of decreasing in G position due to chains to rings transformation could be contrasted by larger aromatic rings.

Kelemen and Fang (2001) and Liu et al., (2012) consider the D-G distance one of the best parameter tor correlate against vitrinite reflectance in a broad range of maturities (ca $0.5 < R_0\% < 4$).

In our study however (Fig. 8.25) data do not show a uniform trend.

In particular we can notice that vitrinite samples PL and graptolites from HCM samples show higher values than LIRA samples.

We are not able to interpret this trend, we can only notice that PL samples show a slight shift of D and G peak position toward lower wavenumber (Table 8.5) which could be at least in part responsible for the different D-G distance. This shift could be itself correlated to an increase in the aromatic character of this set of samples compared to others.

Given the uncertainty in the spectral features and interpretation, we decided not to consider this indicator in our study.

8.4.2 Full Width at Half Maximum of the G band

According to Ferrari and Robertson (2000), the width of the G peak increases as a function of the bond-angle disorder at sp^2 sites (in aromatic rings and olefinic) and its values are maximum for high sp^3 sites content (aliphatic chains) for highly disordered materials. This parameter increases as a function of decreasing temperature or thermal maturity in both regional metamorphism (Beyssac et al., 2002; Lahfid et al., 2010) or increasing coal rank (Ferrari and Robertson, 2000; Guedes et al., 2010a; Jehlička et al., 2003; Kelemen and Fang, 2001; Marques et al., 2009; Quirico et al., 2005; Wilkins et al., 2014).

In agreement with literature studies, we also observe a decrease of FWHM-G as a function of increasing $R_0\%$, or thermal maturity. However, when considering the entire set of samples (Fig. 8.26 a), we observe some data scattering due mostly to measurements on vitrinite fragments, which show lower than normal values, and graptolite measurements, that show higher values for the same $R_0\%$ equivalent.

For this reason, a general correlation was applied only on bulk kerogen analyses (Fig. 8.26 b).

These differences could be due to the different compositions of graptolite and vitrinite versus bulk kerogen. In the case of graptolites, the high H content, expressed by their aliphatic nature (Briggs et al., 1995), would leads to a more disorder of sp^2 sites because of the presence of more chains (aliphatic and olefinic) with respect to aromatic rings. On the other hand, larger aromatic rings and smaller content of olefinic chains in vitrinite from PL could yield lower bond angle disorder at sp^2 sites and smaller FWHM for these samples.

It is interesting to note that our values of FWHM for bulk kerogen are very similar to those found by Guedes et al., 2010 and Quirico et al., 2005 for similar maturity ranges and only just slightly larger than those found for less metamorphosed samples measured by Jehlička et al., (2003) and Beyssac et al., (2002).

On the other hand our FWHM are sistematically smaller with respect to those reported by Kelemen and Fang, (2001) and Wilkins et al., (2014).

The discrepancly could be related to the different fitting procedure adopted by the authors compared to that in this study. In particular with respect to the authors that adopt a two bands fitting (a G band and a D band) for their samples. In our procedure (Fig. 8.4), the G band region was deconvoluted into two bands, the main G band and a Gl band at approximately 1550 wavelength, which well reproduces the asymmetric shape of the G region.

According to our interpretation of the spectra, with increasing thermal maturity we observe a shrinkage of the G region, attributable to both a decrease in the FWHM of the band G and to a decrease in intensity of Gl band (Fig. 8.31). This is in good agreement with the assignment of the Gl band to a , fingerprint of polyacetylene like structures (e.g. polyene chains. Rebelo et al., 2015 and Castiglioni et al., 2004) which are supposed to decrease as thermal maturiy increases. We believe that the two band fitting procedure adopted by Kelemen and Fang, 2001 and Wilkins et al., 2014. strongly overestimates the FWHM of band G in samples in our maturity range where the contribution of the Gl band is not neglectable.



Figure 8.31 Schematic evolution of the GI and the G bands

5.4.3 Area and width ratio parameters (D/G area, RA2, D/G width)

In general, the best calibrated thermal parameters are considered to be those based on D/G area and intensity ratio (ID/IG Tuinstra and Koening, 1970; R2 Beyssac et al., 2002; RA2 Lahfid et al., 2010).

The first study that parameterized Raman spectra based on D and G area and intensity ratios was performed by Tuinstra and Koening (1976, TK relation). The authors found an inverse correlation between the D-G intensity ratio and in-plane graphite crystallite size (L).

In a range of paleotemperatures between 330-650°C Beyssac et al., (2002), found a similar decrease of the D/G intensity (R1 ratio) and of the R2 ratio (D1/ (G + D1 + D2) peak area ratio , see Chapter 2) with increasing temperature. This decrease was attributed to the progressive decrease of the D band with increasing graphitization ranks.

Ferrari and Robertson (2000) also observed an increase in the D/G intensity ratio (TK relation) passing from graphite to nanocrystalline graphite. However, the same relationship did not hold true when dealing with amorphous carbon. The authors stressed that while the intensity ratio behaves similarly to the D/G area ratio for disordered graphite, due to similar D and G width, this is no longer valid for amorphous carbon where the D width shows changes related to the disorder in the structure.

In the low maturity range, as suggested by Ferrari and Robertson (2000), the area ratio should be a more reliable parameter as it takes into account both intensity and width variations.

For instance, at low temperatures, many authors (Guedes et al., 2010a; Jehlička et al., 2003; Liu et al., 2012; Kelemen and Fang, 2001; Marques et al., 2009; Quirico et al., 2005; Sadezky et al., 2005) show a linear increase of the D/G area ratio and parameters related to this ratio (RA1 and RA2, Lahfid et al., 2010) with increasing thermal maturity and/or temperature (between 220-330°C for Lahfid et al., 2010).

The increase in the D/G area ratio is mainly related to the thinning of the G band, which has been interpreted as due to the clustering of the aromatic rings (sp^2 phases, Ferrari and Robertson., 2004, Li et al., 2007). In our set of samples, we observed the following:

- 1) ID/IG ratio does not present any correlation with depth in LIRA well samples (Fig. 8a) or with thermal maturity in other samples.
- 2) D/G area ratio and RA1 and RA2 both increase linearly with thermal maturity in all samples investigated.

These trends area significantly differents from those found by Beyssac et al., (2002) or Lahfid et al., (2010).

To try to understand the process of carbonification in this thermal maturity range and to isolate the contribution of each single band to the RA1and RA2 variation in our set of samples we normalized each band to the G band intensity for samples in the LIRA well (Fig. 32).



Figura 8.32 Ratio of G intensity against : (a) S band area; (b) DI band area; (c) D band area and (d) Dr band area for all sample (not average at each depth) of the LIRA well

In Figure 8.32 the ratio between the G band intensity and the area of the D,S,Dl and Dr bands against an increasing maturation pattern on the x axes is presented. The Figure 8.32 outlines that no great variations are observed in the IG/S_{area} and in the IG/Dl_{area} ratio while a decrease in the IG/D_{area} (e.g. D area band incraese) and an increase of the IG/Dr_{area} ratio (e.g. Dr band area decrease) are clearly observed.

Thus we can conclude that the increase in RA2 ratio can be attributed to the decrease in width and intensity of band G and Gl, already discussed in the previous paragraphs and to the decrease of the satellite band Dr related by different authors to small aromatic (Rebelo et al., 2015) accompanied by a corresponding increase in FWHM of band D (IG/D_{area} decrease).

This decrease, should be related to a progressive loss of hydrogen atoms, loss of chains and corresponding increase in aromatic rings with more than 6-membered (increase in D band width and IG/D_{area}) (Ferrari and Robertson, 2015). In additon, the increase of the area of the D band has been found by Ferrari and Robertson (2000) and Rebelo et al., (2015) to increase with the order.

The general trend of increasing D/G area ratio is thus similar to what observed by Lahfid et al (2010), but the fitting parameters of RA2 equations are not comparable because the contribution of the S and Dl band to the carbonification process appear to be different.

S and Dl band do not show variation both in width and intensity in this thermal maturity range and this is in clear contrast with their behaviour at higher temperatures on the shoulder of the D band (Lahfid et al., 2010).

The reason for these behaviour is not clear. Rebelo et al. (2015) assign these bands to the same vibrational modes of Gl and Dr bands and to the same structural units (small aromatic or polyene domains), so we would expect similar behaviour for these bands at increasing temperature. In here we can only observe a decoupling between S and Gl and Dl and Dr bands and therefore we infer that their assignment must be more complex that previously envisaged. It is possible that those bands are related to similar structural units but slightly different chemical composition(maybe O and N-rich small aromatic rings), which impart a different thermal stability, but obviously more studies are needed to fully address this issue.

In general, RA2 and D/G width represents the paramteres the best fit the entire set of samples.

In particular, RA2 against thermal maturity plotted in Figure 8.28 indicates:

 values calculated on vitrinite are slightly higher with respect to the amorphous rich organic matter of the LIRA well for same thermal maturities; 2) Values calculated on bulk kerogen, dispersed fragments in bulk rock and on graptolite are similar to those calculated on the amorphous rich organic matter of the LIRA well for same thermal maturities, but their trend show slightly different slopes.

Taking into account these differences, a succesfull parameterizations have therefore been determined, according to the following linear equation:

 $RA2 = 0.4415 + 0.4343R_0\%$ ($R^2 = 0.82$, n° of measures = 58) Eq. 4

The D/G width ratio indicates, on the other hand, a more precise correlation not considering values from graptolites, due to their anomalous G band width. The parameterization is described by the following linear equation:

- D/G width ration = $0.89 + 0.6275 R_0\%$ (R² = 0.96, n° of measures = 51) Eq.5

8.5 Conclusion

In this work, we performed Raman spectroscopy measurements of a wide dataset of samples in order to investigate the thermal maturity pertaining to the diagenetic stages.

We considered a wide range of starting materials differing in typology and origin of organic matter. In order to better calibrate and evaluate the applicability and accuracy of Raman spectroscopy to the study of organic matter, different preparation techniques were also explored.

The following materials were analysed:

- Cenozoic shales with interfingered sandstones from cuttings collected from a 5,000 meters depth well drilled in the offshore of Angola (LIRA). In this case, bulk kerogen has been extracted with acid attack (HCl and HF). Kerogen is mainly AOM rich except for the upper part of the well and thermal maturity increases regularly from about 0.3 R_o% at the top to about 1.5 R_o% at the bottom;
- 2) Mesozoic and Cenozoic black shales and siltstone in the Carpathians fold and thrust belt. In this case, we analysed bulk kerogen extracted with acid attack (HCl and HF) and vitrinite fragments dispersed in the bulk kerogen. Kerogen from this samples is composed by many classes of macerals and its thermal maturity ranges from 0.41 to 0.6 R_0 %;
- 3) Paleozoic shales and siltstones from the Holy Cross Mountains. As for the Cenozoic samples, bulk kerogen extracted with acid attack (HCl and HF) was analysed. Moreover, we also analysed single graptolites speciments dispersed in the bulk rock. Kerogen is composed by Paleozoic marine organoclasts and its thermal maturity ranges from 0.81 to 1.09 R_0 %;
- Paleozoic successions in the Podolia region. For this set of samples, we analysed kerogen dispersed in the bulk rock. Kerogen is composed by Paleozoic marine organoclasts. The thermal maturity of the three samples analysed are 0.62, 0.75 and 0.77 R_o%;

Almost all samples are characterized by an intense fluorescence background, increasing with decreasing thermal maturity.

Due to this, before deconvolution of the spectra, we performed a background subtraction procedure based on a third order polynomian curve for all samples. The baseline subtracted spectrum was then deconvoluted according to a six-peak fitting procedure, as this procedure best approximated the spectra (Guedes et al., 2010, 2012). Results of this fitting were expressed in terms of Raman parameters against thermal maturity, as shown in chapters 3,4,5 and 6 using a mutimethods approach.

For the purpose of comparison, thermal maturities were always expressed in vitrinite reflectance equivalent $(R_0\%)$.

For the first case history (LIRA), the following parameters show the best correlation against the increase of thermal maturity: 1) D-G band distance; 2) FWHM of the G band; 3) D/G area ratio ; 4) RA2 ratio (calculated as S+Dl+SD/Dr+Gl+G band ratio) and 5) D/G width ratio.

The LIRA samples show the widest range of thermal maturity going from 0.3 to 1.5 Ro%.

The other case histories show some different correlations.

Parameters related to peak position and peak width are not as sensible indicators of maturation as in the LIRA samples and this is probably due to the narrower range of thermal maturities. However, parameters based on integration of multiple spectral features (RA2 area ratio and D/G width ratio) are still valuable and they can be successfully utilized even for this critical low range of maturities.

We suggest also that, in the presence of macerals from the inertinites group, optical inspection of the sample prior to measurements needs to be performed. This allows to discriminate among different macerals and isolate the contribution of the vitrinite to the Raman signal, which is the most appropriate component to track thermal changes in the organic matter.

Graptolites samples show a different Raman spectra characterized by anomalous width of the G band, which renders D/G width ratio of little use. For this organoclasts RA2 parameter rather than the D/G width ratio can provide better thermal maturity indications.

Starting from these observations, two successful parameterizations have been determined, according to the following equations:

-	$RA2 = 0.4415 + 0.4343R_0\%;$		Eq. 4
-	D/G width ratio = $0.89 + 0.6275 R_0\%$.	Eq. 5	

These two parameterizations can be used for a wide range of thermal maturity, from 0.3 to 1.5 Ro%.

We demonstrated for the first time that at very low diagenetic stages, between immature and mid mature stages of hydrocarbon generation, changes in Raman spectra of undifferentiated dispersed organic matter (excluded macerals of the inertinite group) show quantifiable changes in response to thermal maturation and can be successfully used to parameterize thermal evolution.

It is very interesting to note that the evolution of organic matter varies depending on the maturity stage considered and this is well reflected in the Raman spectra. In fact, as it can be noted in Fig. 8.33, the changes in Raman features going from anthracite to graphite ranks (higher grade metamorphic rocks (i.e. typically greenschist and above; e.g. Wopenka and Pasteris, 1993; Beyssac et al., 2002) are sensibly different from the

change in the features observed in the low volatile bituminous coal to anthracite as well as from those pertaining to this study going from subituminous coals to medium volatile bituminous coals, in the diagenetic stage.

No baseline subtraction

With baseline subtraction



Figure 8.33 The figure shown the evolution of the Raman spectra from high metamorphic stages to the immature stage of HC generation. Raman spectra for temperatures higher than 170°C are redrawn from Lahfid et al., 2010 and Beyssac et al., 2002. Spectra are not in scale on the Y axes. Conversion from vitrinite reflectance in temperature for samples from this work were made only to compared spectra from different works using Barker and Pawlewicz's equation (1994)

In fact, whereas the changes in the Raman spectra for the metamorphic stage are mostly related to the variation of the lattice structure due to the progressive graphitization of the structure, for the low metamorphism and in the immature and mid-mature stages of HC generation, changes can be better described with a molecular

approach (Castiglioni et al., 2004) where a great influence is given by the presence of smaller compounds (e.g. oligomer, linear polyene chains) rather than only big aromatic clusters or only invoking lattice defects.

As far as the band assignment is regarded, we found that the behaviour of the G band agree with the interpretation of most of the authors. The decrease of the Gl band with maturity increase is also consistent with the attribution to polyene chains made by Castiglioni et al., 2004; Rebelo et al., 2015; Tommasini et al., 2004. The FWHM increase of the band D can be interpreted as due to an increae in the size of the aromatic rings with more than six benzene rings due to loss of polyene chains (Gl bands) and smaller aromatic rings (Dl), in agreement with the interpretation of Rebelo et al., (2015) and Ferrari and Robertson (2000). Dr and S bands seem to be largely unaffected by thermal changes in the range of thermal maturities investigated in our study. This behaviour is markedly different from what observed in larger maturity ranges and the reason for this is not immediatly clear.

We can conclude remarking that parameterization of the Raman spectra is extremely temperature sensitive and that for the first time in this study we were able to accurately predict maturity and temperature variation in the low diagenetic stage and our parameterization is perfectly appropriate in the maturity range varying from the immature to the mature stage of hydrocarbon generation.

Chapter 9

Conclusions

Since the eighties of the last century, the introduction -at industrial scale- of thermal modelling in workflows for the assessment of HC prospects have intensely improved exploration efficiency (Katz, 1990). Since then 1 to 3 D modelling packages have been quickly developing, integrating algorithms to properly model kerogen kinetics (based on the basic concepts developed by Tissot, 1969, Tissot & Espitalie, 1975, Lopatin 1971, Waples 1980, Sweeney & Burnham 1990), temperatures and paleo-temperatures (based on Mc Kenzie's -1978-, Sclater and Christie's -1980- and many other authors' work) and subsidence in basins (strarting from the rationales by Watts & Ryan, 1976; Van Hinte 1978).

Great attention has been payed in integrating also the preservation potential of the basins together with depositional history implementing models with low T thermochronological data (Andreucci et al. 2015). In these models, the reliability of quantitative evaluation of quality and quantity of generated and expelled hydrocarbons is strictly related to the robustness of thermal maturity constraints used to calibrate them (Roure et al., 1995; 2010). Despite great effort has been devoted to develop sophisticated numerical modelling tools, the most popular indicator of thermal evolution of kerogen is still vitrinite reflectance. This parameters owes its success to its easy dependence from temperature and time evolution of kerogen (see Lopatin-Waples model, Lopatin, 1971 and Waples 1980) and sensitiveness in the temperature range in which catagenesis and methagenesis of kerogen occur. Thus vitrinite reflectance data are generally abundant even in databases of HC prospects explored since the fifties of the last century. The method of measurement of vitrinite reflectance is even older and dates back to the XVIII century with the onset of industrial revolution and development of coal industry. Nevertheless despite its high reliability and widespread application there are some limitations concerning both the technique and the fields of applications.

The main aim of this thesis has been to develop and test a multimethod approach to assess thermal maturity of sedimentary successions in order to correctly calibrate thermal models of sedimentary basins even when vitrinite reflectance is not available or reliable for a series of reasons. In detail the need to develop a multimethod approach is born from the impossibility of using the most reliable tool for thermal maturity assessment in many case histories where vitrinite is absent, scarce or affected by retardation/suppression phenomena. Furthermore indicators of maximum burial coming from the study of the inorganic fraction of sediments have generally been indicated as less reliable than those derived from kerogen maturity studies. Despite the sensitiveness and reliability of inorganic indicators are generally lower than that of vitrinite reflectance, for example the study of clay minerals reactions can guarantee -together with kerogen study- a denser and cheap control on reconstruction of paleo-geothermal gradients (Hillier et al. 1995; Aldega et al.,

2010; Caricchi et al. 2014). To do this we analysed strongly differing stratigraphic successions both Mesozoic-Cenozoic and Paleozoic in age derived from four different areas representative of sedimentary basins developed in different geodynamic setting (passive margin, fold-and-thrust belt, foredeep) eventually involved in later deformations.

The first area is the offshore Lower Congo Basin (Chapter 3). Here samples were collected from cuttings from a five kilometres deep Oligocene to Miocene marine siliciclastic drilled succession along the passive margin of Angola. It hosts the well-known Malembo formation, containing a highly potential source rock.

The second area is part of the Outer Carpathians fold-and-thrust belt in Ukraine at the border with Romania (Chapter 4). Here samples come from outcrops of the marine marly and arenaceous Lower Cretaceous to Miocene successions, locally rich of organic matter and hosting well known source rocks (Menilite beds and Shypot /Spas Formations).

The third area is the Holy Cross Mountains in Poland, where Paleozoic samples come from Cambrian to Devonian outcrops (Chapter 5). This area is particularly interesting because here the lithotypes that crop out are equivalent in age to those recently drilled further to the east along the so called Golden belt.

The forth area is located in the present-day Carpathian foreland in the Podolia region (Ukraine) in which crop out an Ordovician to Devonian marine succession (Chapter 6). Each of these successions present some of the problems above mentioned that can be encountered when dealing with basin analyses studies focalised on thermal maturity assessment (e.g., absence vitrinite in the dispersed organic fraction (OM), the scarce reliability of its reflectance values or even the almost totally absence of organic matter in sediments). Each of these problems and the way in which we tried to solve them are discussed in this paragraph. In addition, results were summarized showing their implication both for petroleum exploration and the geological evolution of the sedimentary basins (Fig. 9.1).

In the well drilled in the offshore Angola(Chapter 3), the turbiditic successions encountered in the phases of drilling represent the sediments deposited by the fan-delta system of the Congo river from the Oligocene to Upper Miocene times. Here the first problem is represented by the paucity of organic matter of terrestrial origin (e.g. vitrinite) that has been recorded only in the upper portion of the well. In addition there is a misfit between present day geothermal gradient and the paleo-geothermal gradient calculated on the base of measured vitrinite reflectance. Thus vitrinite reflectance retardation phenomena, probably due to the development of overpressures during the deposition of the fan-delta complex or to high H content in kerogen, have been invoked to explain the scarce fitting between modelled and measured vitrinite reflectance. In order to solve such a problem, we coupled analyses on the organic fraction with mineralogical analyses on the < 2 μ m grain size fraction of sediments. In particular we adopted an inorganic pressure independent thermal maturity indicator such as the Illite content in mixed layers Illite-Smectite (%I in I-S). %I in I-S shows a uniform trend along the well indicating the onset of hydrocarbon (HC) generation at shallower depths with respect to those shown by vitrinite reflectance distribution. Based on this evidences

we modelled the thermal evolution of the stratigraphic section using the kinetic equation for the smectite illitization

process proposed by rather than the classical Sweeney and Burnham (1990) kinetic equation adopted for kerogen.

A further investigation on this set of samples was performed through Fourier Transform Infrared Spectroscopy (FT-IR) analyses on the organic matter collected at different depths in the angolan well (Chapter 7).With the use of this techniques it was possible to directly analyse the evolution of the entire organic facies (directly related to the HC production) overcoming the absence of vitrinite in the lower part of the well. FT-IR results indicate that OM, surprisingly show a uniform evolution with depth and any retardation phenomena is not recorded by FT-IR parameters. In addition, comparing our results derived from the ratio of the integrated area bands related to both aromatic and aliphatic absorption derived from the FT-IR spectra, with values from previous works (Chen et al., 2012; Ganz et al., 1990; Ibarra et al., 1996; Iglesias et al., 1995; Lis et al., 2005; Petersen et al., 2008) we defined the thermal maturity interval developed in the well section. It corresponds to equivalent vitrinite reflectance between about 0.3 and 1.5 R_o%. This result further confirms the conclusions carried out in Chapter 3 on the entire successions on the base of vitrinite reflectance and clay minerals data, but focusing on the evolution of organic facies by means of FT-IR. These results are the base for the correlation work described in Chapter 8 on Raman spectroscopy analysis.

The FT-IR contribution allowed us to correctly define the various stages of HC generation (e.g. oil or oil and gas generation) that were scarcely defined before this thesis only on the base of vitrinite reflectance. In addition a significant increase in the sedimentation rate during the Lower Miocene occurs in the Lower Congo Basin was evidenced in the reconstruction reported in Chapter 3.

In the outer sector of the Carpathians fold and thrust belt (Chapter 4), the studied samples come from successions deposited in a deep to near shore environments interbedded by three major anoxic events that are in age from the Lower Cretaceous to the Lower Miocene times. The successions were then thrusted starting from Upper Miocene along major decollements represented by the black shales, in the compressional phases of the Alpine orogenesis (Roure et al., 1993). Different stratigraphic successions were sampled in three distinct tectonic units that from the West to the East are the Chornogora, the Skiba and the Boryslav-Pokuttya units.

The organic matter found in these facies show a very complex composition being composed by several macerals components. These macerals that pertain to the inertinite group generally show very high reflectance values than those of vitrinite fragments. Furthermore, bitumen or macerals of the bituminite group have been detected with reflectance values slightly lower than vitrinite.

			Thermal maturity	Resul	ts
	Areas	Problems	indicators	Implications in HC exploration	Geological implications
Lower Congo Basin		 Scarcity of OM of terrestrial origin (e.g. vitrinite) Retardation phenomena of vitrinite refletance 	- % I in I-S mixed layers - Thermal model using smectite illitization kinetic - FTIR spetroscopy	- Correct assesment of HC, in particular gas generation	- Overpressure phenomena due to high sedimentation rate form Oligocene times
Outer Carpathians	CARNONIAN BASIN	- Hetereogeneity of the OM composition	- Organic petrography - Tmax from Pyrolysis Rock Eval	 Assessment of the source rocks in the area Maturity of the source rocks assess with thermal modellign 	- Differences in the amount of tectonic loading for the different tectoni units
Holy Cross Mountains		- Absence of vitrinite	 Organic petrography on paleozoic organoclasts % I in I-S mixed layers Tmax from Pyrolysis Rock Eval Raman spectroscopy on Cambrian OM 	 Assessment of the source rocks in the area Time of HC generation assess with thermal modellign 	- Similar thermal evolution since Cambrian for the two tectonic blocks
Podolia	Provide the state of the state	- Scarcity of organic matter	- Organic petrography - % I in I-S mixed layers	- No source rocks were found in the area	 Asimmetric basin with maximum depth to the west of the EEC Far-field influence of the Cimmerian orogenesis on the Triassic uplift

Figure 9.1 The figure summarized the problems encountered for each areas in the assessments of thermal maturity, the methodologies used to overcome these problems and the implication in HC exploration and the geology of each areas carried out from our results

In this case, carefully performed optical analyses were necessary to discriminate vitrinite from similar macerals. Vitrinite reflectance data were also successfully compared with Tmax values obtained from Pyrolysis Rock Eval.. R_0 % and Tmax data were also used to calibrate the maturation pattern in thermal models. Models were performed creating two pseudo-wells according to Nöth et al.,(2001) and Oncken (1982) for the Chornogora and the Skiba unit, respectively. Not enough data were present in the Boryslav-Pokuttya unit to performed a proper thermal model.

The heat-flow (HF) value adopted in these models was constant and similar to the present-day one, in agreement with many authors' choice (Andreucci et al., 2015; Castelluccio et al., 2015; Koltun et al., 1998; Kutas, 1977; Pospil, 2006).

Thermal modelling, coupled with Pyrolysis Rock Eval analyses, allowed us to define the most prospective stratigraphic intervals for HC generation. These are the black shales of the Shypot formation in the Chornogora unit and the black shales of the Melinite formation in the Skiba Unit. These source rocks are mostly gas prone. Thermal modelling indicate that the Shypot formation entered the oil window at the end of Cretaceous times (Fig. 15 Chapter 4), whereas only the lower part of the Melinite beds reached thermal maturity level for oil generation at the boundary between Oligocene and Miocene times (Fig. 4.17, Chapter 4).

Furthermore, our models indicate that the thermal maturity reached by Cretaceous successions that crop out in the Chornogora unit and by Oligocene-Miocene successions that crop out in the Skiba unit don't always acquired their thermal signature in the original sedimentay basin, as assessed by Koltun et al. (1998) and Kotarba and Koltun (2006).

In detail, the Chornogora unit underwent only sedimentary burial, while in the model of the Skiba unit 2 km of additional burial beyond original sedimenray thicknesses are necessary. We suggest that the additional burial was due to a tectonic loading, eroded during the exhum ation phase that was set at 5 My, according to the recent work of Andreucci et al. (2015).

The Holy Cross Mountains (Chapter 5) represents one of the few structures in Poland where the sedimentary successions that developed on the Baltica margin from Lower to Upper Paleozoic times crop out. This area is composed by two tectonic blocks, called Kielce block to the south and Łysogory blocks to the north, divided by a major fault called Holy Cross Fault (HCF). In these Lower Paleozoic successions vitrinite fragments are totally absent in the dispersed organic matter. Nevertheless organoclasts other than vitrinite were used in this thesis, for assessing thermal maturity by organic petrography (Cole, 1994; Goodarzi, 1984; Goodarzi and Norford, 1987, 1989). According to several authors (Bertrand, 1990; Bertrand and Malo, 2012; Bustin et al., 1989; Goodarzi and Norford, 1987; Suchý et al., 2002) a correlation between the reflectance of chitinozoas, scolecodont and graptolites can be found. On the HCM samples, we focused optical analyses on vitrinite-like and graptolite fragments dispersed in the whole organic facies. We coupled thermal maturity indicators from optical analyses with those carried out from mineralogical analyses (e.g., I% in I-S) and from Pyrolysis Rock Eval (Tmax) and Raman spectroscopy for the organic matter present in Cambrian rocks . FT-IR

analyses were not performed on this set of samples, because most of the samples are in a thermal maturity ranges higher than 0.7-0.8 R_0 % in which a low band absorption in the infrared spectra can make difficult to obtain reliable FT-IR parameters and would have not improved significantly the thermal maturity dataset (Chen et al., 2012).

All thermal maturity indicators in the HCM indicate significant differences in thermal maturity between the two blocks. Our results agree with those of previous works that found a similar pattern of thermal maturity on the base on thermal alteration index of achritarcs (Szczepanik, 1997, 2001), conodont alteration index (Belka, 1990; Narkiewicz, 2002) for samples from Lower Paleozoic or vitritnite reflectance (Dadlez, 2001; Marynowski et al., 2001; Poprawa et al., 2005) for samples younger than Silurian.

In addition, Pyrolysis Rock Eval results were produced on the original set of our samples and used to characterized the HC potential of the rocks in the area. Our results indicate that only some Silurian, Devonian intervals in the Kielce region and the Jurassic interval sampled in the northern block could act as fair to good source rocks.

In order to reconstruct the thermal evolution of this area, we used indicators carried out from optical analyses to calibrate the maturity curve of two pesudo-wells. The pseudo-wells were located were we have more data (Bodzentyn syncline for the Łysogorybloc and Bardo syncline for the Kielce block). In addition we also used thermal indicators measured for the first time in this work or collected from previous works on the overlying Mesozoic succession.

We fitted our thermal indicators using different burial/thermal histories for the two blocks (Chapter 4). Two main phases of exhumation were recognized in both blocks: the first predating the Permian unconformity as a result of Variscan orogeny and the second, corresponding to the Laramide phase of deformation at bout 50 My, fully constrained by termochronological data. Best fitting thermal models are based on a generally constant heat flow with a thermal peak at Carbonifeours.times in agreement with the thermal models performed in nearby areas by various authors (Botor et al., 2002; Carrozzo et al., 2012).

In the model, we focused our attention on the thermal evolution of the Lower Silurian graptolite-rich shales, that are one of the main targets for gas exploration in northern Europe . Our models indicate that a main burial occurred in the Lysogory region during Paleozoic in the Kielce region and during Mesozoic times. This means that the Silurian interval during Paleozoic times entered in the gas window in the northern block and only in the oil window in the Kielce region. In this last region, higher temperatures suitable for gas generation were reached only after a further phase of burial during Mesozoic time.

Furthermore our reconstruction suggests a similar thermal evolution for the two blocks where the main differences consist in thickness variations. This is in contrast with paleogeographical reconstruction proposed by many authors that interpret the two blocks as distinct terranei that merged only since Upper Paleozoic times (Belka, 1990; Dadlez, 2001; Narkiewicz and Narkiewicz, 2010; Narkiewicz, 2002).
The last case history is devoted to study of the Podolia region (Ukraine) that is, together with the Holy Cross Mts one of the few areas in northern Europe where the Paleozoic sedimentary successions extensively crop out (Chapter 6). Samples analysed and presented in Chapter 6 were collected along the Dniestr River

The Paleozoic and the unconformably lying Mesozoic and Neogene successions exposed in the area represent part of an epicontinental basin system extended along the Western margin of the Eastern European Craton. Samples collected in the area offer a good example of how, even in a case of scarceness of organic matter dispeserd in sediments, we can obtain thermal maturity indicators to model thermal history of Paleozoic rocks. In fact, due to scarcity in organic matter, neither Tmax from Pyrolysis Rock Eval nor FT-IR analyses on bulk kerogen could be performed and organic petrography provided weak contraints. We replaced organic indicators mainly with mineralogical and thermochronological ones.

We produced a new dataset of thermal maturity indicators based on the I% in I-S mixed layers , from mineralogical analyses of the $<2\mu$ m grain fraction size. Our results indicated a high thermal maturity (e.g., late diagenetic zone) for different Paleozoic stratigraphic intervals collected from the east to the west along the Dniestr river. Taking into account that the Mesozoic regional unconformity covers progressively younger and thicker Paleozoic successions moving from the EEC to the West, we could reconstruct the burial history of the Podolia basin by means of three dinstinct 1-Dmodels. We assumed in thermal modelling that changes in heat flow occurred similarly to the evolution defined in nearby areas (e.g., Lublin basin, according to Botor, 2002, Poprawa et al., 2005 and Carrozzo et al., 2012).

Our results outlined that the Podolia Paleozoic basin is an asymmetric basin where sediments accommodation space got thinner moving from the West toward the European Craton and was much higher than that estimable only on the base of field observation. From an applicative point of view the Ordovician to Devonian outcropping lythotypes do not know any potential for HC generation, despite they are located along the south-eastern continuation of the so called Golden Belt in Poland.

Nevertheless, our models indicate important implication for the tectonic evolution of the area, in particular due to the anomalous ages of exhumation found. In particular thermocronological data were useful to costrain a Mesozoic phase of exhumation in the performed models. The recognition of an exhumation in the Late Triassic-Early Jurassic is surprising as it is not related either to the Variscan orAlpine orogenesis. On the other hand we suggest that an important far-field stress derived from the Cimmerian orogenesis whose collisional front was located some hundreds of km away from the Podolia region could be the origin of the major uplift that led the Paleozoic successions to exhume in the Mezozoic.

As seen in the previous paragraph and in Chapters 3, 4, 5 and 6, thermal maturity of analysed samples has been carefully assessed by the cross correlation between different thermal maturity indicators and their modelling.

Based on this robust framework of thermal maturity and thermal evolution of the studied successions, we analysed organic matter dispersed in sediments usign Raman spectroscopy. This further work allowed us in

order to correlate indicators carried outwith this methodology in a thermal maturity range relative to diagenesis (Chapter 8).

In detail we analysed: 33 samples from Angola offshore, 7 samples from Carpathians, 8 samples for the Holy Cross Mts and 3 samples the Podolia region. We were not able to performed Raman analyses on the entire dataset because of the scarcity of OM in some samples. We choose samples on which we could compare Raman indicators with R_0 % or R_0 % eq.

Raman investigation on kerogen was choosen to be tested as a new methods for thermal maturity assessment because:

- it is not time-consuming;
- can be performed on bulk kerogen or directly on plugs prepared for organic petrography;
- provides an insight on the short-order range chemical processes and thus can provide a quantitative assessment on the molecular changes that can occur during thermal maturation of kerogen

Our results demonstrated, for the first time, that even at very low diagenetic stages, between the immature and mid mature stages of hydrocarbon generation, Raman spectra of undifferentiated dispersed organic matter, show quantifiable changes in response to thermal maturation and can be successfully used to parameterize thermal evolution of kerogen and hosting sedimentary successions.

In particular five quantitative parameters (D-G distance, FWHM-G, D/G area ratio, RA2 and D/G width ratio) vary regularly with increasing thermal maturity, whereas that D-G distance, FWHM-G show significant changes with respect to different materials (e.g. vitrinite, bulk kerogen, graptolites).

Moreover two successful parameterizations have been determined, according to the following equations:

$$- RA2 = 0.4415 + 0.4343R_0\%; Eq. 4$$

Eq. 5

- D/G width ratio = $0.89 + 0.6275 R_0\%$.

Eq.4 realates to all samples analysed in this work, while Eq.5 does not take into account data on graptolites because of their anomalous FWHM-G, indicating that this parametr strongly depend on the kind of material. On the nature of this last feature further investigation are needed. What is very important to note is that analysing disordered cabon materials (kerogen at very low thermal maturity) and comparing these results with Raman spectra at higher thermal maturity, changes in the Raman spectra have different meanings at different stages of maturation.

For the metamorphic stage, changes in spectra are mostly related to the variation of the lattice structure due to the progressive graphitization of the carbon structure with increasing metamorphic stage, while for the low metamorphism and in the immature and mid-mature stages of HC generation, changes can be better described with a molecular approach (Castiglioni et al., 2004) where a great influence is given by the presence of smaller compounds (e.g. oligomer, linear polyene chains) rather than only big aromatic clusters or only invoking lattice defects (Fig. 9.2).





lower maturities is related to the high H content. An incraese of the D-G distance is observed related to the shift of the D band t lower wavenumbers due to rise of bigger aromatic clusters. In relatio to the lower content of sp³ sites content, FWHM-G increase with increasing temperature. At low maturity ranks spectra is characterize by the presence of bands related to the presence of small aromatic rings (Dr and DI) or polyacetilene-like structures (S and GI).

- ID/IG : no trend

- RA2 : increase

- D/G width ratio : increase

Figure 9.2 The figure shown the evolution of the Raman spectra from high metamorphic stages to the immature stage of HC generation. Raman spectra for temperatures higher than 170°C are redrawn from Lahfid et al., 2010 and Beyssac et al., 2002. Conversion from vitrinite reflectance in temperature for samples from this work were made using Barker and Pawlewicz's equation (1994)

In conclusion, this work shed new light in the research field of application of Raman spectroscopy in the study of carbonaceous materials, whose application has been quickly growing in the last years.

Thus, our parametrizations cannot be considered conclusive but a solid base that opens new horizons for new researches that in the near future will provide further contributions in the field of characterisation of complex materials such as organic matter.

This can be envisaged not only for applications to hydrocarbons exploration, but also to renewable energies (e.g., bioenergy). This jump of knowledge will need further development and improvement of Raman spetroscopy techniques and a substantial increase of available databases on which to perform Raman analyse.

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