Abiotic CH_4 in ultramafic rocks: follow the Sabatier reaction rules

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Methane (CH_4) occurring in surface manifestations (seeps, hyperalkaline springs) and drillholes in serpentinized ultramafic rocks and Precambrian shields is typically considered to have a dominant abiotic origin, related to Fischer-Tropsch Type (FTT) Sabatier reaction, $CO_2 + 4H_2 = CH_4 + 2H_2O$. Experimental geochemists assumed that geological environments are better represented by aqueous systems and FTT laboratory tests were performed in water, simulating hydrothermal fluids with dissolved carbon compounds. These experiments often started the sequence of the reactions with olivine hydration, miming serpentinization. From early experiments [1] to more recent reviews [2], Sabatier reaction in rocks has been repeatedly reported in the form: $CO_{2(aq)} + 4H_{2(aq)} = CH_4 + 2H_2O$, where $CO_{2(aq)}$ may be HCO_3^- or, in hyperalkaline conditions, CO_3^{2-}. Many of these experiments provided ambiguous or negative results, without significant CH_4 production. A recurrent conclusion is that FTT may not be an important CH_4 generation pathway in serpentinization systems [2]. This claim should only refer to aqueous FTT and to those experiments that do not respect Sabatier rules. As known in industrial chemistry, aqueous FTT is practically impossible with heterogeneous catalysis, especially at low temperatures; dissolved C forms are hardly chemioadsorbed on the metal surface, and the reaction cannot proceed towards H_2O and CH_4. In addition, starting with olivine hydration does not guarantee that H_2 is sufficiently produced to respect the ratio $H_2/CO_2 \geq 4$. In some cases there is no control of catalysts either, as they are assumed to form autonomously (e.g., magnetite during serpentinization). It is not a suprise, then, that many of these experiments did not produce CH_4. It is important to consider that geological systems are not necessarily aqueous and that FTT synthesis can occur in unsaturated rocks and gas filled fractures. Published [3,4] and new experiments rigorously following the Sabatier rules (gas-phase, $H_2/CO_2>4$, catalyst) successfully produced CH_4 over a wide range of temperatures, even <100°, i.e. in continental peridotite conditions. Seep/spring data (e.g., $^{14}C_{CH4}$, CH_4-H_2O disequilibria, seepage distribution) support the hypothesis that CH_4 is not formed in water.

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