

Laboratory organic matter maturation at high pressures: heat-up effect on vitrinite reflectance

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Abstract A laboratory study was conducted to assess the effect of heat-up to high diagenetic to low metamorphic temperatures on vitrinite reflectance (*VR*) at high pressures using the same heat-up processes, apparatus and starting material as those employed in prior experimental studies on huminite/vitrinite maturation. “Heat-up” is the isobaric increase in temperature of an organic matter maturation experiment from room temperature to the desired run temperature T^{ehu} (T^{ehu} = temperature at the end of heat-up). The experiments were performed on xylite of swamp cypress and used a heating rate of 50 °C/min. These confined system maturation experiments were carried out at 10 kbar and involved temperatures T^{ehu} ranging from 175 to 450 °C. Additional experiments were conducted at pressures of 5, 20 and 25 kbar to evaluate the influence of pressure on the effect of heat-up on *VR*. At 10 kbar, results of this study show that heat-up does not influence *VR* for $T^{ehu} < \sim 270$ °C. This absence of maturation is viewed as the result of an activation time delaying vitrinite maturation at these diagenetic to very low metamorphic temperatures. For $T^{ehu} > \sim 270$ °C, heat-up has a significant effect on *VR* at 10 kbar: *VR* greatly increases with T^{ehu} during the short heat-up event. This effect of heat-up on *VR* points out the rapid kinetics of the initial *VR* increase. Increasing pressure reduces *VR* increase gained during heat-up. Obviously, pressure retards the initial *VR* increase and thus controls organic matter maturation. In addition to temperature, the formulation of *VR* evolution rate equation

must consider pressure, activation time and *VR* gained during heat-up.

Keywords Textinite/telinite · Vitrinite reflectance · Organic matter maturation · Confined laboratory maturation · Heat-up effect · Pressure effect

1 Introduction

Petrologists have a whole set of methods to carry out metamorphic studies in terranes consisting of diagenetic and very low to low temperature–low to high pressure silico-calcic metasedimentary rocks (i.e. sub-greenschist, greenschist and blueschist metamorphic facies rocks). There are many reasons to study metamorphism of these terranes, but all are ultimately related to a better understanding of the Earth’s geodynamic evolution. This is because the histories of pressure–temperature (P – T) conditions, i.e. the P – T paths, followed by metamorphic rocks/terranes and estimated by studying metamorphism reflect the depth and thermal state histories and consequently the geodynamics of these rocks/terranes. Obviously, such P – T paths are a critical parameterization of geodynamics and are therefore essential for reconstructing and understanding the geological evolution of terranes. At present, the available methods that are mostly employed to estimate the conditions of pressure (P) and/or temperature (T) in diagenetic to low temperature metamorphic rocks rely on fluid inclusions microthermometry, illite Kübler Index determination, smectite-to-illite reaction progress, K-white mica b cell dimension and the P – T stability fields of minerals and/or mineral assemblages. Nevertheless, these techniques suffer from systematic problems. Whereas the thermodynamic properties of a specific chemical system in fluid

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inclusions is well known, the timing of fluid formation, entrapment and its related microstructural setting are poorly constrained. Nowadays, it is known that fluid entrapment does not usually coincide with *P*- or *T*-peak conditions of a metamorphic *P*–*T* path (Frey and Robinson 1999). Illite Kübler Index determination and smectite-to-illite reaction progress are two semiquantitative metamorphic indicators that define and depend on the geodynamic settings and therefore on the *P*–*T* evolution of diagenetic to low temperature metamorphic terranes (Frey and Robinson 1999). Although illite Kübler Index determination and smectite-to-illite reaction progress are useful to estimate the metamorphic grade (i.e. diagenesis, anchizone and epizone) and geodynamic setting, both of these indicators have their kinetics and thermodynamic properties that are not well defined. In particular, the kinetics of smectite-to-illite reaction was experimentally demonstrated (e.g. Huang et al. 1993) as dependent on K^+ , Ca^{2+} and Mg^{2+} concentrations in solutions. K-white mica *b* cell dimension is a practical semiquantitative indicator of paleopressure conditions in diagenetic to low temperature metamorphic terranes (e.g. Frey and Robinson 1999). Nonetheless, this indicator shows limitations because it is based on the comparison between K-white mica *b* cell dimensions measured in rocks with those previously determined in rocks from constrained geodynamic settings (Frey and Robinson 1999). The *P*–*T* stability fields for single minerals and/or mineral assemblages extracted from petrogenetic grids and/or modeling phase-assemblage diagrams give restrained information on the *P*–*T* conditions and paths followed by metasedimentary terranes at high diagenetic to low metamorphic temperatures. In particular, using modeling phase-assemblage diagrams to estimate *P*–*T* stability fields for mineral assemblages is restricted by the lack of reliable thermodynamic properties and/or solid-solution models for minerals occurring at high diagenetic to low metamorphic temperatures and by the uncertainty in the effective bulk rock composition and/or fluid activities (Le Bayon et al. 2006).

However, the presence of huminite/vitrinite phytoclasts in sedimentary and very low to low temperature–low to high pressure metasedimentary terranes provides a valuable aid to quantify and understand the evolution of metamorphism and maturation in these terranes and thus the geological history of these terranes. Huminite/vitrinite is Type III organic matter (in the van Krevelen terminology) and derives from the decomposition and transformation of lignin and cellulose of plant tissues. A useful and reliable parameter and method to monitor the maturation of organic material from immature to graphite is vitrinite reflectance (*VR*). This stems from the established correlations between *VR* and coal rank and chemistry (e.g. van Krevelen 1953; Teichmüller and Teichmüller 1954; Tissot and Welte 1984;

Taylor et al. 1998). *VR* is the proportion of perpendicularly incident monochromatic light that is reflected from the surface of the huminite/vitrinite maceral group. Hence, *VR* is used as coalification parameter in coals and serves as a powerful tool to estimate the degree of organic matter maturity with respect to hydrocarbon generation in sedimentary rocks and basins. Furthermore, *VR* is the most widely employed calibration parameter in basin modeling and became an indicator of metamorphic conditions in metasedimentary terranes. Nonetheless, the usefulness of *VR* as a tool in modeling and interpreting the evolution of maturation and metamorphism in huminite/vitrinite-bearing sedimentary and metasedimentary terranes depends on how well we understand and quantify *VR* increase and its dependence on time and environmental variables such as temperature and pressure.

Consequently, tremendous effort has been directed towards a better understanding of vitrinite maturation and reflectance over the past 50 years. In particular, several studies were devoted to recognize and estimate a variety of factors influencing *VR*. Both heating time and temperature were recognized as important parameters controlling *VR* at low pressure (van Krevelen 1961; Lopatin 1971; Hood et al. 1975; Burnham and Sweeney 1989; Sweeney and Burnham 1990; Hunt et al. 1991). These early studies were supported by recent experiments (Huang 1996; Dalla Torre et al. 1997; Ernst and Ferreiro Mählmann 2004) showing that, whereas time is important, the major variable that determines *VR* over geological time intervals is host-rock temperature. Several empirical (Waples 1980; Burnham and Sweeney 1989; Larter 1988; Waples et al. 1992; Suzuki et al. 1993) and experimentally based (Huang 1996; Ernst and Ferreiro Mählmann 2004) kinetic models were formulated as a function of temperature. These laboratory based rate equations were calibrated at low pressures: 0.5 kbar (Huang 1996) and 2 kbar (Ernst and Ferreiro Mählmann 2004). The kinetic formulations of *VR* increase are useful tools to model and reconstruct the geological history of metamorphic and sedimentary terranes and therefore to predict source rock maturity in sedimentary basins that is one of the many problems confronting hydrocarbon exploration community.

Moreover, *VR* became a useful tool to estimate the metamorphic conditions in vitrinite-bearing terranes occurring in various geological settings where pressure is an important metamorphic agent such as in subducted, exhumed and collided terranes in orogenic wedges (e.g., Frey et al. 1980; Burkhard and Kalkreuth 1989; Dalla Torre et al. 1996; Ferreiro Mählmann 2001; Árkai et al. 2002; Rantitsch et al. 2005). Nevertheless, the effect of pressure on the maturation of huminite/vitrinite—Type III organic matter remains largely debated (for an overview, see Le Bayon et al. 2011, 2012a and references therein).

This lack of a clear statement on the influence of pressure on *VR* is surprising if one considers the strong pressure dependence of the well-known graphitization process from experimental studies (e.g. Bonijoly et al. 1982) and the importance of pressure as a metamorphic agent in most geological settings. However, a recent study (Le Bayon et al. 2012a) elucidated the effect of pressure on *VR* at 400–450 °C. It was shown that increasing pressure retards vitrinite maturation when $VR < 1.34 \pm 0.29 \%$ and promotes it when $VR > 1.34 \pm 0.29 \%$. Additionally, Le Bayon et al. (2011) proposed an isothermal rate law for *VR* increase at 400 °C. Nevertheless, knowledge and accurate experimental determination of the effect of pressure on *VR* evolution kinetics are still needed at other temperatures to better quantify the diverse processes that control *VR* evolution. However, it is essential to evaluate the laboratory effect of heat-up to high diagenetic to low metamorphic temperatures at high pressures prior to experimentally investigating the influence of pressure on the kinetics of *VR* increase at these low geological temperatures in further studies.

“Heat-up” is the isobaric increase in temperature of a huminite/vitrinite maturation experiment from room temperature to the desired run temperature T^{ehu} . T^{ehu} stands for “temperature at the end of heat-up”. Heat-up is the experimental procedure that precedes any isobaric-isothermal laboratory maturation of huminite/vitrinite at T^{ehu} . Dalla Torre et al. (1997) stated that experimental heat-up has no effect on *VR* as long as T^{ehu} is reached in less than 30 min. This would involve very slow kinetics of the initial *VR* increase during and after (i.e. during isobaric-isothermal maturation experiment that follows heat-up) heat-up. This led Dalla Torre et al. (1997) to consider that the isobaric-isothermal vitrinite maturation (i.e. maturation following heat-up) involving short heating duration is sluggish and thus is negligible in the kinetic analysis of *VR* evolution. Hence, Dalla Torre et al. (1997) calibrated the formulation of their experimentally based *VR* evolution rate equation on an immature starting material having *VR* equal to 0 %. Nonetheless, their series of isobaric-isothermal laboratory vitrinite maturations were carried out on a starting material having a *VR* post-heat-up. Moreover, Le Bayon et al. (2011) experimentally investigated the effect of heat-up to 400 °C at various pressures. These authors pointed out the significant effect of heat-up on *VR*, even though a rapid heating rate of 50 °C/min is used. In addition, Le Bayon et al. (2011) demonstrated the strong influence of heat-up on the kinetic formulation of *VR* increase. However, they provided directions on how to correct *VR* evolution kinetic equation for the effect of heat-up. Nevertheless, this previous laboratory study was limited as it considered only one temperature T^{ehu} . The lack of consideration of the possible influence of heat-up to various T^{ehu} on *VR* is surprising in the light of the

sensitivity of organic matter maturation to temperature. The effect of heat-up to high diagenetic to low metamorphic temperatures on vitrinite maturation at elevated pressures now awaits a stringent detailed experimental investigation.

Consequently, the central objective of the present laboratory study is to determine the effect of heat-up to high diagenetic to low metamorphic temperatures on *VR* at high pressures. In addition, the influence of pressure on the effect of heat-up on *VR* is addressed. For these purposes, this study employed the same experimental heat-up procedures (i.e. heating rate, T^{ehu} and pressure conditions), Type III organic starting material and apparatus as those used in previous laboratory studies of vitrinite maturation (e.g. Dalla Torre et al. 1997; Le Bayon et al. 2011, 2012a). Furthermore, these laboratory procedures will be also employed in forthcoming experimental studies of vitrinite maturation. Accordingly, the implications of heat-up on further isobaric-isothermal laboratory vitrinite maturations and kinetic analysis of *VR* evolution are discussed. This effort is one step towards an accurate experimentally calibrated kinetic formulation for *VR* evolution as a function of pressure and temperature. Such a kinetic equation of *VR* evolution will be a useful tool to model *VR* in geological settings and to evaluate and compare the effects of various parameters on *VR* and thus on organic matter maturation. Lastly, the effect of pressure on huminite/vitrinite maturation is commented.

2 Experimental and analytical procedures

A laboratory study of the maturation of Type III organic material was performed to evaluate the effect of heat-up to various temperatures T^{ehu} on *VR* at 10 kbar using the same experimental heat-up procedures as those employed in previous studies (Dalla Torre et al. 1997; Le Bayon et al. 2011, 2012a). Additional experiments were carried out at 5, 20 and 25 kbar to examine the influence of pressure on the effect of heat-up on *VR*. At the desired run pressure, the experiments consisted of the isobaric increase in run temperature from room temperature to the desired temperature T^{ehu} at a rate of 50 °C/min. Then, the experiments were immediately quenched when T^{ehu} was attained. The investigated T^{ehu} ranged from 175 to 450 °C.

2.1 Starting material

The starting material was identical to that used in Le Bayon et al. (2011, 2012a, 2012b). It consisted of a xylite of swamp cypress (*Taxodioides taxodium*). The sample of xylite is Middle Eocene in age and was collected in the Helmstedt open-pit mine from peat seam 6 of the

Wulfersdorf group, in the eastern Helmstedt syncline, Braunschweig mining area, Germany. The Wulfersdorf seam group represents a coastal swamp paleoecosystem. The sample was stored at ambient conditions and untreated before the experiments. The sample of xylite displays an easily recognizable cellular microstructure (Fig. 1): the bright (on a grey scale) cell walls consisting of textinite that surrounds the darker structureless infilling of the cell lumens (corpohuminite). The sample of xylite lacks liptinite macerals that are known to suppress *VR* due to their high hydrogen content (for an overview, see Carr 2000 and references therein). A vitrinite reflectance $VR = 0.168 \pm 0.020 \%$ was measured in the starting material (Fig. 2), indicating that the initial organic matter was immature prior to the experiments. This allows the investigation of the largest possible *VR* range because maturation prior to the experiments does not interfere with the results. The botanical origin and maceral composition indicate a Type III organic matter. A low atomic H/C ratio of 1.27 ± 0.03 was measured in the sample of xylite (Le Bayon et al. 2011). According to Tissot and Welte (1978) (see their Fig. II.7.6), this low H/C ratio defines the immature Type III organic starting material as lignin in the van Krevelen diagram. Thus, the starting material employed in this laboratory study is the archetype of the botanical and chemical precursor of the huminite/vitrinite maceral group. Consequently, this xylite sample of swamp cypress is an ideal botanical, chemical and physical (low *VR*) starting material on which to perform huminite/vitrinite maturation experiments. However, it is to be noted that the nature of the Type III starting material (conifer or hardwood) did not affect the rate of huminite/vitrinite maturation in previous experiments (Ernst and Ferreiro Mählmann 2004).

2.2 Experimental methods

The experiments of vitrinite maturation were performed using a high pressure piston-cylinder apparatus. This stems from the findings of Monthioux et al. (1985, 1986), Monthioux (1988) and Lewan (1993). These authors demonstrated that natural maturation of organic matter can be reproduced by laboratory maturations only if conducted in confined systems (i.e. in sealed gold or platinum capsules under external pressure) in as much as organic matter heated under confined laboratory conditions follows the same evolution path of H/C versus O/C atomic ratios as natural coalification. In contrast, maturation studies in open systems (under vacuum or inert gas) do not yield geochemical data compatible with natural systems.

The experimental procedures were identical to those described in Le Bayon et al. (2011). The experiments were carried out using the end loaded high pressure piston-cylinder apparatus of the Institut für Geowissenschaften, Abt.

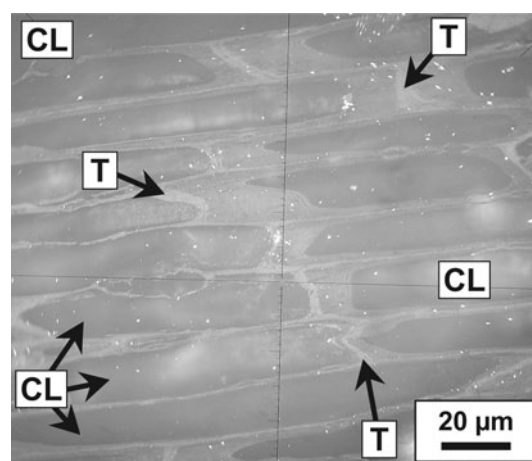


Fig. 1 Photomicrograph of the starting material that consists of xylite of swamp cypress (*Taxodioidea taxodium*) under incident white light and oil immersion. This xylite sample is Middle Eocene in age. The cellular microstructure displays the cell walls consisting of textinite that surround infilling of the cell lumens. The bright spots consist of diamond powder remaining after the last polish. *T*, textinite (cell wall); *CL*, cell lumen (corpohuminite)

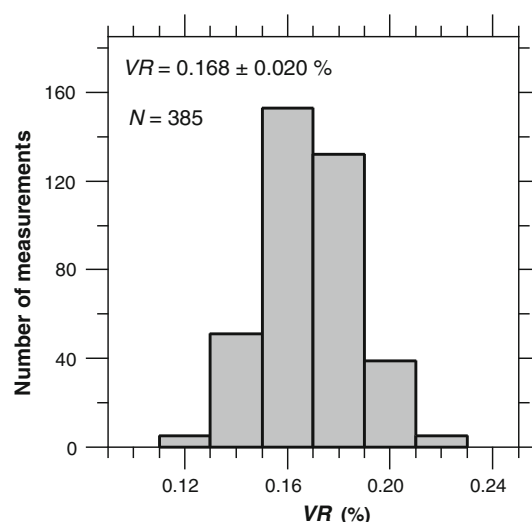


Fig. 2 Distribution of 385 measurements of *VR* conducted on the starting material before experimental maturation. The indicated value *VR* is the mean value of vitrinite reflectance \pm one standard deviation

Petrologie und Geochemie, J.W. Goethe-Universität, Frankfurt am Main, Germany. Pt capsules, NaCl pressure-medium assemblies and graphite resistance furnaces were employed in a 12.7 mm diameter piston-cylinder pressure vessel. A cross-section of the piston-cylinder assembly used in this study is shown in Le Bayon et al. (2011). It is to be noted that a graphite disk was added at the bottom of the graphite cylinder to improve the formation of a reliable heating circuit through the cell. The capsule body (3.03 mm outer diameter and ~ 4 mm long after closure) contained the pressed swamp cypress xylite, which was previously gently disaggregated to coarse and fine particles

(0.1–1.0 mm in length, ~ 0.1 mm thick) in an agate mill. The capsule was cold sealed rather than welded in order to avoid a potential thermal alteration of the charge. The experiments were pressurized to the desired run pressure at room temperature. Then, the experiments were isobarically heated to T^{ehu} at a rate of 50 °C/min. This led to a heat-up time of ~ 190 s at 175 °C, ~ 260 s at 240 °C, ~ 340 s at 300 °C, ~ 460 s at 400 °C, and ~ 520 s at 450 °C. Temperature was controlled automatically by a programmable EUROTHERM power controller using a Pt₇₀Rh₃₀–Pt₉₄Rh₆ (type-B) thermocouple inserted into the experimental assemblage and located at a distance of 0.6 ± 0.03 mm above the flat top of Pt capsule. Thermal gradient is negligible across the capsule. This stems from the small size of employed capsules, the large amount of capsule-forming Pt metal, the reliable heating circuit through the cell and the short distance between the thermocouple and the capsule. During the experiments, temperature was kept constant to within ± 1 °C. Temperatures reported in this study are thermocouple readings. Pressure was kept constant for the duration of the experiment by manual adjustment if necessary (i.e. if loss or gain of pressure generated by the apparatus itself occurred). Pressure is considered to be accurate to ± 1 kbar. When the experiments attained the desired temperature T^{ehu} , the runs were quenched to room temperature in less than 10 s by switching off the power to the heater whilst maintaining quasi run pressure. The very short quench times stemmed from the very small sizes of capsules and piston-cylinder assemblies employed in this study. Afterwards, pressure was decreased in ~ 30 min to ambient.

2.3 Analytical methods

After the experiments, the capsules were recovered and cut diametrically in half for *VR* analysis. The preparation of vitrinite mounts consisted of plucking numerous vitrinite particles from the recovered samples, embedding them in epoxy resin and then polishing the mounts at room temperature using 3, 1 and 0.5 μm diamond powder and felted wool for the last polish to avoid scratches that cause relief and shadows, which change reflectance (e.g. Buiskool Toxopeus 1983). The same preparation procedure for vitrinite mounts was applied to the initial material prior to the experiments. The measurements of *VR* were performed at the Unit of Petrology of the Institut für Geowissenschaften of the Technische Universität Darmstadt, Germany. *VR* was measured according to the standard procedures (Stach et al. 1982), but varied in some points. The 546 nm wavelength monochromatic light reflected from the surface of vitrinite mount is measured using a photomultiplier coupled to a Leitz Orthoplan-photometer microscope calibrated with a single standard. The microscope is equipped with a 125 \times oil-immersion objective

coupled with a 10 \times ocular. This high magnification was optimal for measuring *VR* in the starting material and experimental products. It would have been impossible to measure *VR* in this study by employing a smaller magnification. This stems from the very small material surface where reflectance measurement had to be performed. This high magnification did not result in any optical complication (e.g. blurring). A non-drying immersion oil with a refraction index $n_c = 1.518$ (at 23 °C and for 546 nm wavelength monochromatic light) was used for the reflectance measurements. *VR* measurement equipment was placed on a sturdy work bench to avoid vibration during the measurements. In addition, the measurements were operated in dim light at about 23 °C. The calibration was done according to the standard procedures detailed by Stach et al. (1982). The standard used for the calibration was yttrium–aluminum–garnet, which has a reflectance $R = 0.880\%$. The calibration quality was checked every 20–30 min during the measurements. The measured *VR* is the mean random vitrinite reflectance because *VR* measurements on the starting material and run products show isotropic reflectance. This is supported by the measured *VR* that are all below 1.3 % (Table 1) i.e. that are in the range of *VR* displaying isotropy (Taylor et al. 1998). For $VR < 0.5\%$, *VR* measurements were performed only on textinite, which is a maceral of the huminite group having $VR < 0.5\%$ and consisting of clearly recognizable cell walls of plant tissue (Taylor et al. 1998; ICCP 2005). For $VR > 0.5\%$, *VR* measurements on run products were performed only on telinite. Telinite is a maceral of the vitrinite group having $VR > 0.5\%$ and consisting of clearly recognizable cell walls of more or less intact plant tissue (ICCP 1998; Taylor et al. 1998). The number of *VR* measurements for each run product obeyed a good compromise between statistical and practical considerations.

Table 1 Conditions and results of maturation experiments

Run no.	P (bar)	T^{ehu} (°C)	VR^{ehu} (%)	s_{VR}^{ehu} (%)	N
RLB-e77	5,000	300	0.319	0.022	330
RLB-e37	10,000	175	0.159	0.015	140
RLB-e31	10,000	240	0.163	0.017	260
RLB-e78	10,000	300	0.250	0.010	80
RLB-e103	10,000	400	0.647	0.022	170
RLB-e57	10,000	450	0.708	0.019	120
RLB-e104	20,000	400	0.589	0.017	170
RLB-e68	20,000	450	0.628	0.015	120
RLB-e85	25,000	450	0.592	0.022	100

P , pressure; T^{ehu} , temperature attained at the end of heat-up; VR^{ehu} , measured vitrinite reflectance at the end of heat-up to temperature T^{ehu} at pressure P ; s_{VR}^{ehu} , standard deviation of VR^{ehu} ; N , number of measurements

It is to be noted that the dimension and orientation of the measuring aperture were adjusted to cover equidimensional or elongate shapes of the thin textinite/telinite as advised by Taylor et al. (1998). Evidently, the calibration was redone after each change of size and/or shape of the field of measurement. No *VR* variation was detected on the standard and samples by employing various sizes and/or shapes of the measuring aperture.

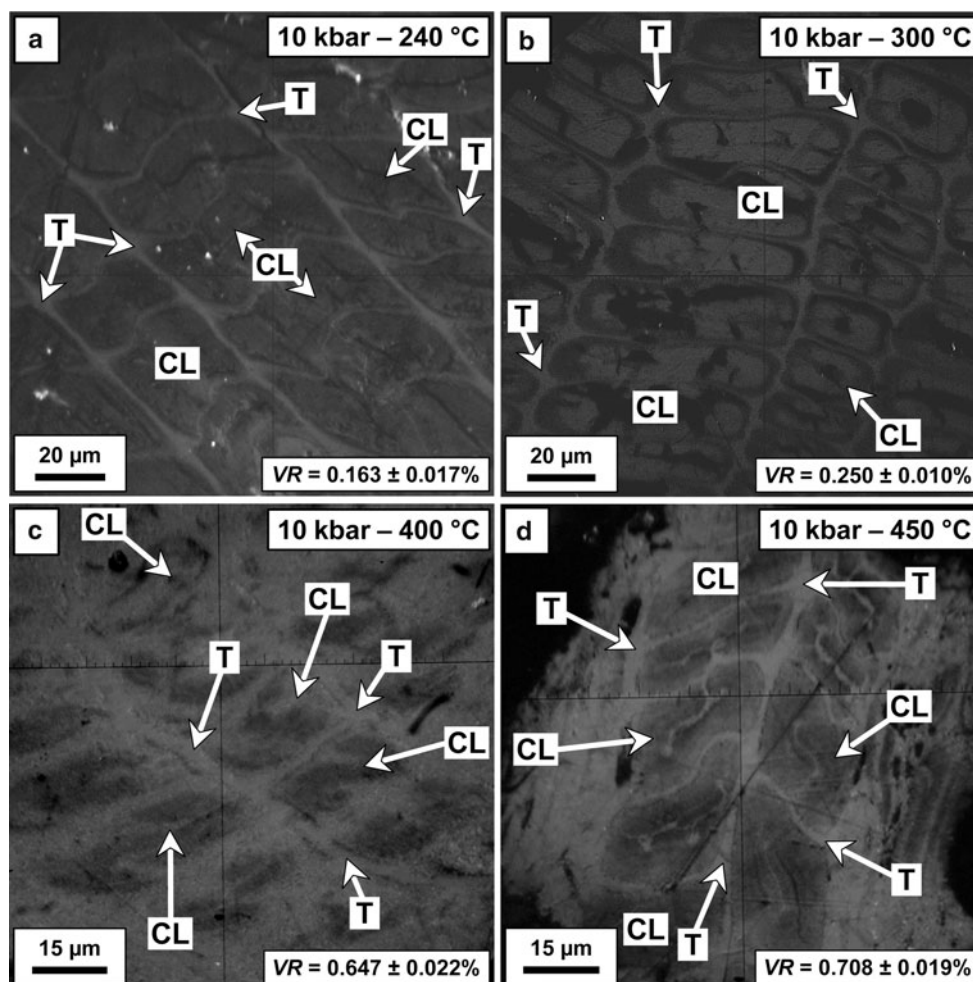
3 Experimental results

3.1 Microscopic observations

After the experiments, several critical aspects of the maturation of organic matter were observed in the laboratory matured xylite. The initial cellular wood microstructure (cell walls and cell lumens) was recognizable in all of the experiments of heat-up (see Fig. 3a–d for the results of heat-up at 10 kbar). Hence, the distinction between textinite/telinite of cell walls from infilling of cell lumens (corpohuminite/corpocollinite) was straightforward in all

of the run products. Gelification and deformation did not occur in the experimental material. Under incident white light, no laboratory maturation was observed at $T^{ehu} = 240$ °C (Fig. 3a) inasmuch as the experimental product presented the same aspect as the starting material. In contrast, the experiments of heat-up to $T^{ehu} \geq 300$ °C showed that laboratory maturation occurred. In particular, corpohuminite/corpocollinite was significantly transformed (Fig. 3b–d). Nevertheless, cell infillings displayed heterogeneous brightening and decomposition arguing for the non-uniform maturation of cell-filling organic material (Fig. 3b–d). However, the experiments of heat-up to $T^{ehu} \geq 300$ °C showed that the cell walls homogeneously brightened with T^{ehu} indicating uniform maturation of textinite/telinite (Fig. 3b–d). The homogeneous brightening/maturation of the cell walls results from their homogeneous chemical composition consisting of pure lignocellulosic material. In contrast, the heterogeneous brightening/maturation taking place in cell-filling material stems from the various substances (i.e. various maceral varieties of huminite/vitrinite present in the original cell lumens) that impregnate the lignocellulosic material of cell lumens (Taylor et al. 1998).

Fig. 3 Photomicrographs of run products from heat-up experiments to various temperatures T^{ehu} (temperature at the end of heat-up) at 10 kbar under incident white light and oil immersion. **a** $T^{ehu} = 240$ °C, **b** $T^{ehu} = 300$ °C, **c** $T^{ehu} = 400$ °C, **d** $T^{ehu} = 450$ °C. The indicated value *VR* for each run product is the mean value of vitrinite reflectance \pm one standard deviation (Table 1). *T*, textinite for *VR* < 0.5 % or telinite for *VR* > 0.5 % (cell wall); *CL*, cell lumen (corpohuminite/corpocollinite)



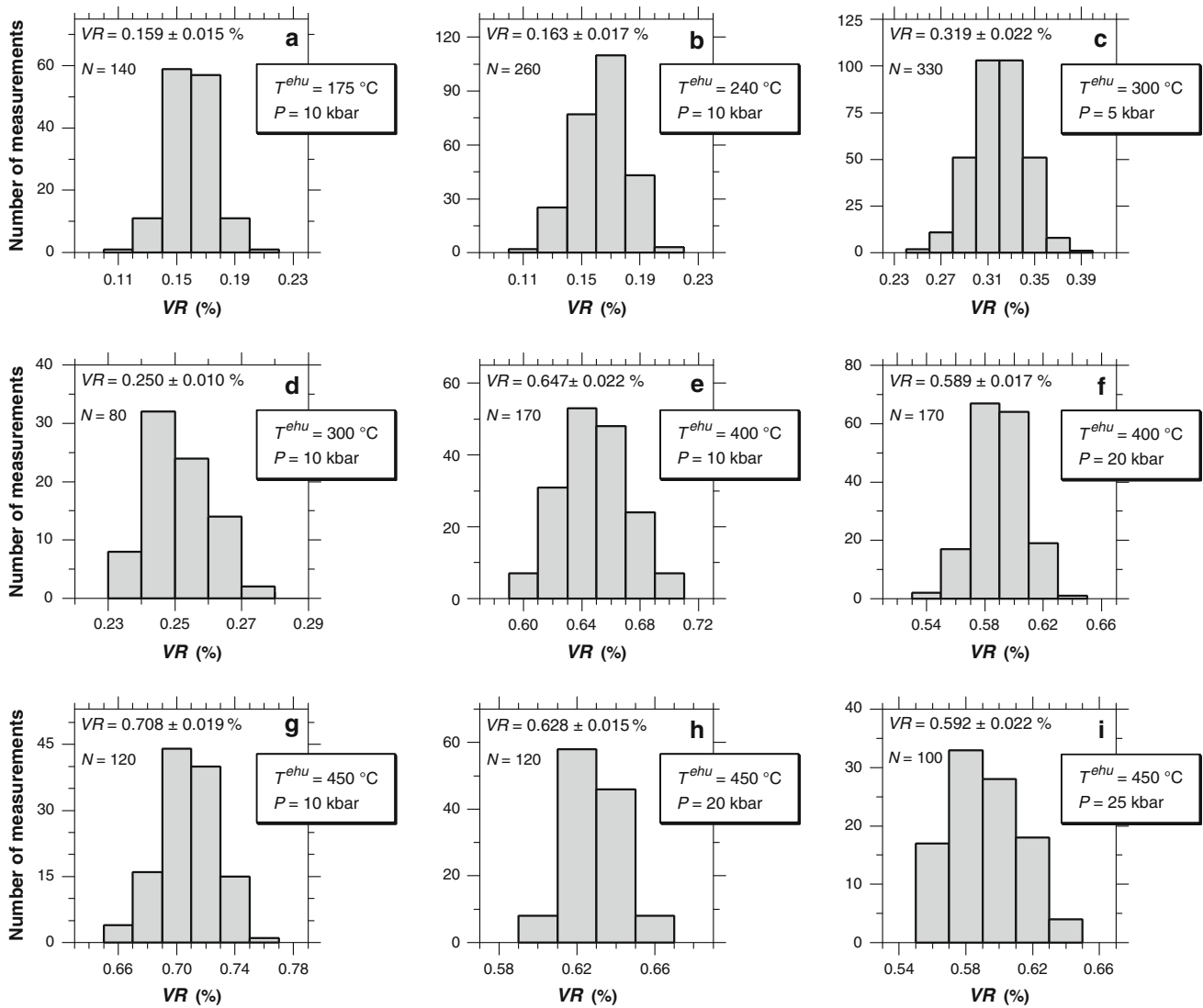


Fig. 4 Distribution of N measurements of VR performed on textinite/telinite of the run products from the isobaric heat-up experiments to temperatures T^{ehu} (temperature at the end of heat-up) at pressures

P . The indicated value VR for each run product is the mean value of vitrinite reflectance \pm one standard deviation. VR data are listed in Table 1

3.2 Vitrinite reflectance

VR results from the experiments of heat-up to various T^{ehu} and at four different pressures (5, 10, 20 and 25 kbar) using a heating rate of 50 °C/min are presented in Fig. 4 and Table 1. These experimental results are plotted in VR^{ehu} versus T^{ehu} diagram (Fig. 5). VR^{ehu} is vitrinite reflectance attained at the end of heat-up to temperature T^{ehu} .

3.2.1 Effect of heat-up to T^{ehu} on VR

The experiments of heat-up to $T^{ehu} = 175$ °C and $T^{ehu} = 240$ °C at 10 kbar (Table 1; Figs. 4, 5) show VR^{ehu} data similar to VR of the starting material. At all pressures, a significant VR^{ehu} increase was measured in all of the run products for $T^{ehu} \geq 300$ °C. In particular, a large and rapid

isobaric increase in VR^{ehu} with T^{ehu} is observed at 10 kbar (Table 1; Fig. 5): from an immature material with $VR^{ehu} = 0.163 \pm 0.017$ % attained at the end of heat-up to $T^{ehu} = 240$ °C, VR^{ehu} changes to 0.25 ± 0.01 % after less than 1.5 min of heat-up time to $T^{ehu} = 300$ °C, 0.647 ± 0.022 % after less than 3.5 min of heat-up time to $T^{ehu} = 400$ °C and 0.708 ± 0.019 % after less than 4.5 min of heat-up time to $T^{ehu} = 450$ °C. It is evident from Fig. 5 that a temperature T^{ehu} between 240 °C and 300 °C is required before a change in VR^{ehu} of the run material is detected at 10 kbar when an experimental heating rate of 50 °C/min is used. T^{ehu} of ~ 270 °C is estimated as temperature at which VR starts to increase during heat-up at 10 kbar. It is to be noted that all of the run products at $T^{ehu} \geq 400$ °C surpass the onset of oil generation commonly fixed at $VR = 0.5$ % for Type III

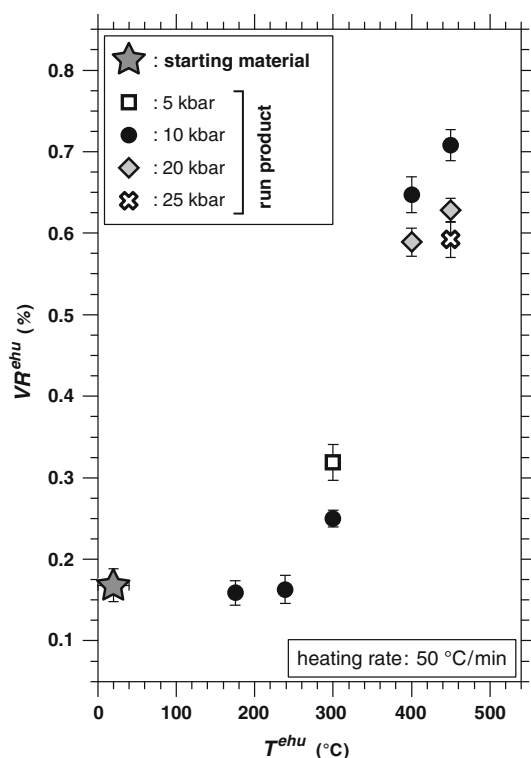


Fig. 5 Variation in VR^{ehu} (vitrinite reflectance attained at the end of heat-up to temperature T^{ehu}) of the run products as a function of T^{ehu} (temperature at the end of heat-up) at various pressures. The error bars in VR^{ehu} are \pm one standard deviation $s_{VR^{ehu}}$. The error bars in temperature are ± 1 °C for the run products and ± 20 °C for the starting material

organic matter (e.g. Taylor et al. 1998) after very short heat-up times. These results demonstrate the strong effect of heat-up on VR and thus on organic matter maturation when $T^{ehu} > \sim 270$ °C, even by using very short heat-up durations. This points out the rapid kinetics of the initial VR increase. At 10 kbar, the lack of maturation indicated by the plateau of VR observed for $T^{ehu} < \sim 270$ °C (Fig. 5) is regarded as the result of an activation time that delays vitrinite maturation at these diagenetic to very low metamorphic temperatures.

3.2.2 Pressure influence on heat-up effect on VR

As seen in Fig. 5, pressure has a significant influence on the effect of heat-up to low metamorphic temperatures on VR for the range of VR examined in this laboratory study (i.e. between ~ 0.25 and ~ 0.71 %): increasing pressure diminishes the effect of heat-up on VR inasmuch as VR^{ehu} decreases with pressure at each investigated T^{ehu} when a rapid heating rate of 50 °C/min is employed. Even an increase in pressure of a few kilobars clearly decreases VR^{ehu} for a same low T^{ehu} . This is illustrated at $T^{ehu} = 300$ °C where VR^{ehu} is equal to 0.319 ± 0.022 % at 5 kbar and 0.25 ± 0.01 % at 10 kbar. This indicates that

pressure retards the initial VR increase, even though a very short heat-up time and a low temperature T^{ehu} are used. Obviously, VR increase/organic matter maturation is not only a thermally activated process, it is also pressure controlled.

4 Discussion and conclusions

For $T^{ehu} > \sim 270$ °C, this laboratory study clearly shows the rapid kinetics of the initial VR increase at 10 kbar as VR strongly increases during the rapid heat-up. This argues for important changes in VR during isobaric-isothermal maturation experiments involving short heating times (between a few minutes and a few hours) after heat-up. In contrast to recent studies carried out at 400 and 450 °C (Le Bayon et al. 2011, 2012a), the previous laboratory huminite/vitrinite maturation study conducted at elevated pressures (Dalla Torre et al. 1997) was focused on gaining VR data attained after isobaric-isothermal experiments involving only long heating durations (several days) at very low to low metamorphic temperatures. Consequently, Dalla Torre et al. (1997) ignored the rapid kinetics of the initial isobaric-isothermal VR increase taking place after heat-up. The study of Dalla Torre et al. (1997) aimed to formulate a kinetic equation for VR evolution with temperature and pressure. These authors described the evolution of VR with heating time, temperature and pressure by a power law rate equation in the form of $VR = kt^n$ where t is time, k is a rate constant depending on temperature and n is a constant unchanged over the experimental temperature and pressure range. The use of a power law equation implies that both short and long heating duration experiments are needed to formulate such a kinetic equation as shown in Le Bayon et al. 2011, 2012a, 2012b). In addition, the power law formalism implies that small discrepancies in the initial VR –heating time data result in large errors in the constants k and n . Thus, the experimental kinetic studies must consider isobaric-isothermal huminite/vitrinite maturation experiments (i.e. maturation occurring after heat-up) involving short heating durations (runs of a few minutes to a few hours) at various P – T conditions. This aims to consider the rapid kinetics of the initial isobaric-isothermal VR increase in the kinetic analysis of VR evolution and therefore to formulate an accurate general rate equation of VR increase that will permit to correctly model VR evolution in natural systems. Nevertheless, long heating duration maturation are still needed for the kinetic analysis of VR evolution.

The absence of maturation during heat-up to very low T^{ehu} (e.g. to $T^{ehu} < \sim 270$ °C at 10 kbar) argues for performing isobaric-isothermal laboratory vitrinite maturation involving short heating times in order to detect the start of

the isobaric-isothermal *VR* increase that follows heat-up at various pressures and diagenetic to very low metamorphic temperatures. This aims to identify and quantify an activation time before measurable maturation begins during the isobaric-isothermal maturation at different *P*–*T* conditions as shown in Le Bayon et al. (2011). This stems from the recognition that activation time strongly influences the power law formulation and its associated constants that describe the kinetics of *VR* evolution at 400 °C (Le Bayon et al. 2011). Thus, activation time pointed out in the present study must be taken into account for the kinetic formulation of *VR* evolution at high *P*–very low *T* conditions. Possibilities on how to handle activation time in the kinetic formulation of *VR* evolution were presented in Le Bayon et al. (2011).

The existing experimentally based pressure–temperature dependent *VR* evolution rate equation and its associated constants are defined for a starting *VR* equal to 0 % (Dalla Torre et al. 1997). This previous study ignored the effect of heat-up on *VR* and postulated that no maturation occurs during heat-up. This is in disagreement with the results of this study when T^{ehu} exceeds a critical value (e.g. $T^{ehu} \sim 270$ °C at 10 kbar), even though VR^{ehu} decreases with *P*. Vitrinite reflectance gained during heat-up must be taken as the starting *VR* in all of the isobaric-isothermal laboratory and kinetic studies that aim to quantify *VR* evolution. Indeed, any isobaric-isothermal huminite/vitrinite maturation experiments following heat-up are carried out employing a starting material having vitrinite reflectance VR^{ehu} . Furthermore, VR^{ehu} was demonstrated to have a large impact on the kinetic formulation of *VR* evolution at 400 and 450 °C (Le Bayon et al. 2011, 2012a). Le Bayon et al. (2011, 2012a) provided explicit directions on how to take into account VR^{ehu} in the empirical formulation of a kinetic equation of *VR* evolution.

This study demonstrates that pressure has a significant effect on *VR* inasmuch as pressure retards the initial *VR* increase. Hence, in addition to temperature, pressure must be considered as a maturation-controlling parameter in understanding organic matter maturation and therefore in further laboratory huminite/vitrinite maturations and formulations of kinetic equations of *VR* increase. Furthermore, future huminite/vitrinite maturation experiments and kinetic analysis of *VR* evolution carried out at low pressure must consider the effect of heat-up to diagenetic to low metamorphic temperature on *VR* because at lower pressure, a more significant effect of heat-up on *VR* occurs. The retarding effect of pressure on *VR* that is detected for the range of *VR* examined in this study (from ~ 0.25 to ~ 0.71 %) corroborates prior experimental results, which demonstrated that pressure retards vitrinite maturation for $VR < 1.34 \pm 0.29$ % (Le Bayon et al. 2012a). It is of interest to examine the influence of pressure on the overall chemical and physical changes taking place during

huminite/vitrinite maturation retarded by pressure, i.e. for $VR < 1.34 \pm 0.29$ %. For this purpose, one uses the direct relationship between *VR* and maturation stages, at which specific physico-chemical processes occur (Levine 1993). According to Levine (1993), the maturation of Type III organic matter for $VR < 1.34 \pm 0.29$ % follows the sequence of maturation stages after peatification: dehydration → bituminization. Thus, pressure has a retarding effect on the overall rate of chemical and physical changes that take place during dehydration (i.e. loss of oxygen-bearing groups and generation of carboxylic acids, CO₂ and H₂O) and bituminization (i.e. generation of hydrocarbons, depolymerization and increased hydrogen bonding). These observations involve that pressure retards the initial increase in *VR* and therefore the generation of hydrocarbons in sedimentary terranes. This is in agreement with observations in sedimentary basins that documented retarded *VR* profiles with the onset of overpressure (for an overview, see Carr (1999) and references therein; Hao et al. 2007). Nonetheless, the retarding effect of pressure and its relative influence with respect to the promoting effect of temperature on the initial maturation of Type III organic matter in sedimentary basins require to be accurately estimated through future experimental studies. Moreover, the observed role of pressure in organic matter maturation in sedimentary basins strengthens the necessity to include pressure as variable in the formulation of a general rate law describing the increase in *VR*. Such a pressure dependent kinetic equation of *VR* increase will improve organic matter maturation modeling in sedimentary basins and thus basin modeling. Therefore, the reconstruction of the geological evolution of sedimentary terranes and the prediction of hydrocarbon source rock maturity degree will be enhanced. This is of high interest for current hydrocarbon explorations inasmuch as they are focusing their interests on sedimentary terranes that deeply occur or were deeply buried and thus on sedimentary rocks that are or were subjected to deep maturation (these sedimentary terranes are located or were buried at a depth of more than 3 or even 10 km and therefore at a pressure of more than 0.8 or even 2.5 kbar).

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