



## **Methane adsorption and micropore characterisation of Posidonia shales and isolated kerogen**

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Gas in shales is stored in three different states: adsorbed, compressed (free) and dissolved; quantifying each underpins calculations of gas storage capacity and also the mechanisms by which gas must be transported from pore (surface) to fracture to well. While compressed gas dominates in meso- and macropores, it is often assumed that (a) sorbed gas occurs mainly in micropores (< 2nm) and (b) micropores are mainly associated with organic matter. Here, we test those ideas by characterising the porous structure of six shales and isolated kerogens from the Posidonia Formation by low-pressure sorption techniques and in combination with high pressure methane sorption isotherms at 45, 65 and 85°C. Together, these data help us to understand the extent to which (a) small pores control CH<sub>4</sub> sorption and (b) whether small “sorption” pores are associated with the organic and inorganic phases within shales.

Samples were selected with vitrinite reflectance of 0.6, 0.9 and 1.45%. Pore volumes – named sorption pore volumes here - were determined on dry shales and isolated kerogens by CO<sub>2</sub> isotherms measured at -78°C and up to 0.1 MPa. These volumes include micropores (pore width < 2nm) and narrow mesopores; according to the Gurvitch Rule this is the volume available for sorption of most gases. Sorption pore volumes of both immature and gas window shales range from 0.010 to 0.021 cm<sup>3</sup> g<sup>-1</sup>, accounting for 33 - 43% of total porosity. For shales in the oil window, sorption pore volumes are 55 – 87% of total porosity. Whilst sorption pore volumes of isolated kerogen are much higher, between 0.095 – 0.147 cm<sup>3</sup> g<sup>-1</sup>, normalization by TOC shows that only half the shales’ sorption pore volume is located within the kerogen.

Methane sorption isotherms at 45°C for shale show excess maxima between 0.07 – 0.12 mmol g<sup>-1</sup>. Uptake on isolated kerogen is much higher, varying from 0.47 mmol g<sup>-1</sup> in immature kerogen to 1.02 mmol g<sup>-1</sup> in gas window kerogen. Combining kerogen and shale isotherms shows that around half the CH<sub>4</sub> sorption in shales occurs within the organic matter, entirely consistent with the division of sorption pores between organic and inorganic phases. There is a very strong correlation between the maximum methane excess uptake and the sorption pore volume indicating that methane sorption capacities are indeed governed by this volume. Our experiments were performed on dry shales; in the subsurface, it is possible that inorganic pores are water-filled and thus unavailable as sorption sites.