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Upscaling the porosity of the Callovo-Oxfordian mudstone from the pore scale to the formation scale; insights from the 3H-PMMA autoradiography technique and SEM BSE imaging

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ABSTRACT

The Callovo-Oxfordian mudstone (Meuse/Haute-Marne, France) is currently considered as the host rock barrier for a deep geological repository. The intimate relationships between the porosity and mineralogy of this host rock were investigated at the small scale (μm–mm) and large scale (m–hm). At the small scale, we have adapted the ^{3}H-PMMA autoradiographic method to map the porosity of the Callovo-Oxfordian mudstone. The ^{3}H-PMMA autoradiographic method was improved in terms of its spatial resolution. ^{3}H-PMMA porosity maps were then compared to homologous mineral maps (clay minerals, carbonates and tectosilicates) built from scanning electron microscopy images (using back-scattered electron imaging). Based on an inversion procedure, the specific porosity of each mineral group was estimated from the mineral and porosity maps. We found that the spatial distribution of porosity at the small scale is mainly controlled by the spatial distribution of the clay matrix (the average porosity of the clay matrix is 40–45%), whereas quartz and carbonate mineral grains have low porosities (0–4%). At the geological formation scale, the porosity and mineralogy distributions were determined by logging tool techniques (nuclear magnetic resonance and spectral gamma-ray). The coupled evolution of clay content and porosity with depth was analyzed according to the porosity/mineralogy relationship defined at the small scale. Finally, we modeled the evolution of the porosity of the Callovo-Oxfordian mudstone with depth by considering the clay content and the effect of physical compaction during burial.

1. Introduction

In France, the Callovo-Oxfordian (COx) clay-rich sedimentary layer of the Paris basin is currently considered as the potential host formation for a future deep underground repository for high-level and intermediate-level long-lived radioactive waste. One of the main issues raised in this framework is the evaluation of the mobility of released radionuclides through the rock formation. The mineralogy of the COx formation consists of a heterogeneous assemblage of clay minerals (clay content: 30–50 wt.%), carbonates, tectosilicates and secondary minerals such as pyrite (Sammartino et al., 2003; Robinet et al., 2012). The bulk porosity ranges from 10 to 20% and mainly consists of nanometer-sized pores. The pore space properties of the COx mudstone induce low diffusion coefficients for radionuclides and a low hydraulic conductivity (Descostes et al., 2008; Altmann et al., 2012; Harrington et al., 2012). However, the mineral contents and porosity vary through the geological formation, with the lower two-thirds of the layer being more clayey compared to the carbonate-rich upper part (Gaucher et al., 2004). To predict radionuclide migration through the entire COx formation, a quantitative description of the spatial distribution of porosity and mineralogy is required from the scale of pores and mineral grains to the hectometer scale of a geological formation (hereafter denoted small scale and large scale, respectively). At the large scale, the quantification of the spatial distribution of porosity and mineralogy was previously performed using logging tool techniques including nuclear magnetic resonance (NMR) and spectral gamma-ray tools to determine the porosity and clay mineral content, respectively (Battani et al., 2011; Cosenza et al., 2014). However, the conjoint evolution of porosity and mineralogy currently remains not fully understood at the large scale. The evolution of mineralogy and porosity at the large scale derives basically from their small scale distributions, where the pores and minerals can be observed. Several studies previously focused on the small scale structure of the COx clay-rich rock (Sammartino et al., 2002, 2003; Esteban et al., 2007; Yven et al., 2007; Robinet et al., 2012). From the micrometer to centimeter scale, the COx mudstone is classically described by a two-domain medium, represented by the clay matrix and micrometer-size carbonate and tectosilicate grains (Sammartino et al., 2002, 2003; Robinet et al., 2012). At the scale of nanometers, the clay matrix is supposed to be organized according to the clay layers, particles and

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aggregates (see, for instance, the work of Houben et al., 2013 applied to the Mont Terri mudstone).

At the small scale, the spatial distribution of porosity can be investigated using various imaging techniques such as electron microscopy, X-ray tomography and autoradiography based on radioactive beta-emission imaging. One of these methods specifically adapted to our purpose is based on the complete impregnation of the pore space of porous materials by ^{14}C doped methyl methacrylate (^{14}C-MMA), the polymerization of MMA into PMMA (polymethyl methacrylate), and the quantitative mapping of the spatial distribution of radioactive tracers filling the connected pore space using a film or digital autoradiography technique (Hellmuth et al., 1993; Siitari-Kauppi et al., 1998; Sammartino et al., 2002, 2003; Siitari-Kauppi, 2002; Prêt et al., 2004; Sardini et al., 2006, 2007, 2009, 2015; Gaboreau et al., 2011, 2012; Jeong et al., 2013). Applying this method to the COx mudstone, Sammartino et al. (2002, 2003) identified two types of porous sets characterized by distinctly connected porosity distributions. Using qualitative scanning electron microscopy (SEM), the authors highlighted that the mineralogy of two porous sets is different; the clay-rich areas are characterized by a higher porosity than the carbonate-rich areas. The ^{14}C-PMMA technique has been used together with chemical etching to determine the spatial porosity of the main minerals in coarse grained granitic rocks (Oila et al., 2005; Cassiaux et al., 2006; Kelokaski et al., 2006; Sardini et al., 2006; Voutilainen et al., 2012). The technique uses homologous maps of porosity and mineralogy to quantify the connected porosity of each mineral composing a rock, thus elucidating the variations in the bulk porosity against the primary mineral contents. Unfortunately, the spatial resolution of ^{14}C-PMMA autoradiography (more than 20 μm) and mineral mapping by chemical etching is not adapted for clay-rich sedimentary rocks because the sizes of non-clay mineral aggregates range from ~1 to ~100 μm. Using SEM techniques, Prêt et al. (2010a, 2010b) studied the relationship between minerals and porosity for fine grained bentonite. Homologous mineral and porosity maps were provided by the numerical treatment of electron microprobe X-ray elemental maps. The resolution of both the mineral and porosity maps was greatly improved; however, the porosity map determined by SEM cannot discriminate connected and isolated pores, which are not involved in transport phenomena. To better understand and quantify the relationship between the mineral contents and the connected porosity of the fine grained rocks (such as shales, including the COx), there is still a need to adapt the ^{14}C-PMMA method. The spatial resolution of the ^{14}C-PMMA method could be improved by ^{3}H (tritium)-doped MMA because the spatial resolution given by ^{3}H is better than that given by ^{14}C. This highest spatial resolution for ^{3}H is due to the difference in the emission energies of beta particles from ^{3}H (E_{max} = 18 keV) or ^{14}C (E_{max} = 156 keV), leading to shorter ranges of ^{3}H beta emission in the PMMA. ^{3}H doped MMA was successfully used only a few times on granitic rocks (Siitari-Kauppi et al., 1998). In particular, routine application is not feasible due to the handling of high ^{3}H activities, which are required for the impregnation of granites with porosities lower than 1%. Clay materials and shales that have higher porosities than granitic rocks are better candidates for ^{3}H doped MMA impregnations because high ^{3}H activities are not required. The ^{3}H-PMMA method is a promising tool for distinguishing non-clay grains from the clay matrix regardless of their porosity contrast (Gaboreau et al., 2011), but further resolution improvements are still required.

The aim of our work is first to improve the ^{3}H-PMMA method with the objective to study the relationship between the porosity and mineral distributions at the small scale. The ^{3}H-PMMA autoradiographic method is applied on the COx mudstone and the spatial resolution of the autoradiography technique is optimized. Mineral mapping is performed by SEM imaging in back-scattered electron mode (BSE) for two regions of interest (ROI) identified on the ^{3}H-PMMA porosity map. The spatial correlations between the ^{3}H-PMMA porosity and SEM BSE mineral maps allow linking the porosity to the mineralogy in the COx; in particular, the relationship between the clay content and connected porosity is pinpointed. At the large scale, wireline logging is used in a borehole crossing the COx formation to quantify the clay content and porosity. The large scale relationship between porosity and mineralogy is interpreted with regard to small scale observations and quantifications.

2. Materials and methods

2.1. Materials

The COx mudstone is located in the eastern part of the Paris Basin (~300 km east of Paris). It was studied by Andra (French National Radioactive Waste Management Agency) over a 250 km^2 area. In this area, Andra had performed several drilling campaigns and constructed an Underground Research Laboratory (URL) at a 490 m depth in the COx layer. The thickness of the COx formation is approximately 135 m at the URL. The overall COx mineralogy is composed of phyllosilicates (20 wt.%–60 wt.%, mainly illite and interstratified illite/smectite, kaolinite, mica, and chlorite), tectosilicates (10 wt.%–40 wt.%, mainly quartz and feldspars), carbonates (15 wt.%–80 wt.%, mainly calcite and dolomite) and pyrite (0%–3 wt.%) (Gaucher et al., 2004). From the base to the top of the layer, the COx formation was divided into four lithostratigraphic units (C2a to C2d) and several petrophysical units (UA1, RIO, UA2, UA3, UT, USC1, RSO and USC2) defined for the purposes of the Andra project (Pellenard et al., 2014). These petrophysical units allow the identification of fine variations in the mineral, physical and mechanical properties occurring within the COx formation. The UA units represent the mostly clayey levels of the formation (C2a and C2b), whereas the UT and USC (C2b2/C2c/C2d) units are siltier and more carbonated compared to the UA units. At the scale of the study area, the mineral proportions vary according to depth mainly due to geological sedimentary cycles (Lefranc et al., 2008); the clay mineral content is roughly anti-correlated to the carbonate content. The rock physical–chemical and petrophysical properties of the COx mudstone are also relatively well known thanks to a large set of studies based on core samples extracted from several boreholes (see, for instance, Gaucher et al., 2004; Yven et al., 2007; Esteban et al., 2007; Cosenza et al., 2014).

The core sample (Ø = 6 cm, L = 25 cm) used for this study (EST26095, −508.86 to −509.07 m) was taken from the DIR1001 borehole drilled from a technical gallery at the URL. The mineralogy of this sample was quantified by means of a combined X-ray powder diffraction and bulk chemical method analysis. A detailed description of this method can be found in Chen et al. (2014). The mineral composition of sample EST26095 is as follows: clays = 44 ± 9 wt.%, tectosilicates = 19 ± 7 wt.% and carbonates 37 ± 9 wt.% (Table 1). The water content measured immediately after drilling by weighing before and after heating at 105 °C and 150 °C for 48 h was 5.4 and 5.8, respectively (% dry base), leading to a bulk porosity of 13–14% assuming a grain density of 2.7 g/cm^3 and full water saturation. Prior to this study, the core sample EST26095 has also been extensively studied in terms of petrological and microstructural properties (X-ray tomography, synchrotron X-ray tomography, optical microscopy… cf. Robinet, 2008; Robinet et al., 2012). This sample was chosen for this work due to the good completeness of its previously acquired dataset and its representativeness regarding the URL level.

2.2. Methods at the small scale

2.2.1. The ^{3}H-/^{14}C-PMMA autoradiographic technique

The ^{3}H-/^{14}C-PMMA method consists of filling the connected pore space of a hand scale rock sample with MMA monomer ($C_5H_8O_2$) labeled by ^{3}H or ^{14}C radioactive isotopes. MMA was selected due to its low dynamic viscosity (0.584 10^{-3} Pa·s at 20 °C compared to 1.005 10^{-3} Pa.s for water), its small size (0.19 nm^3) and because its dipolar moment is close to the dipolar moment of the water. These properties allow MMA to penetrate into the interlayer space of clays involving