International Journal of Coal Geology 157 (2016) 52–73

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

Vitrinite and vitrinite like solid bitumen reflectance in thermal maturity studies: Correlations from diagenesis to incipient metamorphism in different geodynamic settings

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A R T I C L E I N F O

Article history:
Received 14 February 2015
Received in revised form 17 December 2015
Accepted 17 December 2015
Available online 21 December 2015

Keywords:
Vitrinite like solid bitumen reflectance
Vitrinite reflectance
Bitumen classification
Correlation
Diagenesis
Incipient metamorphism

A B S T R A C T

Vitrinite reflectance (VR) is a useful and reliable parameter to monitor the level of organic matter maturation from the immature stage to graphite. Additionally, VR is a useful and essential tool in modelling the temperature–maturation time path. Huminite/vitrinite-bearing sedimentary and meta-sedimentary rocks can be used to reconstruct the thermal history of basins or orogenic terranes throughout their geological history. The usefulness of VR evidently depends on the presence of huminite/vitrinite phytoclasts. However, pre-upper Silurian rocks and many organic-rich marine rocks (e.g. sapropelic sediments) lack of huminite/vitrinite particles. Furthermore, vitrinite is sparse in carbonate sediments.

However, the presence of bitumen in rocks lacking Type III kerogen provides a valuable aid via its reflectance (vitrinite like solid bitumen reflectance — VIBR, and/or solid bitumen reflectance — BR) to fulfil the above-described tasks that VR enables. This study presents basically a relationship between BR/VIBR and VR for various types of geodynamic settings and over the largest possible range of maturation levels so that VIBR may be used as a substitute for VR.

Whereas the effort to correlate VR with BR is not novel, it is the first time that the VR/BR correlation is re-judged, discriminating bitumen from VIB. Moreover for the first time the correlation is established for various geodynamic settings. The investigated geological contexts are:

(1) sedimentary basins (e.g., the Saar, Ruhr, Ohio, West Virginia, and Petrosani basins);
(2) metasedimentary terranes occurring as inverted basins in orogenic belts (e.g., from the Subalpine-Molasse, Helvetic, Austroalpine and Danubian nappe systems) and having suffered from very low to low grade metamorphism (from anchizone to greenschist facies);
(3) metasedimentary terranes (e.g., slates and schists from the Franciscan and Alpine belts) that were subducted at anchizone to blueschist facies conditions; and
(4) metasedimentary rocks affected by contact metamorphism.

Together, the frequent geological settings are referred and most of the earth geothermal conditions and heat fluxes considered. Despite temperature, pressure, and heating time, also heat flow gradient dependences cannot be ignored.

1. Introduction

1.1. Vitrinite — bitumen studies and scope of the project

It is widely accepted that vitrinite reflectance represents a diagnostic tool to determine the maturation of organic matter (Teichmüller, 1958, 1986; Taylor et al., 1998). Vitrinite is a diagenetic product of higher plant debris that is widely dispersed in clastic sedimentary rocks. The decomposition of ligno-cellulose biopolymers due to burial and consequent increase in temperature and lithostatic pressure results in changes in the optical properties, especially, an increase in reflectance and anisotropy (Karweil, 1956; Suggate, 1959; Taylor et al., 1998). Buchardt and Lewan (1990) strongly emphasized the use of vitrinite-like macerals (originating from bitumen) to evaluate the thermal maturation in pre-Devonian sedimentary rocks or those rare in vitrinite (see also Taylor et al., 1998).

Organic matter in sediments and meta-sedimentary rocks is made up of insoluble material (kerogen) and soluble material (bitumen). While bitumen is geochemically defined (Hunt, 1996), the term “bitumen” is also used in a petrographical sense, including terms like e.g. pyrobitumen, solid bitumen and migrabitumen (see also

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http://dx.doi.org/10.1016/j.coal.2015.12.008
0166-5162/

Mohnhoff et al., 2016–in this issue). During expulsion and migration solid bitumen precipitates and frequently can be found as migrabitumen dispersed in sheered rocks in fault zones as well as in younger stratigraphic porous rocks on top of the organic matter source rock. Studies on bitumen/bitumen reflectance (Bertrand and Héroux, 1987; Schönherr et al., 2007) or vitrinite-like particles (Petersen et al., 2013) were often not systematically controlled using other parameters to determine paleo-temperatures, to determine heat fluxes, to predict geotherms or petroleum and gas formation. In this study Mesozoic to Miocene rocks are analysed and vitrinite-like particles (Petersen et al., 2013, references therein) of the Early Palaeozoic are not further discussed. The focus is thus to systematically examine the vitrinite reflectance and vitrinite like bitumen reflectance of Devonian to Miocene rocks through field studies from peat to "optical graphite" (*sensu* Diessel et al., 1978) correlating with "diagenesis to amphibolite facies" (*sensu* Winkler, 1979) determined in the different areas studied.

A systematic maturity study is needed because the determination of bitumen reflectance progress is also not empirically expressed from diagenesis to amphibolite facies. The pressure–temperature estimation used to correlate with organic matter reflectance studies must be critically re-interpreted, because the knowledge about the thermal history of the basins and about the factors of pressure (P), temperature (T), time (t), deformation (D) and rock chemistry (X), having an influence on the thermal indices measured in literature, has progressed and/or changed. In some cases thermal history has to be reconsidered completely. This was obligatory for some basins sampled in the presented study: Stadler and Teichmüller (1971) versus Büker et al. (1995), Rahn et al. (1995) versus Ferreiro Mählmann et al. (2012a), Suchý et al. (1997) versus Árkai et al. (2002); or Hower and Rimmer (1991), Spötl et al. (1998) versus Ruppert et al. (2010). New genetic interpretations on the organic matter evolution and the controlling factors (P, T, t, D, X) rose up also instantaneous to the publications on the vitrinite and vitrinite like bitumen reflectances in the past, thus "not allowing previous models to be used" (Vigneresse, 1993). The knowledge in the petrologic fields has increased also since 1993 and at least new mineralogical calibrations and empirical temperature estimations have to be adapted to the maturity determination. In the diagenesis and very low-grade to low-grade metamorphism many P–T–X–t stability fields of facies indicative minerals have been recalculated, better kinetically expressed or also thermodynamically constrained (Frey and Robinson, 1999). In the presented study the thermal maturity determined using vitrinite reflectance will be compared to petrologic mineral and geochemical data to assess thermal or diagenetic to metamorphic grade and used for correlations with vitrinite like bitumen reflectance.

Illustrating maturity data in a map or determination of thermal maturity in drillings is fundamental for the exploration of the hydrocarbon potential of sedimentary basins and tectonically inverted basins such as found in orogenic belts. The second basin type is economically increasingly important in accretional wedges; thus a better understanding of the factors P–T–t–D–X on the maturity progress is needed (e.g. Sakaguchi, 1999; Allen and Allen, 2013). Some organic matter reflectances together with clay mineralogical indices are presently used as principal tools for mapping regional variations in maturation and establishing a zonation of diagenesis and low-grade metamorphism (for a review see Ferreiro Mählmann et al., 2012a,b). Heating rocks with or nearly without elevated pressure "leads to systematic changes in its" (organic matter) "structure, bulk composition and molecular geochemistry. These changes are routinely used in the petroleum industry to evaluate the thermal history of petroleum source rocks and crude oils" (Robert, 1988; see also Polissar et al., 2011). The maturity of organic matter reflects the integrated time-temperature-pressure genesis during rock diagenesis and metamorphism (Le Bayon et al., 2011).

Economically important "deadlines" and thresholds of hydrocarbons occur in the anchizone (main metamorphic range of grade studied in the present paper and defined by the illite Kübler-Index (Frey and Robinson, 1999; Ferreiro Mählmann et al., 2012a,b and references therein). For example in this zone, the natural gas deadlines (wet gas/dry gas) correlate with certain hydrothermal deposits (e.g. Houseknecht and Spötl, 1993) and with formation limits of intra-formational thermally altered mineral and organic material concentrations as of course anthracite deposits.

In petroleum industry exploration now also takes place in deep shelf areas and in internal orogenic settings of mountain belts (Ganser, 2012). Hydrostatic overpressure and lithostatic pressure have to be considered in these tectono-sedimentary regimes in terms of subnormal gradients (Schlumberger, 2015). In recent time some hydrocarbon blowouts were reported to have its origin in underestimating pressure in the reservoir but also the factor pressure on the production of hydrocarbon volatiles has to be considered (hyper-pressured gas).

It is known that optical properties of organic matter are pressure dependent, e.g. for vitrinite see Chandra (1964), Dalla Torre et al. (1997) or (Le Bayon et al., 2011), and for alginite and bitumen see e.g. Price and Wenger (1992), Ferreiro Mählmann (1995, 1996) and Carr et al. (2009). The recognition of characteristic optical changes is used to predict different lithostatic pressure conditions.

The chemical kinetics that governs maturation (mostly expressed as thermal maturation) is still thought to be strongly temperature dependent (e.g. Polissar et al., 2011). Because the organic reactions of aromatisation and the release of aliphatic molecules are irreversible it is believed that maturation indices measured are extremely sensitive to peak temperatures (Stach et al., 1982; Frey, 1987; Taylor et al., 1998). In the case of vitrinite it is evidently demonstrated that vitrinite reflectance is at least not only temperature and time dependent (reaction time at near peak temperatures), but also from the rate of the temperature and pressure increase (Le Bayon et al., 2011, 2012a,b; Le Bayon, 2012). Kinetics for vitrinite reflectance (VR) increase is much better known than for bitumen reflectance (BR), expressed both in $\%R_{max}$. It is thought that the application of BR shows "substantially lower R_r- and R_{max}-limits compared to vitrinite. Only speculations were possible because neither ultimate nor structural analyses exist for this maceral" (Koch, 1997). The upper limit of the R_{max} BR measurement method was postulated at 5.0% (Buchardt and Lewan, 1990; Koch, 1997) but discussed by Ferreiro Mählmann (1994, 1995), Ciulavu et al. (2008), and Ferreiro Mählmann and Giger (2012) showing that in some cases BR may indicate accurate maturity determinations in the range between VR 1.0 to 8.0 $\%R_{max}$. In this paper a systematic study will be presented.

Until the formation of a three-dimensional crystal structure (mineralogical graphite), organic matter is thermodynamically metastable. Hence devolatilization and decomposition with concomitant increase in reflectivity of the persisting vitrinite is a complex rate process depending on many variables (Franklin, 1951; Teichmüller and Teichmüller, 1954). Because organic matter maturation is best described by multiple reaction pathway kinetics that are sensitive to heating rate (Burnham and Braun, 1989; Burnham and Sweeney, 1989; Sweeney and Burnham, 1990) and probably pressure (Le Bayon et al., 2011; Ferreiro Mählmann et al., 2012a) the results are considered as a first approximation.

Comparing VR and BR/VlBR including "solid bitumen" according to Jacob (1967) some frequently used equations in very low-grade studies are presented, but do not consider the complete coalification range from peat to graphite:

$$VR\%R_r = 0.618 * BR\%R_r + 0.4, BR\%R_r = \%R_o - \text{solid} \quad (1)$$

(Jacob, 1967)

$$VR\%R_r = (BR\%R_r + 0.41)/1.09 \quad (2)$$

(Landis and Castaño, 1995)

$$BR\%R_{max} = -0.519 + 1.341\ (VR\%R_{max}) - 0.0977(VR\%R_{max})^2 + 0.0151(VR\%R_{max})^3. \quad (3)$$

(Ferreiro Mählmann, 1994; Ferreiro Mählmann and Frey, 2012)