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Optical characteristics of graptolite-bearing sediments and its implication for thermal maturity assessment

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ABSTRACT

Graptolite reflectance was thought to be one of the most useful thermal maturity indicators for graptolite-bearing sediments, however, the relationship between graptolite reflectance and vitrinite reflectance is not well-established. Graptolites, especially in the Wufeng–Longmaxi Formations from the Ordovician to Silurian of South China, have been mistaken for vitrinite-like particles or solid bitumen, which results in inconsistent data on the thermal maturity. In this paper, we have employed optical microscope techniques to describe the detailed optical characteristics of graptolites and solid bitumen in the Wufeng–Longmaxi Formations. Laboratory simulation of maturation was used to determine the relationship between graptolite reflectance and vitrinite reflectance.

The organic constituents in the Wufeng–Longmaxi Formations are mainly composed of graptolites and solid bitumen. Granular and non-granular graptolites were observed in the Wufeng–Longmaxi Formations, with non-granular as the most common texture. Solid bitumen can be distinguished from non-granular graptolites by its coarse surface, weaker anisotropy, and lower random reflectance. The combination of non-polarized and polarized light is very helpful to distinguish solid bitumen from graptolite. For comparison, organic material from the early Ordovician Alum Shale Formation of Sweden and Estonia was also studied. The macerals of the Alum shales are mainly composed of lamalginites, mineral-bituminous groundmasses, graptolites, and solid bitumen. The major textures of the graptolites in the Sweden and Estonia sediments are non-granular and granular, respectively.

Both non-granular graptolite and vitrinite reflectances display a systematic increase with the increase of heating temperature and time. The granular graptolites in the Estonian sample were gradually changed to non-granular graptolites following laboratory simulated maturation, indicating that granular graptolites can transform into non-granular graptolites with maturation. Solid bitumen in the Wufeng–Longmaxi Formations was derived from the solid residue of kerogen and/or post-oil bitumen. The graptolite random reflectance is a better thermal maturity indicator than graptolite maximum reflectance and is more precise due to the smaller standard deviation. Several equations are proposed to determine the thermal maturity of the graptolite-bearing sediments based on graptolite random reflectance, graptolite maximum reflectance and solid bitumen random reflectance.

1. Introduction

The thermal maturity is of great importance to hydrocarbon exploration in the conventional and/or unconventional systems, and vitrinite reflectance is generally thought to be the most robust thermal maturity indicator for post-Devonian rock sequences (Stach et al., 1982; Hackley and Cardott, 2016; Luo et al., 2016, 2017b). The reflectance of bitumen, zooclasts and vitrinite-like particles has been widely used to evaluate the thermal maturity in pre-Devonian rocks lacking vitrinite (Kurylowicz et al., 1976; Teichmüller, 1978; Clausen and Teichmüller, 1982; Goodarzi, 1984, 1985; Goodarzi and Norford, 1985; Goodarzi et al., 1985; Bertrand and Heroux, 1987; Goodarzi and Higgins, 1987; Goodarzi and Norford, 1987, 1989; Bustin et al., 1989; Jacob, 1989; Riediger et al., 1989; Bertrand, 1990; Buchardt and Lewan, 1990; Goodarzi et al., 1992a,b; Landis and Castaño, 1995; Zhong and Qin, 1995; Xiao et al., 2000; Suchý et al., 2002; Schoenherr et al., 2007;

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Petersen et al., 2013; İnan et al., 2016; Lavoie et al., 2016; Luo et al., 2016, 2017b). Graptolites, chitinozoans, and scolecodonts were present in the Lower Palaeozoic rocks, and their optical properties have been widely studied, which indicates that graptolite reflectance is more suitable to determine the organic maturity due to their greater abundance (Bertrand, 1990; Tricker et al., 1992; Cole, 1994; Petersen et al., 2013).

The relationship between graptolite reflectance and vitrinite reflectance is not well-established. Goodarzi and Norford (1989) indirectly correlated the graptolite maximum reflectance with vitrinite reflectance using conodont alteration indices (CAI) and described that vitrinite has a lower reflectance value than graptolite for the same CAI. The graptolite maximum reflectance falls between 0.7% and 1.7% for the oil window (Goodarzi et al., 1992a; Gentzis et al., 1996). However, Bustin et al. (1989) alternatively suggested that the graptolite reflectance is close to the vitrinite reflectance based on laboratory simulated maturation, which is consistent with the results of Bertrand (1990). At low thermal maturity, the vitrinite reflectance is greater than that of graptolite, whereas at high maturity the graptolite reflectance is greater (Link et al., 1990). Zhong and Qin (1995) tried to establish the relationship between graptolite reflectance and equivalent vitrinite reflectance (EqVR$_o$) based on data from Chinese Lower Palaeozoic sediments. Recently, Petersen et al. (2013) and Synnott et al. (2018) determined a relationship between graptolite random reflectance and vitrinite random reflectance through the intermediate conversion of Rock-Eval T$_{max}$ values, and illustrated that the graptolite random reflectance is higher than vitrinite random reflectance.

The Wufeng–Longmaxi Formations are one of the most important graptolite-bearing sediments with high thermal maturity in China (Chen et al., 2000, 2004, 2005; Luo et al., 2016, 2017b), and have become the key exploration target for shale gas in China (Zou et al., 2011; Dai et al., 2014, 2016; Zou et al., 2016; Nie et al., 2018). However, the thermal maturity evaluation of the Wufeng–Longmaxi Formations has been a big problem due to lack of vitrinite (Luo et al., 2016, 2017b), with the bitumen or vitrinite-like particles generally used to determine the thermal maturity (Teng et al., 2006; Wang et al., 2009; Li and Li, 2010; Chen et al., 2011; Nie et al., 2012; Hu et al., 2017). The graptolite maximum reflectance was employed to assess the organic maturity by Luo et al. (2016, 2017b), who also described that the macerals measured in other studies might be primarily graptolites. The graptolites can be easily misidentified as bitumen or vitrinite-like particles due to poor polishing and uncertainties concerning the optical characteristics of graptolites (Luo et al., 2016, 2017b). The Alum shale is a widely studied graptolite-bearing sediment in Europe and contains abundant low-maturity graptolites (Petersen et al., 2013; Luo et al., 2017b).

In this study, the graptolite-bearing sediments of the Wufeng–Longmaxi Formations, the Pingliang Formation and the Alum Shale Formation from China, Sweden and Estonia were studied, and laboratory simulated maturation was conducted on low-maturity graptolite-bearing sediments and coals, in order to determine the correlation between graptolite reflectance and vitrinite reflectance, and the nature of the major organic components and their origin in the Wufeng–Longmaxi Formations.

2. Geological setting

During the Early–Middle Ordovician, intense tectonic compression resulted in the formation of marginal uplifts, which led to changes in depositional environments from an open ocean to an extensive semi-enclosed low-energy, anoxic environment in the studied area (Chen et al., 2004). During this time, organic-rich graptolite-bearing shales were extensively deposited on the Yangtze Platform (Chen et al., 2000, 2004, 2005; Mu et al., 2011). The Wufeng–Longmaxi Formations have been classified into 13 graptolite biozones in order to aid correlation between different locations, a division which is easy to use by non-palaeontogists (Chen et al., 2015, 2017). According to the graptolite biozones and geochemical characteristics, the *Dicellograptus complexus* Biozone (WF2), *Paraorthograptus pacificus* Biozone (WF3), and *Akidograptus ascensus* Biozone (LM2) to *Demirastrites triangulates* Biozone (lower part of LM6) were thought to be the best sediments for the shale gas exploration (Chen et al., 2015, 2017). The Wufeng–Longmaxi Formations are mainly composed of dark grey–black siliceous/carbonaceous shale, silty shale and dark grey argillaceous siltstone.

The Pingliang Formation was deposited in carbonate slope facies, with a mean thickness of 500 m, and is mainly comprised of shale, marlstone, limestone and siltstone (Sun et al., 2008). The total organic carbon (TOC) is low in the marlstones of the Pingliang Formation, with an average of 0.52%, and non-granular graptolites are major organic components in the Pingliang Formation (Luo et al., 2017b). The graptolite faunas in the Pingliang Formation belong to the *Climacograptus bicornis* zone (Lin, 1996).

The Alum Shale Formation is mainly composed of dark to black shales with minor limestone or sandstone layers (Nielsen and Schovsbo, 2006), which was thought to be deposited in an epicontinental sea with anoxic or euxinic conditions (Thickpenny, 1987). The graptolite-bearing Alum shales were mainly developed during the Tremadocian (early Ordovician *Rhabdinopora flabelliformis* zone). These shales are characterized by high TOC (up to 25 wt%), high hydrogen index, and abundant lamalginites and non-granular graptolites (Nielsen and Schovsbo, 2006; Petersen et al., 2013; Luo et al., 2017b). Detailed stratigraphic columns of the Wufeng–Longmaxi Formations, the Pingliang Formation and the Alum Shale Formation can be found in Figs. 3 and 5 in Luo et al. (2017b).

The graptolite-bearing Alum shale Formation (known also as the “Türisalu Formation”) in Estonia was deposited under shallow water (Hints et al., 2014). These sediments are mainly composed of massive dark brown kerogenous argillite and yield abundant graptolites and rare scolecodonts (Hints and Nõlvak, 2006).

3. Sampling and methods

A total number of 33 samples was collected from China, Sweden and Estonia. The Wufeng–Longmaxi shales were collected from Chongqing, Sichuan, Hunan, Hubei, Yunnan and Guizhou provinces (Fig. 1). The upper Alum Shale Formation (Tremadocian stage) was collected from Östergötland, Öland island, and Scania of Sweden (Fig. 4 in Luo et al., 2017b). One sample of Estonian Alum shale was collected from Pakerort section (Sample No. E1; Fig. 2). The accurate stratigraphic position could not be identified for the Alum shale samples.

The samples were cut perpendicular to bedding into blocks and were polished on a Buehler automatic grinding and polishing machine (EcoMet 250 with AutoMet 250) to give a smooth surface for the microscopic examination. The measurements of graptolite maximum reflectance (polarized light) and random reflectance (non-polarized light) were conducted on a Leica DM4500P reflected light microscope equipped with a CRAIC microscope photometer. The microscope was linearly calibrated with standard materials before measurement (Saphir 0.589% R$_o$, Gadolinium-gallium-garnet 1.725% R$_o$, Cubic zirconia 3.08% R$_o$, and Strontium Titanate 5.36% R$_o$). The number of readings was generally > 30 for the random reflectance and > 20 for the maximum reflectance (Malinconico, 1992; Luo et al., 2017b). The maceral observation was conducted under both reflected light and fluorescent light.

A coal of Carboniferous Shanxi Formation (sample No. ZJJ-C4), with a vitrinite reflectance of 0.56%, was selected to conduct the laboratory simulated maturation with graptolite-bearing sediments (samples No. E1 and AS-DD-LG). These three samples were cut into small blocks and were placed in the same vessel simultaneously and heated under the conditions as follows. The lithostatic pressure and hydrostatic pressure were set at 100 MPa and 50 MPa, respectively. The samples were heated at temperatures of 350, 400, 450, 500 and 550 °C