Abiotic synthesis of methane in ultramafic rocks: just let them dry!

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Fluids within actively serpentinizing systems often exhibit significant methane (CH₄) enrichment that is thought to derive from Fischer-Tropsch type (FTT) reactions. Despite numerous experimental endeavors, the precise conditions conducive to CH₄ abiotic synthesis in ultramafic settings remain elusive. In particular, the role and physical state of water which is central to these reactions remains poorly explored. It is known that Fischer-Tropsch and Sabatier reactions can only occur with reagents in the gaseous state and cannot proceed for compounds dissolved in aqueous liquid (Etiope and Whiticar, 2019; Etiope, 2017; Duyar, 2015; Miguel et al., 2015 ; McCollom, 2013). Even with abundant dissolved H₂ (>0.1 mol/kgH₂O), it now appears that the serpentinization reaction alone is incapable of substantial abiotic hydrocarbon production on laboratory timescales and temperature ranging from 300 to 400°C (McCollom, 2016). Gaseous CO₂ and H₂ can form CH₄ at 20-90°C using a dry ruthenium catalyst (Etiope and Ionescu 2015), but the catalytic availability of Ru reaction sites in natural igneous rock is highly uncertain, and may be negligible if shielded by the mineral host or adversely affected by water. Here, we document the CH₄ and CO production when reacting natural chromitite with CO₂ and H₂ at $100 - 200^{\circ}$ C. We reveal that CH₄ is produced only when the system is dry (no liquid or vapor water). Under such condition complete reduction of CO2 into CH4 occurs within few hundreds of hours at 200°C. Thus, if CH4 is produced through FTT reactions in ultramafic settings, our observations imply that dry areas may exist next to the serpentinization zones. Such a conclusion is supported by preliminary observations made in a deep chromite mine in the Bulqizë massif (Albania) (Truche et al., 2023).