FAST ABIOTIC PRODUCTION OF METHANE AT TEMPERATURES <100°C

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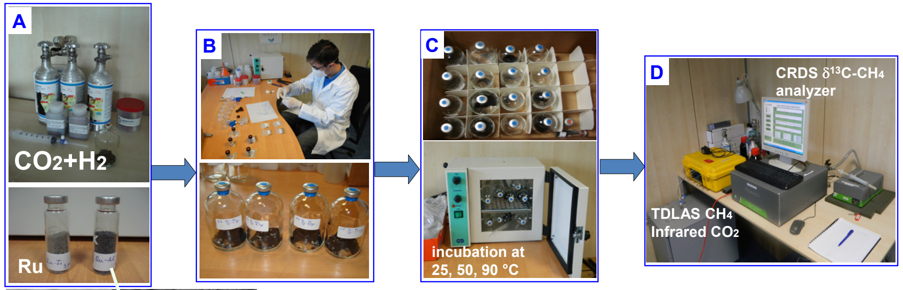
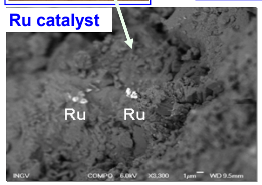
Fischer-Tropsch Type (FTT) reactions, e.g., the Sabatier synthesis between H_2 and CO_2, are considered a main source of abiotic methane (CH_4) on Earth and other planets. Several laboratory FTT experiments demonstrated abiotic CH_4 production at T > 200°C, by using Fe, Ni or Cr catalysts, simulating hydrothermal conditions in peridotite-hosted submarine systems. Nevertheless, Fe-Ni-Cr catalysts cannot support CH_4 generation at T < 100-150°C, which are those of continental serpentinization systems.

In **2014** we reported rapid production of considerable amounts of CH4 (>800 ppmv in 155 mL bottles after 1 day, up to 6.5 vol% after 1 month) via Sabatier reaction at 90, 50 and 25°C, using concentrations of non-pretreated ruthenium equivalent to those occurring in chromitites in ophiolites or continental igneous complexes (*Etiope and Ionescu, 2015; Geofluids, 15, 438-452*).



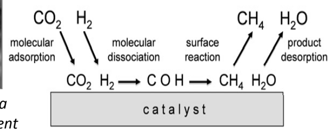
Ru catalyst

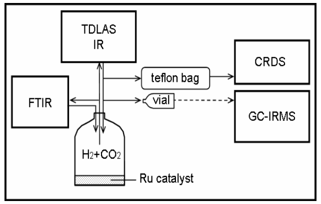


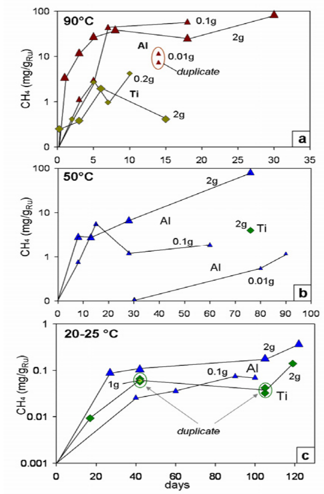
FESEM image of ruthenium on alumina support, used in the Sabatier experiment

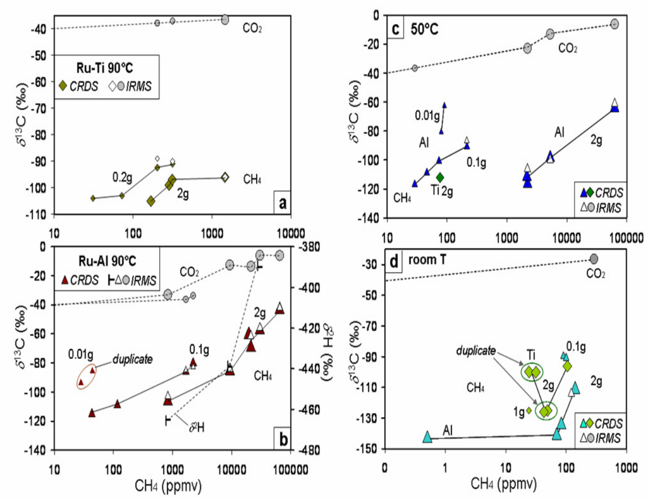
SABATIER REACTION

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$







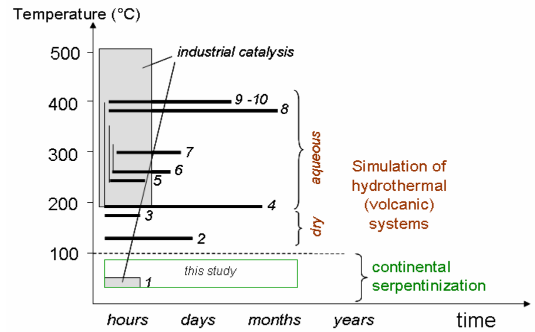


In **2015** we repeated the experiments by using [13]C-enriched CO2 and we confirm fast production of CH4 at percentage levels.

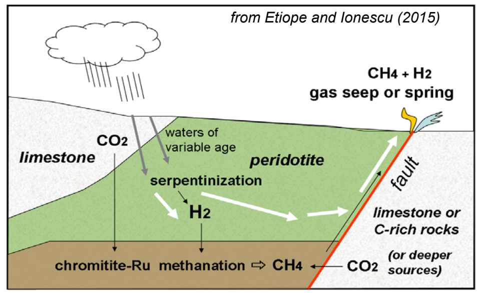
The experiments so far performed show that:

1. **large CH4 amounts can be produced in dry conditions below 100°C using extremely small quantities of ruthenium**
2. **under the same experimental conditions (<100°C), Fe, Ni and Cr oxides do not produce methane**
3. **low T FTT reactions can produce CH4 with a large C isotope fractionation between CO2 and CH4, leading to relatively "light" ([13]C-depleted) CH4, resembling microbial gas**
4. **CO2-CH4 isotope separation decreases over time and by increasing the temperature**
5. **minor amounts of C2-C6 hydrocarbons are also generated**

LABORATORY FTT EXPERIMENTS - INDUSTRY vs GEOLOGY



Schematic plot of temperature and time scales considered in FTT experiments in geology and industrial catalysis. All geologic experiments were conducted at T> 100°C. Our study is the first to report CH4 generation and its isotopic composition below 100°C, which is the T of continental serpentinization.
1. Thampi et al. (1987); Jacquemin et al. (2010); 2 .Lancet et al. (1970); 3. Medina et al. (2000); 4. Horita and Berndt (1999); 5. Taran et al. (2010); 6. Ni and Yin (2011); 7. Taran et al. (2007); 8. Foustoukos and Seyfried (2004); 9. Fu et al. (2007); 10. Zhang et al. (2013). The "industrial catalysis" field is based on Wang et al. (2011) and references therein.



Schematic representation of CH4 production at a land-based ultramafic serpentinization site. Methane-rich seeps and hyperalkaline springs are typically found in correspondence with faults, often in tectonic contacts between peridotites and limestones or carbon-rich metasedimentary rocks.

Our laboratory data are compatible with the isotopic patterns of naturally occurring CH4 in land-based seeps and hyperalkaline springs. Our experiments suggest that Ru-enriched chromitites could potentially generate methane at low T on Earth and other planets. For example, since ruthenium was reported in Martian meteorites, low T Sabatier reaction may produce abiotic CH4 in Martian Ru-bearing rocks (*Etiope, Ehlmann and Schoell, 2013, Icarus, 224, 276-285*).

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