

# Approaching the porosity values of Cretaceous carbonate deposits in Araxos peninsula and Kastos Island (North-Western Peloponnese, Greece) for the characterization of reservoir quality.

N. Bourli<sup>1</sup>, M. Kokkaliari<sup>1</sup>, I. Iliopoulos<sup>1</sup>, A. Zelilidis<sup>1</sup>

(1) Department of Geology, University of Patras, 26504 Patras, Greece, n\_bourli@upnet.gr

# Introduction

According to Bourli et al., (2019) upper Cretaceous–Lower Eocene deposits of the Ionian basin is the major target in hydrocarbon exploration as they represent the expected reservoir rocks. These deposits are mostly composed of calciturbidites interbedded with breccia-microbreccia deposits. Calciturbidites can be of great economic importance and they can serve as viable reservoir rocks because of their high porosity and permeability values, which can be additionally enhanced by the development of nodules that in turn increase secondary porosity. Studied Cretaceous limestones in Araxos peninsula (NW Peloponnesus, internal Ionian sub-basin) and Kastos Island (external Ionian sub-basin) showed that both lower Cretaceous "Vigla limestones" and upper Cretaceous "Senonian limestones" are characterized by the presence of siliceous nodules. Siliceous nodules within the Vigla limestones are of smaller in relation to the Senonian limestones. The above difference in nodules size could be related with the different porosity of hosted deposits. Pelagic limestones of lower Cretaceous Vigla limestones must have reduced pores or lower porosity than the porosity of calciturbidites.

## Material and methods

Nitrogen absorption-desorption was performed with the Quantachrome Nova 2200e at the Research Laboratory of Minerals and Rocks, Department of Geology, University of Patras. The relative pressure against the nitrogen adsorption was used and a full isotherm diagram was produced based on the adsorption and the desorption isotherms. For determination of the specific surface area, the BET equation (Brunauer, Emmett, & Teller, 1938) was used in the form of a linear plot. The BJH method (Barrett, Joyner, & Halenda, 1951) was applied within the range from 2 to 50 nm and average cumulative surface of pores (S<sub>BJH</sub>), average volume of mesopores (V<sub>BJH</sub>) and average diameter of mesopores (D<sub>BJH</sub>) were calculated. According to IUPAC (Sing et al., 1985), pores are classified into three groups according to their diameter: micropores (diameter < 2 nm, mesopores (diameter 2 - 50 nm), and macropores (diameter > 50 nm). Moreover, results processing with software NovaWin helped us classify isotherms according to Sing et al. (1985), where five (5) groups (I to V) were determined and isotherm hysteresis loops into four types (H1-H4).

#### Data analysis

Lower Cretaceous limestone samples (V1, V3, I5, GN1 and GN2) and Upper Cretaceous limestone samples (S1, Ark7 and Ar40d), from both studied areas were analyzed for their specific surface area ( $S_{BET}$ ) and the average diameter of mesopores ( $D_{BJH}$ ) by Nitrogen porosimetry. Porosity measurements for both areas showed that the isotherms of the samples, according to IUPAC classification (Sing et al., 1985), are type IV, indicating mesoporous (2 – 50 nm) studied rocks. The characteristic feature of type IV isotherm is the presence of the hysteresis loop, typical for the mesoporous material, which is associated with pore condensation (Fig. 1). The hysteresis loop of the studied type IV isotherms classified in the H3 type, indicating pores with slit shape overall of the sample, from non-rigid aggregated of platy particles. Also, if the network consists of macropores, then these are not completely filled with the condensate (Thommes et al., 2015). Furthermore, the H3 loop hysteresis suggests the presence of mainly accessible pore network, because otherwise it would not create hysteresis (Liu et al., 2014). The adsorption and desorption branches of some



Figure 1. Representative diagrams of N2 adsorption of samples V3 (Lower Cretaceous shales from Kastos Island) and GN2 (Upper Cretaceous calciturbidites from NW Peloponnesus).

samples approach a nearly vertical direction above the 0.8 relative pressure indicating the presence of outer surface, which is characteristic of isotherm II (red circle in figure 1A). The above could support the idea that although the studied samples were classified into the type IV due to the presence of the hysteresis loop, the pores present broad size distribution and could also suggest the presence of some larger porous, perhaps of type II. In cases where an incomplete equilibrium during the measurements occur, an open loop hysteresis is observed (Bertier et al., 2016) at very low relative pressure (red circle in Fig. 2) that refers to the slow diffusion of adsorptive in micropores, structural deformation of the sample or even chemisorption (Rouquerol et al. 2014). On the other hand, the hysteresis loop for the rest of the samples has a narrower shape indicating the presence of slit-shaped mesopores with a non-uniform size (red box in Fig. 1B).



Figure 2: Representative diagrams of N2 adsorption of sample V1 (Lower Cretaceous shales from Kastos Island)

Nitrogen sorption isotherms of the studied samples have similar shape, classified as an H3 of the type IV isotherm. According to the BJH method the pore volume ( $V_{BJH}$ ) ranges from 0.001 to 0.002 cc/g, the pore diameter ( $D_{BJH}$ ) ranges from 3.550 to 3.663 nm and the cumulative surface area ( $S_{BJH}$ ) ranges from 0.376 to 0.826 m<sup>2</sup>/g while the total specific area ( $S_{BET}$ ) through the BET calculations ranges from 0.577 to 0.933 m<sup>2</sup>/g. Only one sample had different values as far as the BJH pore volume (0.007 cc/g) and the BJH cumulative surface area (2.321 m<sup>2</sup>/g), even though the BJH pore diameter is 3.550 nm, while the BET specific surface area with the BET calculation is 3.193 m<sup>2</sup>/g.

### Results

According to the above and taking into account that both, Early Cretaceous Vigla limestones and Late Cretaceous Senonian calciturbidites, showed that now they are mesoporous, a secondary higher increase of pores within Early Cretaceous Vigla limestones than in Late Cretaceous calciturbidites, could be caused due to fracturing owed to the nodules development, as suggested by Spence and Finch (2015).

#### Acknowledgements

Nicolina Bourli is a PhD student and she was financially supported by the "Andreas Mentzelopoulos Scholarships for the University of Patras".

#### References

- Barrett, E.P., Joyner, L.G., Halenda, P.P., 1951. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. Journal of the American Chemical Society 73, 373-380.
- Bertier, P., Schweinar, K., Stanjek, H., Ghanizadeh, A., Clarkson, C.R., Busch, A., Kampman, N., Prinz, D., Amann-Hildenbrand, A., Krooss, B., Pipich, V., 2016. On the use and abuse of N2 physisorption of the pore structure of shales. The Clay Minerals Society Workshop Lectures Series 21, 151–161.
- Bourli, N., Pantopoulos, G., Maravelis, A.G., Zoumpoulis, E., Iliopoulos, G., Pomoni-Papaioannou, F., Kostopoulou, S., Zelilidis, A., 2019. Late Cretaceous to Early Eocene geological history of the eastern Ionian Basin, southwestern Greece: An integrated sedimentological and bed thickness statistics analysis. Cretaceous Research 98, 47-71.
- Brunauer, S., Emmet, P.H., Teller, E., 1938. Adsorption in gases in multimolecular lyers. Journal of the American Chemical Society 60, 309-319.
- Liu, J.Y., Qiu, Z.S., Huang, W.A., Luo, Y., Song, D.D., 2014. Nano-pore structure characterization of shales using gas adsorption and mercury intrusion techniques. Journal of Chemical and Pharmaceutical Research 6, 850–857.
- Rouquerol, F., Rouquerol, J., Sing, K.S.W., Llewellyn, P., Maurin, G., 2014. Adsorption by Powders and Porous Solids: Principles, Methodology and Applications, 2nd ed. Academic Press, Oxford, UK.
- Sing, K., Everett, D., Moscou, L., Pierotti, R., Rouquerol, J., Siemieniewska, T., 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity International union of pure and applied chemistry. Pure and Applied Chemistry 57, 603-619.
- Thommes, M., Kaneko, K., Neimark, A.V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S.W., 2015. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure and Applied Chemistr, 87, 9–10.