Influence of water hydrogen on hydrogen stable isotope ratio of methane at low versus high temperatures of methanogenesis

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Our laboratory experiments simulated hydrocarbon gas generation from source rocks by using low-temperature (≤ 200 °C) and long-term (1 month and 5 years) heating of pre-evacuated and sterilized immature shales and coals (vitrinite reflectance (Ro) values of 0.21 to 0.47%). Source rock powders and chips were sealed in gold and Pyrex® glass tubes in the presence of waters with variable hydrogen isotopic compositions (i.e., δ^2Hwater values of –137‰ and +1246‰) to assess the influence of water-derived hydrogen on generated gaseous hydrocarbons. In addition, hydrous pyrolysis (HP) experiments using pre-extracted shales at 330 °C and H-isotopically distinct waters were performed for comparison. The isotopic transfer of water-hydrogen to hydrocarbons generated at both low and high temperatures was quantified. Isotopic mass-balances indicate that the methane to butane hydrocarbon gases from high-temperature HP experiments received an average of 53% of their hydrogen from water, whereas at low-temperatures the hydrogen transfer from water to methane ranged only from ~1% to ~13% of organic hydrogen.

A possible explanation for differences in the extent of hydrogen transfer is that during lower-temperature hydrocarbon gas generation carbon-carbon bond breaking occurs close to the interface between minerals and organic matter, where hydrophobic organic microdomains limit the access of water. At higher temperatures, the physico-chemical properties of water are altered compared to those at lower temperatures. Therefore, by comparing the results obtained at low-temperature and high-temperature conditions, our laboratory experiments offer insights into the mechanisms controlling the contribution of water hydrogen to hydrocarbon gas generation in sedimentary basins.