Effect of Organic Matter Type and Thermal Maturity on Gas Adsorption in Shale-Gas Systems

Tongwei Zhang¹, Geoffrey S. Ellis², and Stephen C. Ruppel¹
Bureau of Economic Geology, The University of Texas at Austin, Austin, TX
²U.S. Geological Survey, Denver, CO

Natural gas stored in shale-gas reservoirs is thought to exist in one of three forms: 1) free gas in pores and fractures, 2) sorbed gas in organic matter and inorganic minerals, and 3) dissolved gas in oil and water. Understanding the relative proportions of gas stored in these different forms is critical for accurate assessments of shale-gas resources and the design of effective production strategies. Although the critical role of organic matter gas storage in shales is well documented, the details of the mechanism are not well understood. In particular, the effect of kerogen type and thermal maturity on gas sorption in shales is unclear. In this study, we investigated the sorption of methane onto whole rock and isolated kerogen samples of the Barnett Shale, Green River Formation, Woodford Shale, and Cameo coal to examine how differences in organic matter type and thermal maturity affect natural gas adsorption. The total organic carbon (TOC) content of theses samples is 7.9, 20.7, 17.2, and 72.2% respectively, with thermal maturity values ranging from 0.56 to 0.58 % $R_{\rm o}$. Thermal maturity effects were determined on an additional three Barnett Shale samples with measure vitrinite reflectance values of 0.58, 0.81, and 2.1% $R_{\rm o}$ and TOC contents ranging from 6.6 to 7.9%.

For all samples, the total amount of methane adsorbed is directly proportional to the TOC content of the sample, and on average the maximum amount of gas sorption was 721 scf of methane per ton of kerogen. These results indicate that sorption on organic matter plays a critical role in shale-gas storage, which is further illustrated by our observation that significantly larger amounts of gas can be adsorbed onto isolated kerogen than onto the whole rock (on a per unit-weight basis). Under our experimental conditions, differences in kerogen thermal maturity showed no significant effect on the total amount of gas sorbed; however, adsorption equilibrium was reached at a faster rate for the shales with higher thermal maturity. Specifically, the Langmuir pressure constant (which represents the pressure at which gas storage capacity equals one half of the maximum gas adsorption capacity) is 1.92 Mpa at 50°C for the highest maturity sample (% R_o >2.1), whereas the lowest maturity sample (% R_o =0.56) has a significantly larger Langmuir pressure constant (5.08 Mpa) under the same temperature conditions.

The experimental adsorption data show good agreement with a Langmuir isotherm, which assumes the following conditions: 1) the maximum amount of gas adsorbed at different temperatures is constant and is only dependent on the availability of surface area, and 2) the Langmuir equilibrium constant is purely a function of temperature for a given gas/surface system. Quantitative model predictions based on the Langmuir equation parameters can then be applied to specific organic matter properties. In particular, the value of the Langmuir constant increases with kerogen type in the following sequence: Type I < Type II < Type III. The Langmuir constant is related to the affinity of a gas for a surface (i.e., larger values indicate strong bonding) and the observed trend is likely a product of the increasing aromaticity of the kerogen. These findings have important implications for shale-gas resource assessments and recovery technologies.