Quantification of uncertainty related to methane production associated with geogenic hydrogen and carbon dioxide

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We provide a numerical analysis aimed at quantifying uncertainty associated with methane (CH_4) production following geogenic hydrogen (H_2) and carbon dioxide (CO_2) generation. Our study stems from the observation that naturally generated H_2 can potentially be (*i*) reduced through, e.g., mineral-based (abiotic) geochemical processes and/or (*ii*) consumed through (biotic) methanogens. Both scenarios yield methane (CH_4) as a product. Some studies suggest relying on the H_2/CH_4 ratio as a straightforward indicator to assess the origin of methane in the subsurface. For example, Oze et al. (2012) rely on laboratory experiments of serpentinization associated with a given temperature/pressure condition and rock/fluid compositions and suggest that values of H_2/CH_4 larger than 40 are likely to indicate abiotic origin of CH_4. Otherwise, values H_2/CH_4 less than 40 suggest contribution of biotic activity to methane generation. Here, we consider the same types of (abiotic) geochemical reactions analyzed by Oze et al. (2012) and conceptualize the subsurface system as a natural chemical reactor within which a mixture of H_2 (generated from serpentinization) and CO_2 (generated from carbon-clay-reactions) yields a mixture of H_2, CO_2, and CH_4. Our analysis considers that complete mixing of the various chemical species is attained and that geochemical reactions can be evaluated under thermodynamic equilibrium conditions. We then perform a modeling study framed in a stochastic context and relying on a numerical Monte Carlo framework. We aim at quantifying the way uncertainties associated with hydrogen loss (as reflected through the H_2/CH_4 ratio) due to geochemical reactions at reservoir equilibrium condition can depend on corresponding uncertainties related to (*i*) composition of the fluids residing in the system, (*ii*) depth of a reservoir (i.e., as reflected through temperature/pressure conditions), and (*iii*) characterization of the thermodynamic equilibrium model. With reference to the latter point, uncertainties in terms of values of reaction equilibrium constants stem from the observation that temperature and pressure values associated with significant burial depths may fall outside ranges of validity of commonly employed thermodynamic databases and typically used geochemical software. Our stochastic simulation results suggest that (on average) almost 43% of native H_2 is consumed due to the geochemical reactions analyzed. This would correspond to an average value of H_2/CH_4 of about 13 (with first and third quantiles corresponding to 7 and 20, respectively). The ensuing sample probability density function of the H_2/CH_4 ratio displays a clear positive skewness. Our results may practically be used as a simple criterion to identify the probability associated with CH_4 production from geochemical processes involving natural H_2 under reservoir thermodynamic equilibrium conditions.

Keywords: serpentinization, methane, geochemical reactions, uncertainty quantification, H_2/CH_4 ratio.

References

Oze, C., Jones, L. C., Goldsmith, J. I., and Rosenbauer, R. J. (2012). Differentiating biotic from abiotic methane genesis in hydrothermally active planetary surfaces. Proceedings of the National Academy of Sciences, 109(25), 9750-9754. https://doi.org/10.1073/pnas.1205223109.