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Research paper

Effect of thermal events on maturation and methane adsorption of Silurian black shales (Checa, Spain)

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ABSTRACT

The present work is devoted to the study of the relationship among composition, properties and methane adsorption of selected Silurian black shales from the Bádenas Formation, located near Checa town (Spain). These outcropping samples were collected in a formation, which is not considered as target for shale gas exploration. The clay minerals are predominant in the whole-rock samples and mostly composed of illite (both potassium and ammonium phases), rectorite and pyrophyllite with subordinated kaolinite and chlorite. This peculiar mineralogical assemblage is related with burial and thermal events having affected the shales since their deposition. Differences in TOC (1.92–7.62 wt%), BET specific surface (27–34 m^2/g) and thermal maturity (Tmax of 459–484 °C) were observed prior to experimental adsorption. Excess adsorption isotherms for methane were measured on dry bulk samples at 30 °C, 50 °C and 80 °C, up to 3.5 (MPa) by the use of a combined manometric-calorimetric device. The maximum methane excess adsorption capacities within this pressure range varied from 0.021 to 0.168 mmol/g at 30 °C. TOC seems to be the primary factor affecting methane adsorption capacity but nonlinear regression of adsorption capacity with TOC content was observed. A modified Langmuir-type adsorption function, with a term taking into account the volume of the adsorbed phase, provide a good representation of the measured excess adsorption isotherms. Additionally, the heats of adsorption were found nearly constant, with an approximate value of 30 $kJ \cdot mol^{-1}$, indicating that physical adsorption process controls the adsorption of methane molecule to the shale samples.

1. Introduction

Shale gas exploration and production has become a major social issue because of the economic and environmental concerns. The estimation of these unconventional reserves suggests a huge potential, which could modify the oil and gas economy. A major issue is the estimation of the amount of gas contained in the reservoir (Gas In Place, GIP). The gas in the reservoir is at "free" state, in the pores and fractures, dissolved in fluids and at adsorbed state in the rock. This last part represents 50 to 60% (Gasparik et al., 2012) of the total gas in place (GIP), therefore adsorption is a leading criteria governing shale gas production. If the porosity controls the amount of free gas, the selective adsorption on solid surfaces is still waiting for a better understanding despite the increasing number of studies. The factors affecting methane sorption capacity of shales include: total organic carbon content (TOC), clay mineral content, organic matter type and thermal maturity, water saturation and temperature (Gasparik et al., 2012; Cao et al., 2015). Especially clay mineral content and TOC are critical and low-TOC clay-rich shales can show comparable or even higher methane sorption capacities than organic-rich shales (Schettler et al., 1991; Ji et al., 2012; Fan et al., 2014). Anyway, most of the studies reported in the very expanded literature, indicate that the organic matter is the primary component responsible for the methane adsorption in the shales. Many positive correlations were reported between the methane uptake and the TOC content (Ross and Bustin, 2008; Ross and Bustin, 2009; Weniger et al., 2010; Chen et al., 2011; Gasparik et al., 2012; Wu et al., 2015).

The role played by pore structure of shales and their kerogen on BET specific surface and CH4 adsorption has been recently reported by several authors (Kuila et al., 2014; Kennedy et al., 2014; Cao et al., 2015; Löhr et al., 2015; Yang et al. 2015), some of them showing evidences of organic matter nanopores (<100 nm) by means of high-magnification SEM images.

The relatively low adsorption capacity of shales (typically 10–20%) sets very high demands on the accuracy of measurements supporting the interest to study the relationships between the CH_4 adsorption capacity and other properties of shales. Therefore, the aim of the work is to provide simultaneously reliable experimental data of both methane sorption capacity and heat of adsorption on shale systems by means of a homemade manometric - calorimetric apparatus, operating under high pressure and high temperature conditions. Specific attention was performed to calibration standards and optimization of operator-

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defined experimental parameters through the usage of a standardized protocol. The study is focused on Silurian graptolite black shale samples outcropping in the Iberian Range from Central Spain. It is important to specify that these samples are not stemming for a zone of production. In this sense, the present work differs from the extended literature devoted to shale samples of production zone. The choice of the samples was dictated to obtain a set with significant differences in TOC and mineralogy. The following aspects were investigated in the present paper: 1) Characterization of the samples studied including mineralogy, chemistry, BET surface area, porosity parameters and Rock-Eval analysis. 2) Variation of uptake capacity for methane at 50 °C as a function of TOC richness and mineralogical assemblage. Application of a modified Langmuir approach to rationalize the data. 3) Determination of the adsorption heat to characterize the clay mineral-kerogen/methane interaction.

2. Materials and experimental methodology

2.1. Materials

Six samples named CH-0 to CH-5 were collected from Silurian pelitic to metapelitic materials outcropping near Checa town (Guadalajara province) in the Iberian Range from Central Spain (Fig. 1A). These rocks have a complex geologic history including several tectono-thermal events in relation with the superposition of Variscan and Alpine orogenies. The zone has been selected because it allows to study the interaction of experimental methane with shales modified by diagenetic to very low-grade metamorphic events or hydrothermal fluid circulations. This study relied on outcrop samples instead of cores; however, these samples are representative of a great extent in the zone of interest.

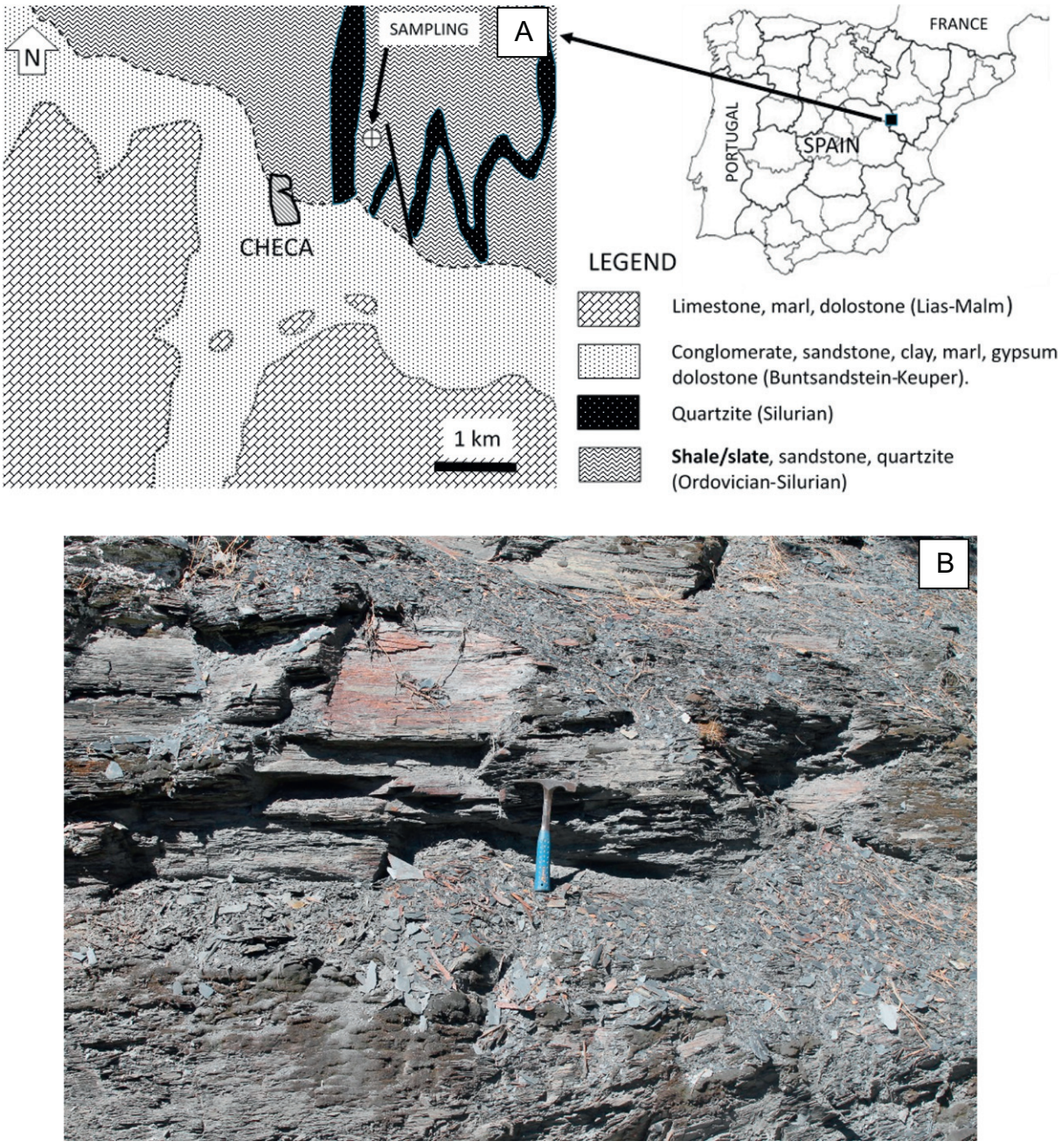

Fig. 1. A. Geological map and location of samples near Checa village (Guadalajara, Central Spain). B. Outcrop view of graptolite black shales showing lamination and incipient slaty cleavage affected by fractures.