International Journal of Coal Geology 150–151 (2015) 74–119

Contents lists available at ScienceDirect

International Journal of Coal Geology

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

Optical thermal maturity parameters and organic geochemical alteration at low grade diagenesis to anchimetamorphism: A review

Christoph Hartkopf-Fröder [a,*], Peter Königshof [b], Ralf Littke [c], Jan Schwarzbauer [c]

[a] Geological Survey North Rhine-Westphalia, De-Greiff-Straße 195, 47803 Krefeld, Germany
[b] Senckenberg Research Institute and Natural History Museum, Senckenberganlage 25, 60325 Frankfurt am Main, Germany
[c] Energy and Mineral Resources Group (EMR), Institute of Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Lochnerstraße 4–20, 52056 Aachen, Germany

ARTICLE INFO

Article history:
Received 6 November 2014
Received in revised form 14 June 2015
Accepted 15 June 2015
Available online 19 June 2015

Keywords:
Vitrinite
Conodonts
Palynomorphs
Invertebrates
Thermal maturity
Organic geochemical alteration

ABSTRACT

Sedimentary organic matter derives from biological precursor material which undergoes systematic, irreversible changes upon burial which mainly reflect increasing diagenetic temperatures, although other factors have also an influence. Several parameters have been established in the last decades to determine the palaeotemperature history of sedimentary rocks based on geochemical or petrographical methods. Organic matter is the most temperature-sensitive solid constituent in sedimentary rocks and vitrinite reflectance (VR), miospore and conodont colour alteration are among the most widely used optical maturity parameters. Despite tremendous interest in estimating maturity parameters in the oil generation zone as well as for high grade diagenesis and metamorphism and despite decades of research only a few of these methods have been well established and compared to each other by now. The focus of this review is on some new aspects with respect to organic matter maturation and optical palaeotemperature parameters, especially for high grade diagenesis and anchimetamorphism. Such a discussion might be a prerequisite for a better understanding of palaeotemperature assessments in different sedimentological and/or geotectonic settings and useful for different fields in applied sciences. Furthermore, suggestions for further research are discussed.

1. Introduction

During the last decades, reconstruction of palaeotemperature histories of sedimentary rocks has become an important discipline in earth sciences, which is widely applied in petroleum exploration. Whereas the present-day temperature regime in sedimentary basins can be studied on the basis of borehole temperatures or temperature logs, the reconstruction of palaeotemperature evolution is more difficult. In many sedimentary basins, present temperatures are much lower than ancient temperatures and the state of the rocks with respect to e.g. petroleum generation and compaction was established during earlier geologic eras at higher temperatures. Especially for these basins, understanding of the palaeotemperature histories is critical and a prerequisite when quantifying diagenesis or modelling petroleum generation.

However, palaeotemperature reconstructions are essential not only for basins and sedimentary rocks which experienced their highest temperatures in the past, but also for those in which Neogene temperatures are the highest. This is because early temperature evolution will have already influenced mineral precipitation and oil or gas generation from source rocks. The knowledge of the extent of such an early phase of generation can be a clue towards an understanding of the extent of the late (Neogene) phase of generation in different parts of a basin and thus an aid in petroleum exploration strategies.

The irreversible changes of organic matter reflect to a great extent the increasing diagenetic temperatures (e.g. Price, 1983), although other factors such as microbial degradation (at shallow depth) and pressure have also an influence. The temperature-related changes can be measured using a variety of optical and chemical maturity parameters. Maturation is a term commonly used in sedimentary basin studies to address thermally induced changes in the nature of organic matter. Maturation reflects organic matter conversion including petroleum generation and thermal gas generation. The driving force is the difference in free energy ($-\Delta G$) between the reactant (immature organic matter) and the product (mature organic matter; see Atkins and de Paula, 2010). Therefore, maturation depends mainly on temperature and the time, during which specific temperatures are maintained. Other factors such as the chemical environment and pressure are generally regarded to be of lesser importance, although there may be exceptions (Carr, 1999; Huang, 1996; Price and Barker, 1985).

The correlation of optical measurements and maturity is based on the thermodynamically driven changes of the molecular composition.

---

* Corresponding author.
E-mail addresses: hartkopf-froeder@gd.nrw.de (C. Hartkopf-Fröder), Peter.Koenigshof@senckenberg.de (P. Königshof), ralf.littke@emr.rwth-aachen.de (R. Littke), jan.schwarzbauer@emr.rwth-aachen.de (J. Schwarzbauer).

http://dx.doi.org/10.1016/j.coal.2015.06.005
0166-5162/

This linkage is obvious especially for the systematic changes of the organic matter. Optical properties in the range of UV and visible light are related to the bond configurations and the corresponding quantized energy levels of the valence electrons. Highly unsaturated and conjugated systems and in particular aromatic moieties, both with delocalized π-electron systems, build up chromophores in the visible light range. With increasing temperature a higher tendency to form aromatic systems of higher cyclization degree can be observed in natural organic matter. A higher aromatic cyclization degree results in a lower energy range of absorption. Hence, with increasing temperature and corresponding increasing aromaticity a shift in visible light absorption from the high energy range to the lower energy range has to be expected. For predicting the colour changes with temperature two further factors have to be considered: the complementary colour system affecting human colour perception and the superimposition of different colours resulting from lower and higher energy absorption at a later stage of maturity. Regarding all these aspects, a shift from light yellow colour towards orange tones at initial state followed by red/brown to dark colour tones resulting from the ongoing superimposition of colours can be expected. In the same way, also fluorescence properties are affected systematically by the changes of the molecular composition with increasing temperature.

In order to quantify thermal maturation of sedimentary rocks, a great number of optical, other physical and chemical maturity parameters have been developed. All these parameters are measured either on total organic matter or parts of the organic matter. Table 1 gives an overview on some of the most common parameters used and their application. The most widely used parameters in the petroleum industry are vitrinite reflectance, miospore colour, and T_{max} values. Furthermore, molecular geochemical parameters are applied, which are especially useful in oil–oil and oil–source rock correlations.

Many of the maturity parameters listed in Table 1 (based on a compilation by Littke et al., 2008a) have been developed for the oil generation zone. Usually, the main zone of oil generation is defined to range from about 0.5–0.6% VR_r (random vitrinite reflectance; oil birth line; Rullkötter et al., 1988) up to 1.3% VR_r (oil death line). It should be noted, however, that petroleum generation depends as well on kerogen type. For example, sulphur-rich kerogen can generate (heavy) bitumen already at low temperature and maturity (Orr, 1986). In terms of maturation stages kerogen in the main zone of oil generation is defined as mature (oil window), below 0.5–0.6% VR_r as immature, between 1.3% VR_r and 2.0% VR_r as postmature and above 2.0% VR_r as overmature (Table 1). In coal petrography, often the term "coalification" is used describing the evolution of peat towards lignite, subbituminous coal, bituminous coal, anthracite and finally meta-anthracite.

Based on organic maturation, an ever increasing number of parameters have been developed over the last decades, providing insights into temperature histories or maximum palaeotemperatures that sedimentary rocks experienced (Harris and Peters, 2012; Peters et al., 2005; Suárez-Ruiz et al., 2012; Taylor et al., 1998). Among optical maturity parameters, vitrinite and huminite reflectance are most commonly used. However, optical and chemical properties of other macerals, palynomorphs, and microfossils with organic compounds embedded in their shell/skeleton, and molecular composition of bitumen also serve as parameters of maturity (Table 1). More parameters have been proposed, e.g. colour changes in foraminifera tests (Foraminifera Colouration Index, FCI, e.g. McNeil et al., 1996), ostracod shells (e.g. Kontrovitz et al., 1992), conchostracan valves (Tasch, 1982), other arthropod cuticles (Bartram et al., 1987), and in ichthyoliths (e.g. Johns et al., 2012). In addition, colour changes induced by the effect of heat have been reported from other fossil groups e.g. thecamoebians (McNeil et al., 2000), microbivalves, microgastropods (Ainsworth et al., 1990), and amniote eggshells (Janssen et al., 2011). However, due to the scarcity of these fossils or because their potential as palaeogeothermometer has not yet been elucidated in detail they have not found application in thermal maturity studies. Furthermore, colour alteration of calcareous shells must not inevitably be coupled with high temperatures but may be a taphonomic indicator for longer exposure times before burial (Kolbe et al., 2011). For the oil window, the change in optical properties of vitrinite/huminite, solid bitumen, conodonts, graptolites, acritarchs and algae/alginite, miospores (spores and pollen grains)/sporinite, chitinozoans and scolecodonts has been investigated partly in great detail (e.g. Bertrand, 1990a; Bertrand and Malo, 2012; Epstein et al., 1977; Goodarzi and Norford, 1985; Hoffknecht, 1991; Petersen et al., 2013; Schoenherr et al., 2007; Staplin, 1969; Taylor et al., 1998).

Many cross-correlation charts have been published showing various organic maturation indicators such as vitrinite reflectance (VR), conodont colour alteration (CAI), miospore colour (TAI, SCS, SCI), miospore fluorescence, often in correlation with hydrocarbon generation (e.g. Batten, 1996b; Harris et al., 1987; Kovács and Árkai, 1987; Traverse, 2008; Taylor et al., 1998). These charts offer a rough correlation of thermal maturity parameters, but are usually limited to few indices. A perfect correlation cannot be reached, because the progress of the various chemical and physical changes follows different kinetics.

Generally correlation between different methods is difficult, particularly in defining the transition between diagenetic to anchizone. After Kovács and Árkai (1987) the transition between diagenesis and anchizone corresponds to CAI 5. A comparative study of CAI and illite crystallinity (IC) by García-López et al. (1997) proposes that the transition between diagenesis and anchizone (180–230 °C, e.g. Kisch, 1990; Frey and Robinson, 1999) corresponds to CAI 4, and the transition between anchi- and epizone (280–320 °C after Bucher and Frey, 1994) occurs at about CAI 5.5. Kovács and Árkai (1987) have correlated CAI and IC in a petrologically heterogeneous set of metamorphic rocks from Hungary. They correlate the transition from diagenesis to anchizone with CAI 5, i.e., with a higher CAI than by García-López et al. (1997).

The purpose of this paper is to review the extensive data on the most useful optical palaeotemperature parameters determined taking particularly also high grade diagenesis to anchimetamorphism into account which has been investigated much less than low grade diagenesis/oil window stage. Also chemical composition and structure of organic matter are treated to some extent, especially in relation to changes in optical properties. Although there exists a huge number of publications dealing with different aspects mentioned above, several open questions still remain which will be addressed.

2. Palaeotemperature parameters

2.1. Vitrinite and solid bitumen reflectance in comparison to geochemical maturity parameters and fission tracks

Arguably the most accurate way to reconstruct temperature histories in the context of sedimentary basin history is numerical modelling (basin and petroleum system modelling; e.g. Littke et al., 2008b). Clearly, the quality of model predictions on palaeotemperature, maturation, petroleum generation etc. depends on the availability of temperature-sensitive data and parameters, which can be used for calibrating these models. The most widely used of these parameters is vitrinite reflectance. Vitrinite is a group of organic particles derived from higher land plants ("wood-like particles", "huminite" in lignites) which are the major constituents of most coals, but also ubiquitous in other sedimentary rocks. Its chemical properties as well as its reflectance change systematically with increasing burial temperatures. Vitrinite reflectance was originally measured on coals, where vitrinite is the most abundant, usually predominant constituent. Later, vitrinite was found to be common in other sedimentary rocks as well, especially in dark-coloured siltstones, sandstones, marlstones and shales. This abundance allowed a wider application as maturity parameter predicting e.g. the stage of oil generation for petroleum source rocks. In particular, it served as calibration tool in numerical modelling of thermal histories of sedimentary basins. The basics of vitrinite reflectance are described in detail in