



## Porosity at the interface of organic matter and mineral components contribute significantly to gas adsorption on shales

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### ABSTRACT

Using CO<sub>2</sub> as a shale fracturing fluid was proposed recently as an alternative to H<sub>2</sub>O fracturing, one of its advantages is enhanced recovery of CH<sub>4</sub>, which is based on the competitive adsorption of CO<sub>2</sub> and CH<sub>4</sub> on shales. Therefore, investigations on gas adsorption in shales are of great importance. Recent researches evidenced that organic matter (OM) in shale is the major control on its adsorption behavior, but in some cases, mineral components (MC) may also play a role. Herein, we focus on the alteration of porosity due to the presence of OM-MC interface and their influence on gas adsorption, these cannot be simply attributed to either OM or MC as frequently reported in the previous publications. In this context, OM from a shale sample was purified following reported methodology, while a universal procedure for extraction of MC was established. Further studies on the porosity and adsorption behavior were carried out on OM, MC, and shale, which were then compared with a hypothetical mixture (HM) from OM and MC bearing the same composition of shale. For the first time, we demonstrate experimentally the profound effect of porosity at the OM-MC interface on gas adsorption of shales particularly at temperatures more relevant to reservoir conditions. The current work deepened the understanding on gas adsorption of shale, and thus shed meaningful lights on related areas such as gas-in-place (GIP) estimation, CO<sub>2</sub> sequestration in shales, and particularly the utilization of CO<sub>2</sub> for enhanced shale gas recovery.

### 1. Introduction

Shale gas generates from biogenic and/or thermogenic processes of organic matter in shale plays, and thus shale is both the source and the reservoir for shale gas (in contrast to conventional natural gas) [1,2]. As a type of unconventional resource, exploration of shale gas develops rapidly in recent years particularly in north America and China. CH<sub>4</sub> in shale reservoir includes free gas (within pores, fractures, voids, etc.), adsorbed gas (enriched on shale surface due to adsorption), and dissolved gas (enriched in the bulk of bitumen, oil, and/or water) [3,4]. Among these, adsorbed gas accounts for 20–85% of the total gas, and thus showing paramount importance to the continual production of shale gas [5,6]. Normally, fracturing of the shale rock with H<sub>2</sub>O is needed to achieve economical production of shale gas, however, recent experience evidenced that the process is environmentally risky,

therefore using CO<sub>2</sub> as a fracturing fluid was proposed as an alternative with several advantages [7]. One very interesting feature of CO<sub>2</sub> fracturing is that CO<sub>2</sub> can be favorably adsorbed onto the surface of shale than that of CH<sub>4</sub>, which leads to enhanced recovery of the adsorbed CH<sub>4</sub>. In principle, the process is competitive adsorption of CO<sub>2</sub> over CH<sub>4</sub>, therefore related understandings are necessary to fulfill effective, beneficial, and large-scale of CO<sub>2</sub> utilization in the area.

In recent years, large efforts were made to investigate gas adsorption on shales, special focus included the effect of total organic carbon (TOC), maturity, mineral composition, and others [8]. For example, several groups have reported the increase of surface areas with the rise of TOC in different shale samples, and thus organic matter is regarded as the major control for gas adsorption [9,10]. On the other hand, Gasparik et al. measured CH<sub>4</sub> adsorption on a wide range of shale samples from Europe and US, a positive correlation between CH<sub>4</sub>

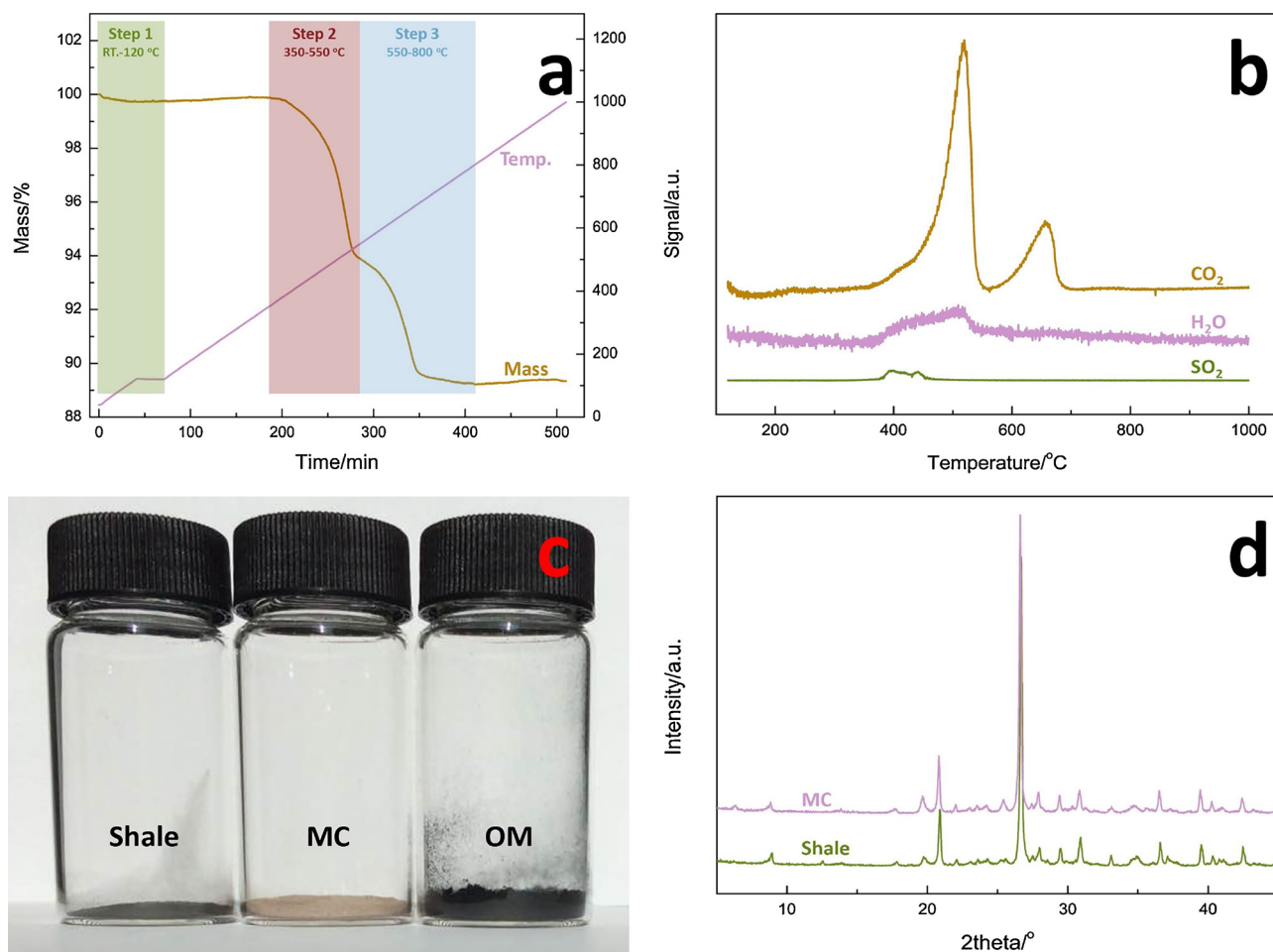
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**Fig. 1.** a) TG curve of shale in an air atmosphere. b) MS signal during TG analysis. c) Photograph of Shale, MC, and OM. d) XRD patterns of Shale and MC.

sorption capacities and TOC was observed, but great deviations from this trend was also noticed [11]. In their further work on analyzing high pressure CH<sub>4</sub> adsorption of shale from the Netherlands, no correlation of excess adsorption capacity with TOC was found, and low-TOC, clay-rich shales showed comparable or even higher CH<sub>4</sub> adsorption capacities as compared with the TOC-rich samples [12]. Similarly, Heller et al. also observed higher gas uptakes on shales with lower TOC [6].

In order to achieve in-depth understanding on the above issue, some researchers attempted to study individual contribution from organic matter (OM) and mineral components (MC) to the overall adsorption of shales. For example, Xiong and colleagues measured gas adsorption on kerogens extracted from shales, and the results were compared with data obtained from different minerals (e.g. quartz, illite, and chlorite), this enabled the authors to conclude that adsorption on kerogen is significantly higher than minerals [13]. Based on adsorption data of minerals in the literatures, Yang and co-workers calculated adsorption capacity of shales by considering individual adsorption capacities and mass ratios of organic matter and different minerals [14].

In general, previous researches established that the highly developed porosity in OM and some of the MC are the major locations for gas adsorption, however, it is reasonable to expect substantial alterations on the intrinsic porosity of OM and MC due to the presence of their interface in a shale sample. Apparently, these changes in porosity, which are expected to have considerable influence on the adsorption behavior of shales, cannot be simply attributed to either OM or MC. For example, Rexer and co-workers removed the clay minerals from shale by acid washing, gas adsorption was then measured on the resulted kerogen samples, combining with mineral adsorption data reported by other researchers, they concluded that approximately 45–60% and

60–70% of the adsorption capacity of shales can be attributed to clays and kerogen, respectively. They also suggested that the interfaces of kerogen and clay minerals might have great influence to the adsorption properties of shales. In this work however, neither direct observations nor characterizations were attempted to understand gas adsorption at the interfaces of kerogen and clay minerals [8].

Herein, extraction of OM and MC from a Longmaxi shale was carried out, characterization of the samples during and after the extraction indicated the effectiveness of those processes, and both the resulted OM and MC stayed intact after extraction with minimized alternation as compared with their counterparts in shale. This is to say that we established a general procedure to extract MC from shale, which can be used for other types of shales, and thus benefits the broad research interests. Furthermore, systematic characterization on the porosity and evaluation on gas adsorption (both CH<sub>4</sub> and CO<sub>2</sub>) were then performed on OM, MC, and shale, which were then compared with a hypothetical mixture (HM) from OM and MC bearing the same composition of shale. For the first time, we demonstrate experimentally and directly that a large amount of the original micropores in OM was actually blocked in shales, and thus are inaccessible for gas adsorption. More importantly, generation of additional narrow mesoporosity was confirmed at the interface of OM and MC (probably due to the presence of OM in the larger pores of MC), which played an important role for gas adsorption particularly at temperatures more relevant to reservoir conditions. These observations deepened current understandings on adsorption behavior and mechanism of shales, thus shed interesting lights on related applications such as gas-in-place (GIP) estimation, CO<sub>2</sub> sequestration in shales, and particularly the utilization of CO<sub>2</sub> for enhanced shale gas recovery.

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