Raman spectroscopy of dispersed vitrinite — Methodical aspects and correlation with reflectance

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Nils Keno Lünsdorf

Georg-August-University Göttingen, Geoscience Center, Department of Sedimentology and Environmental Geology, Goldschmidtstraße 3, D-37077 Göttingen, Germany

ABSTRACT

Raman spectroscopy of dispersed vitrinites needs polished surfaces to safely identify organic particles in whole rock samples. Carbonaceous matter (CM) is very sensitive to the polishing process which leads to erroneous Raman spectra of these materials. It is unknown to which extent Raman spectra of low ordered CM are influenced by the polishing process. Therefore, vitrinites of high volatile bituminous coal, through anthracite to semi-graphite rank to graphitic CM were analyzed by multi-wavelength Raman spectroscopy and measured for minimum and maximum reflectance. A step-wise preparation and measuring protocol allows us to access at which point the Raman spectra are altered by sample preparation. The effect of polishing on the Raman spectra of vitrinites is not significant up to maximum reflectance values of ~7%. The multi-wavelength approach shows that short-wavelength lasers (488 nm and less) invoke far less fluorescence background than long-wavelength lasers, which permits us to measure very low mature vitrinites. Wavelength-dependent frequency shifts in the vitrinite Raman spectra reconstruct a two stage evolution of aromatic compounds during organic metamorphism. The first stage shows a wavelength independent downshift of the defect-band (D-band) from ~1370 to 1330 cm^{-1}, which is assumed to be related to the progressive growth of linear aromatic structures. The second stage is characterized by diverging D-band positions, which is caused by the growth of compact polycyclic aromatic hydrocarbons. Consequently, a strong linear correlation between the reflectance values and the derived Raman spectroscopic parameters was found. Because the comparison was conducted on the single grain level, it is shown that the scaled total area (STA) Raman parameter relates to the true maximum vitrinite reflectance. Thus, a linear and robust maturity index, which covers a maximum vitrinite reflectance range of ca. 1 to 7%, is established.

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1. Introduction

Raman spectroscopy of carbonaceous material (RSCM) indicates the degree of organic metamorphism (Wopenka and Pasteris, 1993; Yui et al., 1996) and is an empiric geothermometer (Beyssac et al., 2002; Rahl et al., 2005; Aoya et al., 2010; Lahfid et al., 2010) that is used to infer the maximum metamorphic temperature (Beyssac et al., 2007; Wiederkehr et al., 2008; Wiederkehr et al., 2011). RSCM is also used to characterize disordered CM (Ferrari and Robertson, 2001) and already Spötl et al. (1998), Keleman and Fang (2001) and later Liu et al. (2013) noted that maturity trends in kerogen and coal were reflected by their Raman spectra. Guedes et al. (2010, 2012) analyzed maturity trends in different coal macerals by Raman spectroscopy and recently, Hinrichs et al. (2014) correlated coal rank parameters to RSCM data. However, there are some analytic pitfalls which must be considered, i.e. thermal alteration of CM during measurement, structural defects due to polishing, orientation effects, spectral curve-fitting strategy, wavelength dependent Raman band dispersion, etc. (Wang et al.,

1990; Wopenka and Pasteris, 1993; Matthews et al., 1999; Beyssac et al., 2003; Lünsdorf et al., 2014). As outlined above, RSCM has the potential to be used as a maturity parameter. Therefore, a methodical framework for the correlation of dispersed vitrinite reflectance and Raman spectroscopy is established by observing factors that influence the shape of the Raman spectrum on samples that experienced increasing coalification and graphitization. The observed factors are 1) the effect of polishing on the Raman spectrum, 2) the wavelength dependent Raman band dispersion and 3) the effect of fluorescent background signal.

Polishing has a major impact on the Raman spectrum of CM (Beyssac et al., 2003; Ammar and Rouzaud, 2012). This is because organoclasts and graphite usually have a high opacity and thus, the penetration depth of the laser light during Raman measurements is very shallow (<1 μm) causing the gained Raman information to be exclusive for the sample surface (McCreery, 2000). Because grinding and polishing especially affect the graphite lattice at the surface, i.e. by shearing off or crumpling of graphene layers or promotion of dislocations, the Raman spectrum does not reflect the pristine sample signal. To avoid erroneous measurements, usually CM beneath a translucent mineral is analyzed (Beyssac et al., 2003) or chemical separation can be applied (Rantitsch

E-mail address: kluensd@gwdg.de.

et al., 2004). However, textural information is lost during this process. In the case of dispersed organic matter (DOM), polished surfaces are needed to locate and identify the organoclasts in the mineral matrix and as the majority of DOM is hosted in (meta-) pelitic rocks (Vandenbroucke and Largeau, 2007) the probability of finding the required geometry is very low. Thus, it is firstly important to know if polishing has an effect on the Raman spectrum of CM of diagenetic pressure and temperature conditions and secondly at which stage during organic metamorphism or sample preparation it becomes significant. Therefore, dispersed vitrinites of a sample set that spans diagenetic to blueschist facies conditions were analyzed by multi-wavelength Raman spectroscopy and measured for maximum and minimum reflectance. To follow the spectral evolution during the step-wise abrasion and polishing procedure, the location of each vitrinite in each sample was noted and the spectral evaluation was carried out by automated curve-fitting (Lünsdorf and Lünsdorf, 2014) to handle the large data amount and to reduce the spectral analysis bias (Lünsdorf et al., 2014).

The used laser wavelength has prime influence on band positions and band intensity ratios in the Raman spectrum of CM (Vidano et al., 1981; Wang et al., 1990; Pócsik et al., 1998; Ferrari and Robertson, 2001) and further determines the fluorescence response of the sample. In aromatics the energy gap of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases with the extent of delocalized electrons and thus decreases with the increasing size of the observed aromatic system (Ruiz-Morales, 2002; Castiglioni et al., 2004). Therefore, resonance and pre-resonance spectra are recorded when the energy gap matches or is close to the laser energy. The multi-wavelength approach revealed a two stage evolution of Raman band dispersion during coalification and graphitization which is related to the size and structure of aromatic compounds in vitrinite and discussed on the basis of molecular models of vitrinite (Mathwes et al., 2001). As the reflectance of vitrinite is also controlled by its aromaticity (Carr and Williamson, 1989) a strong linear correlation between the maximum vitrinite reflectance and the scaled total area (STA) Raman parameter is observed. The characterization of the methodical aspects allows us to formulate a methodical approach to the use of STA-RSCM as a rank indicator.

1.1. Molecular evolution during coalification and graphitization

The primary precursor of kerogen III or vitrinite is lignin (Hatcher, 1990; Hatcher and Clifford, 1997), a polymer of glyceryl methoxyphenol units (Faulon et al., 1994). Thus, in vitrinite and vitrinite rich coals lignin is the major source for aromatic compounds (Hatcher, 1990). Hatcher (1990) suggested that coalification up to the stage of sub-bituminous coal modifies lignin in a series of reactions to form phenols and these react further to diaryl ethers. These reactions are accompanied by a loss of O-bearing groups like –COOH, CO_2 and H_2O (dehydration stage after Levine, 1993), and depolymerization of the macromolecular organic matter. According to Oberlin and Bonnamy (2013) the depolymerization or 'softening' transforms the organic matter into a more or less viscous suspension in which the heavier molecular fragments or basic structural units (BSU) are dispersed in the lighter molecular units. The concept of BSUs or aromatic 'bricks' (Oberlin et al., 1974) and their evolution during artificial and natural maturation were already proposed by Oberlin et al. (1974, 1975a,b), Rouzaud et al. (1983), Beny-Bassez and Rouzaud (1985) and Oberlin (1989). A more recent definition is given in Oberlin and Bonnamy (2013) which states that BSUs are stacks of 2–3 polycyclic aromatic hydrocarbons (PAH) with a size of 0.7 to 1.5 nm. The best model for a BSU is a saturated tri-coronene- or tri-ovalene-like substance (Oberlin and Bonnamy, 2013). It is important to note that a BSU is not equivalent to coronene or ovalene, but can be envisioned as a compound with a hexagonal core saturated at the edges with hydrogen and functional groups (Oberlin and Bonnamy, 2013). Considering this model, the BSUs are probably formed at the rank of sub-bituminous coal. For this rank and

up to low volatile bituminous coal Kruge and Bensley (1994) showed that mono-aromatic units, likely stemming from the lignin, diminish while tri- to tetra-aromatic compounds increase in quantity especially pronounced at about 0.9% R_{max}. Up to this stage, which is equivalent to the bituminization stage after Levine (1993), the BSUs are randomly oriented. At the point of maximum hydrocarbon generation, the BSUs rearrange to form domains of local molecular orientation (LMO) in which the BSUs form columnar arrangements (Oberlin et al., 1999) with a tilt and twist misorientation of the BSUs inside a LMO of 20 to 40° (Oberlin and Bonnamy, 2013). The size and growth of a LMO depend on the balance of hydrocarbon moieties and cross-linking heteroatoms like oxygen and sulfur in the CM (Oberlin et al., 1999; Oberlin and Bonnamy, 2013). Thus, a high oxygen concentration poses a hindrance on the mobility of a BSU which leads to smaller LMOs (~50 Å for Kerogen III and >1000 Å for Kerogen I). During the debituminization stage (Levine, 1993) the concentration of aromatic CH-groups decreases, manifested as release of light weight hydrocarbons. This leads to "dangling" bonds, i.e. aromatic radicals, which allow the recombination of the BSU columnar stacks to form distorted layers. Further annealing gives rise to rapid ring condensation and the aromatic layers increase in size developing the bi-periodic, turbostratic ordering of anthracites (graphitization stage after Levine, 1993). According to Bonijoly et al. (1982) anthracites are microporous media characterized by a statistical long-range preferred orientation superimposed to the local molecular orientation. The long-range orientation results from the flattened pores with their walls being composed of distorted aromatic layers (see above). Following Bonijoly et al. (1982), Buseck and Huang (1985) and Bustin et al. (1995) natural graphitization of anthracites is a process driven by temperature and pressure, because the activation energy of thermal graphitization is too high to be realized by the natural geothermic gradient. Lithostatic pressure will promote the accumulation of shear stress, and thus strain energy, at the boundaries between two distorted aromatic layer stacks and at the pore-wall boundaries (Bonijoly et al., 1982). The increased strain energy leads to the rupture of pore-walls, which promotes the mechanical reorientation and alignment of the aromatic units and thus will facilitate the reduction of defects by diffusion, elimination of bonding vacancies and annealing of aromatic sheets to form triperiodic graphite (Bustin et al., 1995).

1.2. CM Raman spectra during coalification and graphitization

Following the discussed molecular evolution of CM to graphite, the 'graphite-island' model or molecular approach after Negri et al. (2002, 2004) and Castiglioni et al. (2004) is a reasonable approximation to the above outlined structural evolution through coalification. These authors follow the idea that PAHs are molecularly defined graphite sub-units (Negri et al., 2004), which fits well with the observed BSUs that are supposedly build up of PAHs (Oberlin, 1989; Oberlin et al., 1999; Oberlin and Bonnamy, 2013). In the first order region (up to ~2000 cm^{-1}) of the Raman spectrum of CM, two main bands appear at 1582 cm^{-1} and at about 1350 cm^{-1}. The first one is named G-band, after graphite, and is due to a doubly degenerate phonon mode of E_{2g} symmetry (Tuinstra and Koenig, 1970; Reich and Thomsen, 2004; Pimenta et al., 2007), which is the in-plane vibration of the carbon atoms in the graphene sheet. In the case of perfectly crystalline graphite, this is the only Raman active vibration recorded by most Raman systems. The other E_{2g} mode at 42 cm^{-1}, which is the relative sliding of the graphene sheets (Reich and Thomsen, 2004), is often blocked by the filter system. The band at about 1350 cm^{-1} is not present in perfect graphite, but is recorded when the graphite becomes disordered, hence it is termed D-band. Its frequency depends on the used excitation wavelength (Vidano et al., 1981, Wang et al., 1990). Currently two models explain the origin and energy dependence of the D-band. In the solid state model (Reich and Thomsen, 2004) a double resonant Raman scattering process (Pócsik et al., 1998; Thomsen and Reich, 2000; Maultzsch et al.,