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Thermal Analysis of the Kerogen Rich Black Shales from the Upper Devonian in Kowala Quarry, the Holy Cross Mountains, Poland

Piotr ZIÓŁKOWSKI[1], Beata DĄBROWSKA[1], Sage MUTTEL[2], Dougles SYZDEK[2], Johnathan TORRES[2], Kelvin GOODINGS[2], and Janusz GRĘBOWICZ[2]

[1]University of Warsaw, Faculty of Geology, Warsaw, Poland

[2]University of Houston-Downtown, Natural Sciences Department, Houston TX, USA

✉ pziolkow@uw.edu.pl

Abstract

In-situ conversion process for recovery of hydrocarbons from shales requires heating the rock formation to 320°C in order to break down kerogen polymer into fragments small enough to permeate toward collection facility. Thermal analysis is essential for understanding the properties of shales as they change during heating to the target temperature (Grębowicz 2014). The study involved kerogen rich samples derived from the Late Famennian rocks representing global anoxic events: Annulata and Hangenberg. The Upper Famennian Annulata (ABS) and Hangenberg (HBS) Black Shales are exposed in the successions of the Kowala Quarry in the Holy Cross Mountains. The twin Annulata anoxic events are manifest as two organic-rich (TOC up to 23 wt.%), finely laminated black shales, each up to 0.6 m thick, separated by marl or nodular limestone layers (Racka *et al*. 2010). The sampled HBS succession (TOC c.a. 10 wt.%), is divided into seven layers, each being around ten to fifteen centimeters thick (Marynowski *et al*. 2012). For this study a thermomechanical analysis (TMA) and an analysis of anisotropy of magnetic susceptibility (AMS) vs temperature was used. Thermal expansion measurements were conducted in two different directions: perpendicular (vertical) and parallel (horizontal) to the layers from room temperature to 800°C at a rate of 10°C a minute. In AMS analysis samples was measured from room temperature to 600°C, taking measurements every 25°C. The expansion pattern (Fig. 1A) could be divided into three main temperature ranges: (1) low temperature: between 25 and 340–360°C (pre-pyrolysis), (2) transition range: 350–500°C, with the peak around 415–430°C (pyrolysis), and (3) high temperature: above 500°C (post-pyrolysis). Those three ranges are best seen in vertical measurements. At 450°C, overall increase of sample size has reached more than 30%. After passing the peak expansion, the samples quickly shrinks by about 10% at 500°C, followed by slow decrease in size until 800°C. AMS fabrics show typical sedimentary pattern with K_1 and K_2 axes in a bedding plane and a vertical K_3 (Fig. 1B). Magnetic susceptibi-

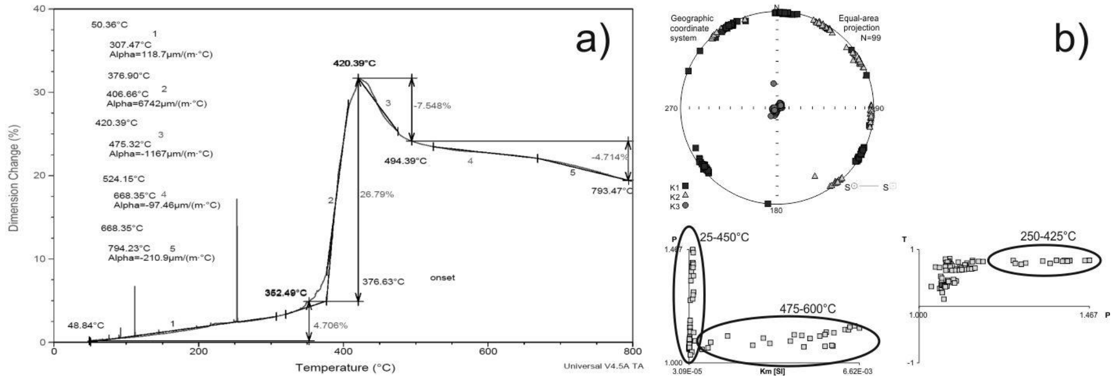

Fig. 1. (a) Thermal expansion results for the Annulata Black Shale sample (vertical), (b) AMS fabrics, P/K, and P/T diagrams for Annulata and Hangenberg Black Shale samples.

lity values at a room temperature ranges from 36 to 50 × 10^{-6} [SI] and the anisotropy degree (P) ranges from 1.05 to 1.09. After heating the anisotropy degree (P) rapidly rises between 250–425°C reaching the peak value (1.47) at 300–325 °C. During further heating (450–600°C) the anisotropy degree (P) falls to the previous values but magnetic susceptibility strongly increases up to 6.60 × 10^{-3} [SI]. This suggests the presence of iron sulphides and, after pyrolysis, the formation of superparamagnetic magnetite grains.

Keywords: oil shales, in-situ conversion process, thermomechanical analysis, anisotropy of magnetic susceptibility.

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