

Low-temperature catalytic CO₂ hydrogenation with geological quantities of ruthenium: a possible abiotic CH₄ source in chromitite-rich serpentinized rocks

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ABSTRACT

Metal-catalysed CO₂ hydrogenation is considered a source of methane in serpentinized (hydrated) igneous rocks and a fundamental abiotic process germane to the origin of life. Iron, nickel, chromium and cobalt are the catalysts typically employed in hydrothermal simulation experiments to obtain methane at temperatures >200°C. However, land-based present-day serpentinization and abiotic gas apparently develop below 100°C, down to approximately 40–50°C. Here, we document considerable methane production in thirteen CO₂ hydrogenation experiments performed in a closed dry system, from 20 to 90°C and atmospheric pressure, over 0.9–122 days, using concentrations of non-pretreated ruthenium equivalent to those occurring in chromitites in ophiolites or igneous complexes (from 0.4 to 76 mg of Ru, equivalent to the amount occurring approximately in 0.4–760 kg of chromitite). Methane production increased with time and temperature, reaching approximately 87 mg CH₄ per gram of Ru after 30 days (2.9 mgCH₄/g_{Ru}/day) at 90°C. At room temperature, CH₄ production rate was approximately three orders of magnitude lower (0.003 mgCH₄/g_{Ru}/day). We report the first stable carbon and hydrogen isotope ratios of abiotic CH₄ generated below 100°C. Using initial δ¹³C_{CO2} of -40‰, we obtained room temperature δ¹³C_{CH4} values as ¹³C depleted as -142‰. With time and temperature, the C-isotope separation between CO₂ and CH₄ decreased significantly and the final δ¹³C_{CH4} values approached that of initial δ¹³C_{CO2}. The presence of minor amounts of C₂–C₆ hydrocarbons is consistent with observations in natural settings. Comparative experiments at the same temperatures with iron and nickel catalysts did not generate CH₄. Ru-enriched chromitites could potentially generate methane at low temperatures on Earth and on other planets.

Key words: abiotic methane, chromitites, CO₂ hydrogenation, ruthenium, Sabatier reaction

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INTRODUCTION

The Sabatier reaction (CO₂ + 4H₂ = CH₄ + 2H₂O), also known as CO₂ hydrogenation or methanation, is a Fischer-Tropsch-type (FTT) synthesis commonly invoked to explain the origin of methane observed in serpentinized ultramafic rocks, in mid-ocean ridges and on continents (McCullom & Seewald 2007; Proskurowski *et al.* 2008; Etiope *et al.* 2011, 2013a,b; Etiope & Sherwood Lollar 2013; Schrenk *et al.* 2013; Szponar *et al.* 2013). The H₂ necessary for the reaction is produced by serpentinization, that is, the hydration of peridotite minerals (McCullom & Seewald 2007; Schrenk *et al.* 2013). The CO₂ may have various origins including the mantle, limestone or the atmosphere. CO₂

hydrogenation is also considered to be a possible step in the origin of life, that is, for the passage from inorganic to organic chemistry (Russell *et al.* 2010). It can be important in atypical petroleum systems, where hydrocarbon reservoirs are formed by igneous rocks (Farooqui *et al.* 2009; Etiope *et al.* 2013b; Etiope & Schoell 2014). It is also a potential source of methane on some planets (Tobie *et al.* 2006; Atreya *et al.* 2007; Etiope *et al.* 2013c). H₂ and CO₂ react on the surface of a metal catalyst, which lowers the activation energy required for the reaction. To date, laboratory experiments aimed at stimulating FTT synthesis in geological settings have produced methane only under ‘hydrothermal’ conditions, generally above 200°C as in mid-ocean ridges (see review by McCullom 2013), using traditional

catalysts, such as iron, nickel, chromium or cobalt (Figure S1). However, the abiotic methane observed in gas seeps and water springs in land-based ultramafic rocks altered by meteoric water (see a review by Etiope & Sherwood Lollar 2013 and Etiope *et al.* 2013b) appears to be produced at temperatures below 100°C, often around 40–50°C (Bruni *et al.* 2002; Etiope *et al.* 2011; Boschetti *et al.* 2013; Suda *et al.* 2014), that is, at temperatures lower than those required for traditional catalysts to function, at least on laboratory timescales. The only catalysts known to be effective below 100°C are rhodium (Rh) (Jacquemin *et al.* 2010) and ruthenium (Ru) (Thampi *et al.* 1987). Rhodium is extremely rare and dispersed in parts-per-billion concentrations in ultramafic rocks. Ru is rare in submarine hydrothermal systems (McCollom and Seewald, 2007; Pašava *et al.* 2007), but within chromitites of many continental ophiolites and igneous complexes, it is a dominant platinum group element (PGE), reaching parts-per-million concentration levels (Economou-Eliopoulos 1996; Garuti & Zaccarini 1997; Prichard & Brough 2009). Ru is mainly in the form of sulphur minerals, such as laurite (RuS₂), ruthenian pentlandite ((Ni,Fe)₈RuS₈), and Ru-Ir-Os alloy or oxide (RuO₂) (Garuti & Zaccarini 1997). These are found in either stratiform or podiform chromitites with the concentrations typically in the range of 0.1–1 ppm (relative to mass chromitite) and up to several ppm in Cr-rich veins (e.g. Page & Talkington 1984; Bacuta *et al.* 1990). In ophiolite sequences, Ru-enrichments are preferentially within tectonite and Moho transition zones, particularly in crustal dunite (Prichard & Brough 2009; Mosier *et al.* 2012). We note a geographic coincidence between the occurrence of Ru-rich chromitites and methane. Following discoveries in the 1980s and 1990s in the Philippines, Oman and New Zealand, new cases of gas-bearing seeps or hyperalkaline (pH >9) springs in present-day serpentinized rocks have recently been documented, with CH₄ isotopic analyses, in Turkey, Canada, Japan, Italy, Greece and Portugal (Etiope *et al.* 2011, 2013a,b; Boschetti *et al.* 2013; Szponar *et al.* 2013; Suda *et al.* 2014). All of these seeps are adjacent to chromite mines or located above ultramafic rocks hosting Ru-enriched chromitites. Examples include the Chimaera fires in Turkey, close to the ancient chrome mines of Cirali (Juteau 1968), the Semail ophiolite in Oman (Page *et al.* 1982), the Othrys ophiolite in Greece (Garuti *et al.*, 1999), the Zambales in the Philippines (Bacuta *et al.* 1990), Newfoundland in Canada (Page & Talkington 1984) and Cabeço de Vide in Portugal (Dias *et al.* 2006). The deep boreholes that provided abiotic gas from crystalline Precambrian rocks at Sudbury in Canada (Sherwood Lollar *et al.* 2008) are located in one of the richest Ru mines in North America (Ames & Farrow 2007). Furthermore, large amounts of methane leading to explosions were reported in what is likely the world's largest Ru mine complex, Bushveld in South Africa (Cook 1998). Could Ru

minerals play a methanation role in these low-temperature geological environments?

To start answering this question, we conducted laboratory methanation experiments at room temperature (20–25°C), and at 50 and 90°C in a closed system (borosilicate glass bottles) using extremely small concentrations of non-pretreated Ru oxide, equivalent to those present in chromitites. Ru catalysis is known in industrial applications but only after special pretreatment of the metal (e.g. reduction under H₂ stream) to enhance its catalytic performance and to obtain substantial amounts of CH₄ within a few hours (Thampi *et al.* 1987). Nonartificially pretreated Ru, where the catalytic activity is reduced by adsorption of humidity from air, is more analogous to natural conditions in rocks. Laboratory prepared C-free catalyst, with known Ru concentration, was preferred in our experiments over natural Ru-bearing minerals or rocks (chromitites) for several reasons. Small rock samples, even if derived from the same chromitite, can in fact have different (and unknown) Ru concentrations and may contain several contaminant carbon forms, including CH₄. Unlike previous experiments in aqueous solutions aimed at stimulating water-rich hydrothermal conditions (see review by McCollom 2013 and Figure S1), we tested methanation under dry conditions, the simplest system for the Sabatier reaction, where solubility factors do not influence CO₂ and H₂ adsorption–desorption at the catalyst surface. Analogous conditions occur in dry fractures and gas-filled pores in unsaturated rocks such as in igneous reservoir gas-caps (Liu *et al.* 1998; Farooqui *et al.* 2009), which might also represent the source of CH₄ in land-based serpentinization systems. FTT reactions are quite sluggish in aqueous solution even at high temperatures (McCollom 2013; Zhang *et al.* 2013), and CO₃²⁻, the only C form in CH₄-bearing hyperalkaline waters (pH >9), does not significantly react with H₂. In practice, CO₂ does not exist in waters with pH >9 and transformation of C (other than CO₂) to methane using H₂ is thermodynamically unfavourable at low temperature (R. Thampi, personal communication). As a consequence, the hyperalkaline waters of land-based serpentinization systems could be just a carrier, but not a producer of CH₄ which is likely generated in and migrated from water unsaturated ultramafic rocks. Therefore, while aqueous FTT experiments are important for simulating high-temperature hydrothermal systems, dry FTT experiments may be better analogues of low-temperature land-based systems, especially those where gas is not associated with groundwater, for example, the microseepage from peridotite outcrops in the Tekirova ophiolite (Etiope *et al.* 2011) and the dry gas seeps of Chimaera in Turkey, Poison Bay in New Zealand and Los Fuegos Eternos in the Philippines.

The carbon and hydrogen isotope ratios of CH₄ generated are fundamental parameters for interpreting gas origins in natural settings, including abiotic methane (Schoell 1980; Whiticar 1990; Etiope & Sherwood Lollar 2013;

and McCollom 2013). Until a few years ago, and based on a limited number of data, the isotopic composition of abiotic gas was considered to be typically enriched in ^{13}C , with $\delta^{13}\text{C}$ values higher than -25‰ . Today, a wider set of isotopic data are available and show the $\delta^{13}\text{C}$ of methane in land-based serpentinized ultramafic rocks can have values up to -37‰ while methane from Precambrian shields can be even lighter (Etiope & Sherwood Lollar 2013). Laboratory experiments have produced abiotic methane with $\delta^{13}\text{C}$ values as depleted as -57‰ , which is comparable to the isotopically 'light' values derived from biological activity (Horita & Berndt 1999). But thus far, carbon and hydrogen isotope compositions have only been measured at 'hydrothermal' conditions, above 200°C (McCollom 2013; see also Figure S1). Here, we present the first methane C and H isotope data for abiotic CH_4 generated below 100°C and down to $20\text{--}25^\circ\text{C}$.

For comparison and control, parallel experiment was performed with Fe and Ni catalysts that are more abundant, with respect to ruthenium, in ultramafic rocks, but they are known to be ineffective for CO_2 hydrogenation at temperatures below 100°C (Wang *et al.* 2011 and references therein; R.Thampi, personal communication).

In brief, this study mainly addressed the following questions: (i) Can methane be produced by Sabatier reaction at temperatures below 100°C using concentrations of non-pretreated ruthenium equivalent to those occurring in chromitites in ophiolites or igneous complexes? (ii) What is the C and H isotope separation between produced CH_4 and initial CO_2 and H_2 , at these low temperatures? (iii) How does this isotope separation evolve with time and temperature? (iv) Is methane the only hydrocarbon produced under these conditions?

This experimental study only initiates the evaluation of Ru as a catalyst in natural geological systems and does not purport whether or not natural Ru minerals actually control or facilitate the low-temperature production of CH_4 in chromitites. The main chemical and mineralogical factors that should be investigated in future are, however, discussed.

METHODS

Experimental set-up

Thirteen methanation ($\text{CO}_2 + \text{H}_2$ mixing) experiments were performed with different combinations of temperature ($20\text{--}25$, 50 and 90°C) and amounts of Ru catalysts (from 0.38 to 76 mg Ru), for $0.9\text{--}122$ days. CO_2 hydrogenation was obtained in borosilicate glass Wheaton bottles (155 ml) filled with 5 ml CO_2 and 50 ml H_2 (high purity 99.99% , Scotty Standards) diluted with argon as make-up gas. Both standards have methane or other hydrocarbons level below detectable limits. The minimum

$\text{H}_2:\text{CO}_2$ ratio for the Sabatier reaction is $4:1$; because some H_2 can react with O_2 occurring in the non-pretreated catalyst support, a surplus of H_2 is beneficial to maintain the essential $4:1$ ratio after the possible H_2 loss. ^{13}C -labelled (99% ^{13}C) CO_2 , which is useful to trace the source of carbon in reaction products and evaluate the extent of contamination, was used in a control test, as described below. We purposefully did not use labelled CO_2 in the experiments because we wanted to study the carbon isotope effects between CO_2 and CH_4 in natural isotope abundances at low temperature. This would not be possible using a ^{13}C -carbon isotope labelled CO_2 . Similarly, the ^{13}C -labelling technique was not used by Fu *et al.* (2007), Taran *et al.* (2007, 2010), McCollom *et al.* (2010) and Zhang *et al.* (2013). Isotopically labelled material was actually not necessary because the amount of abiotic methane synthesized greatly exceeded the potential background sources, as confirmed by the control tests. All bottles were slightly overpressurized with respect to ambient conditions by injecting approximately $20\text{--}30\%$ more argon than bottle capacity to reduce fractionation effects due to depressurization of the bottle during sample taking for analyses. The bottles were sealed with gas impermeable blue butyl septa (Bellco Glass Inc.) and aluminium crimp caps. Prior to use, the septa were boiled in 1 N NaOH to remove trace hydrocarbon contaminants and potentially reactive plasticizers (Oremland & Des Marais 1983).

Two types of Ru catalysts on carbon-free supports, non-pretreated in a H_2 stream, were used: 3.8% Ru on titania (TiO_2) and 3.8% Ru on alumina (Al_2O_3), both prepared by the School of Chemical and Bioprocess Engineering of the University College of Dublin, as described by Thampi *et al.* (1987). Ru was not prerduced in H_2 , and it is predominantly in the form of RuO_2 , with minor amounts of suboxides RuO_x (x between 1.9 and 2). This chemical form is the same of naturally occurring Ru oxides in chromitites (Garuti & Zaccarini 1997). The catalyst preparation procedure ensured nanosized deposits of Ru oxides and suboxides on the alumina and titania supports akin to the most probable condition prevailing in natural geological samples, where Ru occurs in finely dispersed forms. Finely dispersed and nanosized clusters of catalytically active elements tend to show higher reactivity than larger clusters or particles (R. Thampi, personal communication). The amount of catalyst powder used in the experiment (0.01 , 0.1 , 0.2 and 2 g at $3.8\text{wt}\%$ Ru) was equivalent, in terms of order of magnitude, to the range of Ru occurring in $0.4\text{--}760$ kg of chromitite in continental serpentinized ultramafic rocks, considering an average Ru concentration range of $0.1\text{--}1$ ppm ($0.1\text{--}1$ mg Ru per kg of chromitite; Economou-Eliopoulos 1996; Mosier *et al.* 2012). Assuming an average chromitite density (approximately $4000\text{--}4500$ kg m^{-3}) and a typical fracture porosity of serpentinized rocks ($5\text{--}10\%$; Hövelmann *et al.* 2012), the volume

of a 155-ml bottle is equivalent to that of gas in the pores/fractures of approximately 6–14 kg of chromitite, which would contain 0.6–14 mg of Ru; such an amount occurs in approximately 0.016–0.37 g of Ru catalyst powder. Bottles were stored in the dark at room temperature (20–25°C) and in a thermostated oven at 50°C, 90°C, and, for a few initial tests, 200°C, for up to 4 months (Table 2). In total, 58 bottles, including three duplicates (one duplicate = two bottles with the same catalyst amount, temperature and reaction time), were analysed. Each ‘time point’ data refers to ‘one bottle experiment’ (one time point = one sacrificial bottle), not to a time series evolution of gas in the same bottle.

The same procedure was adopted for a parallel, comparative experiment based on Fe and Ni catalysts (Table S1). Twenty-nine bottles were filled with 5 g of magnetite (Fe₃O₄ 95%, powder <5 µm, Aldrich). Eleven bottles were filled with 5 g of nichel catalyst (CRG-F Syntex pellets Ø 3.4 mm × 3.5 mm) composed by NiO (75–81%), SiO₂ (0.2%), K₂O (0.35%) and Al₂O₃ (balance). Seven bottles were filled with a 50% mixture of Fe and Ni catalyst. The samples were stored at room temperature (25°C) and in a thermostated oven at 50, 90 and 200°C, up to 108 days (Table S1).

Gas analyses

The CH₄ and CO₂ in all bottles were analysed by an instrumental package (West Systems, Pontedera, Italy) equipped with TDLAS (tunable diode laser absorption spectroscopy; range 0.1 ppmv – 100%v/v; repeatability, 0.1 ppmv) and a double-beam infrared CO₂ sensor (IR-Licor; range 0–20 000 ppmv with an accuracy of 2% and a repeatability of ±5 ppmv) (Fig. 1). Gas in the bottle entered the detector inlet through a needle in the septa and returned to the bottle via a second needle. The background CH₄ concentration (generally of approximately 2 ppmv) in the air inside the sampling and output line of the

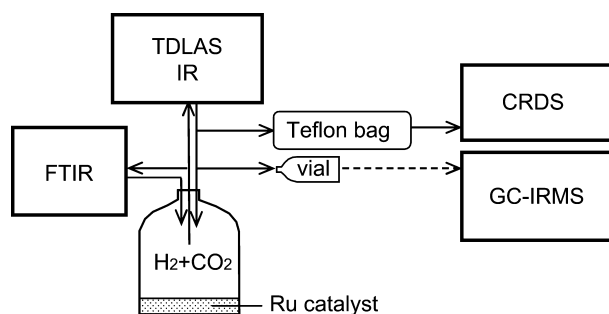


Fig. 1. Sketch of the analytical system used in the methanation experiments. TDLAS, tunable diode laser absorption spectroscopy; CRDS, cavity ring-down spectroscopy; IR, infrared; IRMS, isotope ratio mass spectrometry; GC, gas chromatograph; FTIR, Fourier transform infrared spectrometer.

instrument were measured before each sample analysis. In this manner, CH₄ in the bottle, which exceeded the air concentration, was immediately detected with simultaneous visualization of the CO₂ concentration. Thirty-two bottles were then analysed using a Fourier transform infrared spectrometer (FTIR Gasmeter DX-4030, Gasmeter, Finland,) with a standard spectra library for rapid, semiquantitative (with an accuracy ranging from 10% to 20%) and simultaneous determination of 13 gases (CH₄, CO₂, H₂O, CO, C₂H₆, C₂H₄, C₃H₈, n-C₄H₁₀, i-C₄H₁₀, n-C₅H₁₂, i-C₅H₁₂, C₆H₆ and COS), with typical detection limits of 1 ppmv. Each bottle was analysed once. For bottles with CH₄ above 3 ppmv, approximately 60–100 ml of gas were collected in a Teflon bag and analysed within 10 min, using a cavity ring-down spectroscopy (CRDS) methane carbon isotope analyser (Picarro G2112-I, Picarro Inc., California; precision <0.7‰ at 1.8 ppmv CH₄, 5 min, 1σ, and <0.4‰ at 20 ppmv CH₄, 5 min, 1σ). Fifteen gas samples with at least 100 ppmv of CH₄ (detected by TDLAS) were stored in pre-evacuated 20-ml vials for the analysis of molecular composition (C₁–C₆ alkanes, H₂ and CO₂) by gas chromatography (Shimadzu 2010 TCD-FID, accuracy 2%), and the isotopic composition of CH₄ and CO₂ by isotope ratio mass spectrometry (IRMS, Finnigan Delta Plus XL, precision ± 0.1‰ for ¹³C and ± 2‰ for ²H) at Isotech Laboratories Inc., Illinois. Only a few samples were analysed for the deuterium isotopic composition of CH₄ and H₂ (the large concentrations of hydrogen gas present in the samples interfered with the δ²H_{CH₄} analysis at low CH₄ concentrations). GC-IRMS was also used for the analysis of CO₂ and H₂ standards (the reagents).

Control tests

Prior to methanation experiments, seven types of control tests (CT in Table 1) were executed to evaluate possible isotopic fractionation during gas sampling, storage and transfer, and the absence of background carbon sources (graphite, CO₂, CH₄ or other hydrocarbons) in the catalyst powder and other material involved in the reaction. After the experiments, a conclusive ¹³C-labelling test was performed to verify that all CH₄ is originated from CO₂ and not other C sources. A semiconductor detector (Hydrotech Huberg, Italy; detection limit of 5 ppmv) was used to detect H₂ in the control test CT4 (Table 1). Blank tests performed on bottles with catalysts but without reagents, and empty bottles, demonstrated that CH₄ and C₂₊ hydrocarbons are not released by septa (either pretreated or untreated) or by catalysts after heating up to 200°C for 48 h. The blue butyl septa may release only C₃₊ hydrocarbons if not pretreated with NaOH (Ward *et al.* 2004). Tests on bottles filled with isotopically known CH₄ (δ¹³C: -44‰, 99% CH₄) showed that no CH₄ isotopic fractionation was observed after 60 days, or during gas transfer

from bottles to syringes or Teflon sampling bags. Hydrocarbons were not detected in CO₂ and H₂ standards. Tests at 200°C with Ru catalyst (1 g) and H₂ without CO₂ (CT5, Table 1) and with CO₂ without H₂ (CT6) did not produce any hydrocarbon. A further test with reagent gases without catalyst (CT7), lasting 3 months at 90°C, did not produce any hydrocarbons. CH₄ was always below detection limit (0.1 ppmv with TDLAS). Field emission scanning electron microscopy (FESEM) analyses on both alumina- and titania-supported catalyst powder did not reveal detectable carbon amounts (e.g. graphite) prior to the experiments, according to the catalyst preparation procedure described by Thampi *et al.* (1987).

A final control test (CT8) with labelled ¹³C₂O₂ (99% ¹³C, Aldrich) confirmed that CH₄ is produced exclusively from CO₂ hydrogenation. Three bottles with 1 g of Ru on alumina and the same H₂+CO₂ concentrations used in the experiments (10:1 ratio), after 3 days at 90°C and 50°C and 15 days at 25°C, produced 1400 ppmv, 180 ppmv and 10 ppmv of isotopically labelled methane, respectively (¹³CH₄, as indicated by out of calibration readings, >+100 000‰ VPDB, of the CRDS isotope analyser).

These control tests suggested that the only carbon source in the methanation experiments is the injected reagent CO₂, and no significant isotopic fractionations are expected during the several steps of gas storage and sampling. The methane amounts observed in the experiments were, however, much higher than those that may be induced by microquantities of carbon impurities inside the bottles.

Preliminary methanation tests at 200°C

Preliminary tests were conducted at 200°C (Table 2) to verify quickly CH₄ production by non-pretreated Ru powder. The tests showed a rapid and considerable CH₄ production (up to 17380 ppmv or 37 mg CH₄ per gram of ruthenium after 24 h). Three catalyst samples used in these tests were then left in contact with air for several days and reused, without regeneration: CH₄ production was then significantly reduced and variable (as also its carbon isotopic composition) depending on the catalyst sample. No production of C₂₊ alkanes or CO was observed.

RESULTS

In all experiments with Ru (Table 2), we observed significant methane production that correlates with (i) temperature, (ii) the time elapsed since the initiation of heating and (iii) the amount of catalyst. CH₄ concentrations measured by TDLAS, FTIR and GC are in fair agreement; a slight CH₄ depletion from TDLAS to GC and FTIR (up to about 15%) reflected sample dilution and air contamination during the several steps of gas transfer and analysis. The several catalyst samples, due to random exposition to air, may have acquired different catalytic performance, with different CO₂ adsorption and CH₄ release capacities. This can explain why some samples with longer methanation time produced less CH₄ than others with shorter reaction time. Carbon isotope ratio data ($\delta^{13}\text{C}_{\text{CH}_4}$) by CRDS and

Table 1 Molecular and isotopic composition of gas in control tests

Control Tests (CT)	CH ₄	$\delta^{13}\text{C}_{\text{CH}_4}$	CO ₂	$\delta^{13}\text{C}_{\text{CO}_2}$	H ₂	$\delta^2\text{H}_{\text{H}_2}$	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀
gas standards	50.0 (GC)	-44.0	99.9 (GC)	-40.1	99.99 (GC)	-226.7	bd ^a (GC)	bd ^a (GC)	bd ^a (GC)
(1)	49.1 (GC)	-43.4	n	n	n	n	n	n	n
(2)	47.0 (GC)	-44.7	99.0 (GC)	-40.5	n	-227.5	n	n	n
(3)	bdl (TDLAS)	n	99.0 (GC)	-40.5	n	-227.5	bd (GC)	bd (GC)	bd (GC)
(4)	bdl (TDLAS)	n	bd (IR)	n	bd (SC)	n	bd (GC)	bd (GC)	bd (GC)
(5)	bdl (TDLAS)	n	bd (IR)	n	n	n	bd (FTIR)	bd (FTIR)	bd (FTIR)
(6)	bdl (TDLAS)	n	>20 000 (TDLAS)	n	bd (SC)	n	bd (FTIR)	bd (FTIR)	bd (FTIR)
(7)	bdl (TDLAS)	n	>20 000 (TDLAS)	n	n	n	bd (FTIR)	bd (FTIR)	bd (FTIR)
(8)									
90°C	1400	>+100 000	n	99% ¹³ C	n	n	n	n	n
50°C	180	>+100 000	n	99% ¹³ C	n	n	n	n	n
25°C	10	>+100 000	n	99% ¹³ C	n	n	n	n	n

(1) Check of CH₄ isotopic fractionation by leaks from bottles: long-term storage (50 vol% CH₄, 50°C × 45 days). (2) Check of CH₄, CO₂ and H₂ dilution and isotopic fractionation after gas standards handling from bottles (for TDLAS), to vials (for IRMS) and gas bags (for CRDS). (3) Check of CO₂ and H₂ isotopic fractionation by leaks from bottles and hydrocarbons release from septa: long-term storage (pure standards, 50°C × 45 days). (4) Check of hydrocarbons, CO₂ and H₂ release from ruthenium catalysts or septa (in pure argon, no reagents; 200°C × 48 h). (5) Check of CO₂ and hydrocarbon production at 200°C (3 days) by catalyst (1 g Ru on alumina) + H₂ (50 ml diluted in argon). (6) Check of hydrocarbon production at 200°C (3 days) by catalyst (1 g Ru on alumina) + CO₂ (50 ml diluted in argon). (7) Check of hydrocarbon production without catalyst, at 90°C (3 months) by 10H₂ + CO₂ (50 and 5 ml respectively, diluted in argon). (8) ¹³C-labelled test (¹³CO₂ + 10H₂) with 1 g of Ru (on alumina) at 90°C (3 days), 50°C (3 days) and 25°C (15 days). The $\delta^{13}\text{C}_{\text{CH}_4}$ values are out of CRDS calibration range, just indicative of the produced ¹³C-labelled CH₄. Gas concentration in vol%, except for CT(8) where CH₄ is in ppmv (measured by TDLAS); isotopic composition in ‰ VPDB for C (measured by CRDS for CH₄ and IRMS for CO₂), ‰ VSMOW for H (measured by IRMS). Mean of 2 test runs is reported for all control samples. Analytical technique in brackets (GC, gas chromatography; CRDS, cavity ring-down spectroscopy; IRMS, isotope ratio mass spectrometry; TDLAS, tunable diode laser adsorption spectroscopy; SC, semiconductor; FTIR, Fourier transform infrared spectrometer). CH₄ gas standard used only for control tests (1–2); CO₂ and H₂ standards are the same used as reagents in the methanation experiments; bd, below detection limit; n, not measured; ^aHydrocarbons in both CO₂ and H₂ standards were below detection limit.

Table 2 Results of the methanation tests

T °C	Catalyst (grams)	days	CH ₄ TDLAS	CH ₄ prod*	$\delta^{13}\text{C}_{\text{CH}_4}$		$\delta^2\text{H}_{\text{CH}_4}$		$\delta^2\text{H}_{\text{H}_2}$	CO ₂		$\delta^{13}\text{C}_{\text{CO}_2}$ IRMS	CH ₄ GC - FTIR	CO	C ₂	C ₃	C ₄	C ₅	C ₆₊ GC	benz FTIR			
					CRDS	IRMS	IRMS	IRMS		IR	GC										GC	GC	GC
200	Ru-Al 2 g	0.9	5540	11.9	-78	n	n	n	n	1.04	n	n	n-n	n-n	n-n	n-n	n-n	n-n	n-n	n	n		
		1	17380	37.3	-64	n	n	n	n	0.14	n	n	n-n	n-n	n-n	n-n	n-n	n-n	n-n	n	n		
		1	13600	29.2	-68	n	n	n	n	0.53	n	n	n-n	n-n	n-n	n-n	n-n	n-n	n-n	n	n		
		2	193	0.3	-21	n	n	n	n	1.62	n	n	n-187	n-bd	n-bd	n-bd	n-bd	n-bd	n-bd	n-bd	n	bd	
		6	40	0.1	-48	n	n	n	n	1.57	n	n	n-35	n-bd	n-bd	n-bd	n-bd	n-bd	n-bd	n-bd	n	bd	
		10	36	0.1	-67	n	n	n	n	>2.00	n	n	n-34	n-bd	n-bd	n-bd	n-bd	n-bd	n-bd	n-bd	n	bd	
		1	833	3.6	-105	-102.0	n	n	n	15.1	>2.00	2.12	-32.9	740-n	bd-n	10-n	bd-n	bd-n	bd-n	bd-n	10	n	
		3	9270	12.3	-84	-83.0	n	n	n	9.0	0.77	0.72	-12.5	9060-n	bd-n	120-n	20-n	5-n	bd	40	n		
		5	21200	28.2	-68	-60.4	n	n	n	465	17.8	1.74	-13.4	18120-n	bd-n	210-n	37-n	19-n	3-n	64	n		
		8	30000	40.0	-56	-54.6	n	n	n	439	4.6	0.38	-5.9	25350-n	bd-n	420-n	180-n	42-n	6-n	44	n		
18	19500	26.0	-59	n	n	n	n	n	0.08	0.08	n	n-18203	n-bd	n-142	n-59	n-48	n-10	n	38	n			
30	65000	86.6	-42	-41.2	n	n	n	390	0.4	0.07	-6.0	57000-61600	bd-bd	480-520	200-220	52-20	45-60	29	40	n			
3	43	1.1	-114	n	n	n	n	n	>2.00	n	n	n-41	n-bd	n-bd	n-bd	n-bd	n-4	n	bd	n			
5	116	3.1	-108	n	n	n	n	n	1.36	n	n	n-110	n-3	n-2	n-bd	n-bd	n-3	n	bd	n			
7	1680	44.8	-85	-84.3	n	n	n	n	>2.00	2.47	-36.1	1320-1607	bd-4	28-11	4-9	bd-4	bd-5	17	17	n			
18	2230	59.4	-79	-82.0	n	n	n	n	>2.00	2.18	-33.6	2140-2122	bd-2	50-24	11-8	6-4	bd-8	27	32	n			
14	28	7.5	-93	n	n	n	n	n	>2.00	n	n	20	n-bd	n-bd	n-bd	n-bd	n-bd	n	bd	n			
14	44	11.7	-85	n	n	n	n	n	>2.00	n	n	31	n-bd	n-bd	n-bd	n-bd	n-bd	n	bd	n			
0.25	168	0.3	-105	n	n	n	n	n	>2.00	n	n	n	n	n	n	n	n	n	n	n			
3	285	0.4	-99	n	n	n	n	n	1.75	n	n	n	n	n	n	n	n	n	n	n			
6	1460	1.9	-97	-96.0	n	n	n	n	1.7	0.35	0.37	-36.5	1350-1299	40-91	37-28	13-22	bd-4	bd-5	26	36	n		
15	313	0.4	-97	-97.0	n	n	n	n	n	0.57	n	n	n	n	n	n	n	n	n	n			
2	31	0.4	-104	n	n	n	n	n	n	1.82	n	n	n	n	n	n	n	n	n	n			
5	203	2.7	-92	-89.0	n	n	n	n	11.0	1.66	1.65	-37.8	190-n	97-n	8-n	4-n	bd-n	bd-n	13	n			
7	72	1.0	-103	n	n	n	n	n	n	1.90	n	n	n-68	n-64	n-2	n-2	n-bd	n-2	n-9	n	4		
10	316	4.2	-91	-90.0	n	n	n	n	8.5	1.61	1.62	-37.0	310-308	130-98	14-6	10-11	3-bd	bd-11	15	17			
50	Ru-Al 2 g	8	2200	2.9	-115	-105.2	n	n	n	9.2	1.96	1.92	n	bd-11	58-29	35-30	9-2	bd-4	64	47	n		
		13	2160	2.9	-110	n	n	n	n	1.30	n	n	n	n-2010	n-15	n-33	n-29	n-2	n-4	n	31	n	
		28	5260	7.0	-97	-98.9	-593	n	n	5.8	1.58	1.34	n	6090-4965	bd-bd	151-84	99-48	28-17	8-4	14	37	n	
		76	63000	84	-63	-60.0	n	n	n	n	1.25	n	n	n	n-54240	n-2	n-332	n-134	n-47	n-118	n	40	n
		8	29	0.8	-116	n	n	n	n	n	>2.00	n	n	n-23	n-4	n-bd	n-bd	n-bd	n-2	n	bd	n	
		15	214	5.7	-90	-86.0	n	n	n	6.8	>2.00	2.51	n	200-186	bd-2	9-3	4-3	bd-bd	bd-5	30	5	n	
		28	46	1.2	-108	n	n	n	n	n	>2.00	n	n	n	n-40	n-bd	n-bd	n-bd	n-4	n	bd	n	
		60	73	1.9	-100	n	n	n	n	n	>2.00	n	n	n	n-50	n-bd	n-bd	n-bd	n-2	n	4	n	
		8	0	0	n	n	n	n	n	n	>2.00	n	n	n	n	n-bd	n-bd	n-bd	n-bd	n-2	n	bd	n
		15	0	0	n	n	n	n	n	n	>2.00	n	n	n	n	n-bd	n-bd	n-bd	n-bd	n-2	n	bd	n
28	0	0	n	n	n	n	n	n	1.35	n	-5.9	n	n-bd	n-bd	n-bd	n-bd	n-bd	n-bd	n	bd	n		
80	2.1	0.6	-80	n	n	n	n	n	>2.00	n	n	n	n-bd	n-bd	n-bd	n-bd	n-bd	n-bd	n	bd	n		
90	4.9	1.2	-62	n	n	n	n	n	>2.00	n	-6.0	n	n-2	n-bd	n-bd	n-bd	n-bd	n-bd	n	bd	n		
76	3058	4	-112	n	n	n	n	n	1.78	n	n	n	n-3	n-bd	n-bd	n-bd	n-bd	n-55	n	bd	n		

0.2 to 1.1 mg CH₄/g_{Ru}/day; Fig. 2b). After 76 days, 84 mg of CH₄ (63 000 ppmv) was produced using 2 g of Ru on alumina support. At room temperature, CH₄ production was approximately two orders of magnitude lower than at 50°C (<0.004 g CH₄/g_{Ru}/day; 0.1 mg of CH₄ = 70 ppmv, after 1 month on alumina support; Fig. 2c). Two duplicate samples analysed on days 42 and 105 have similar CH₄ concentration values (49 versus 43 ppmv, and 24 versus 31 ppmv; Table 2). At all temperatures, the catalyst supported by titania appeared to be less productive than that with alumina.

The carbon isotope separation between CO₂ and CH₄ ($\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CH}_4}$) and CO₂ concentrations decreased as the CH₄ concentration increased (Fig. 3). At all temperatures, CH₄ was initially extremely ¹³C depleted ($\delta^{13}\text{C}$ up to 102‰ lower than CO₂) and progressively became ¹³C enriched with time. ¹³C enrichment also directly correlated with temperature. Such a shift in $\delta^{13}\text{C}_{\text{CH}_4}$ with time corresponded to a parallel shift in $\delta^{13}\text{C}$ for residual CO₂. Knowing the initial $\delta^{13}\text{C}_{\text{CO}_2}$ to be -40‰, we measured $\delta^{13}\text{C}_{\text{CH}_4}$ values down to -142‰ for the room temperature experiments. $\delta^{13}\text{C}_{\text{CH}_4}$ approached that of original CO₂ after a month at 90°C. Two duplicate samples with titania support, measured at room temperature on days 42 and 105, have similar

$\delta^{13}\text{C}_{\text{CH}_4}$ values (-125 versus -126‰ and -99.8 versus -100‰, respectively). For the same amount of CH₄ produced, the carbon isotopic separation did not depend on the support type.

Three $\delta^2\text{H}_{\text{CH}_4}$ values determined at 90 and 50°C show that CH₄ produced is strongly depleted in deuterium ($\delta^2\text{H}_{\text{CH}_4}$ up to -465‰) with respect to the H₂ precursor ($\delta^2\text{H}_{\text{H}_2}$: -226.7‰). In all these cases, the residual H₂ is even more ²H depleted (up to -593‰) with respect to the initial H₂.

A substantial production of C₂-C₆ hydrocarbons (C₂₊), on the order of tens and hundreds of ppmv, is produced in samples as low as 50°C (Fig. 4 and Table 2). The C₂₊ concentration, which was generally higher with alumina support, was proportional to CH₄ and increased with both temperature and time.

At 90°C, CO was produced (up to 130 ppmv) only on titania support, and not observed with the alumina support (Table 2). At lower temperatures, CO was present only on the alumina support. COS was not detected; therefore, it is not listed in Table 2.

The experiments with Fe and Ni oxide catalysts show significant CH₄ production only at 200°C (Table S1 in Supporting Information). At temperatures below 100°C, CH₄ was always within the range of the background (up

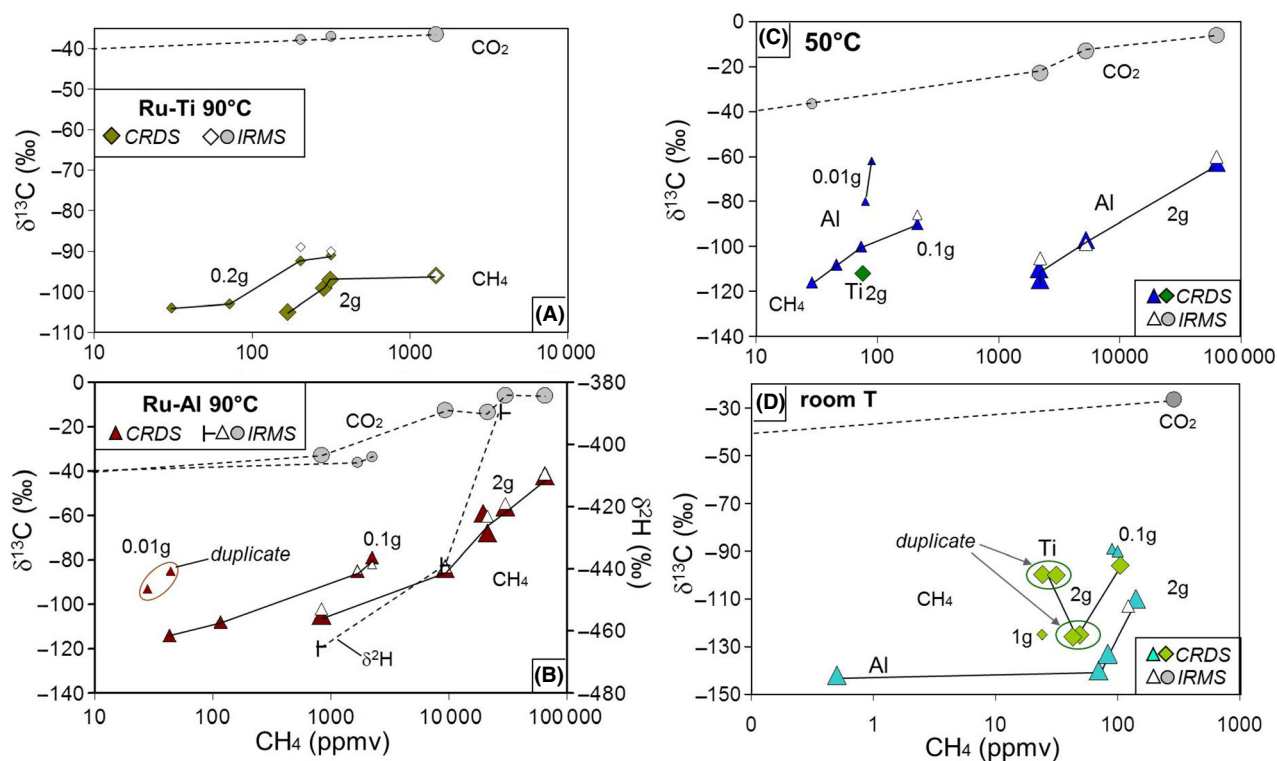


Fig. 3. The isotopic ratios of CH₄ and residual CO₂. Evolution at 90°C with (a) titania and (b) alumina support; (c) 50°C and (d) 20–25°C for both supports. The hydrogen isotopic composition of CH₄ was measured in three samples with alumina support (b). Isotopic analyses were made either by CRDS (cavity ring-down spectroscopy) for $\delta^{13}\text{C}_{\text{CH}_4}$ or by IRMS (isotope ratio mass spectrometry) for $\delta^{13}\text{C}_{\text{CO}_2}$, $\delta^{13}\text{C}_{\text{CH}_4}$, and $\delta^2\text{H}_{\text{CH}_4}$.

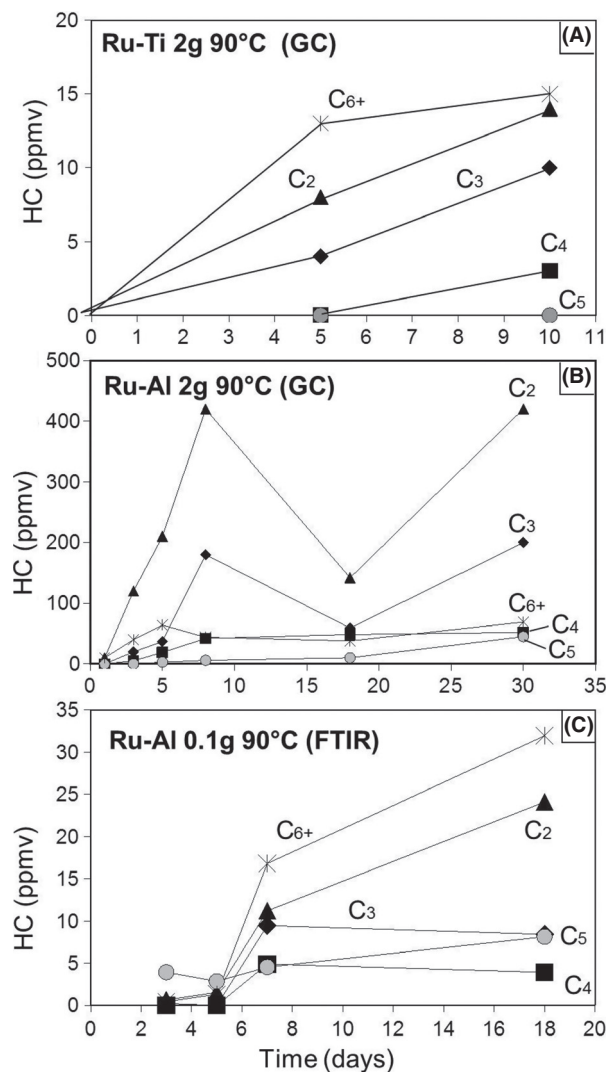


Fig. 4. The production of C₂-C₆ hydrocarbons at 90°C. Concentrations (in ppmv developed in glass bottles) with 2 g of catalysts on (a) titania, (b) alumina and (c) 0.1 g of catalysts on alumina.

to 14 ppmv with Fe, and <1 ppmv with Ni) observed in control tests without CO₂ and H₂. The few ppmv of CH₄ observed with Fe also in control tests are likely due to the carbon occurring in magnetite powder. The experiments confirm the sharp difference in the low T catalytic activity between Ru and the more traditional catalysts based on Fe and Ni.

DISCUSSIONS

Methane production

CH₄ was generated using extremely small concentrations of ruthenium, down to 0.38 mg Ru, equivalent to those occurring in only 4 kg of classical chromitite. Methane

generation was rapid, and the production rate apparently decreases with time. This is typical of catalytic methanation (e.g. Thampi *et al.* 1987; McCollom *et al.* 2010), and it may be attributed to the accumulation on the catalyst of liquid water (produced in the Sabatier reaction) which inhibits the reaction (Thampi *et al.* 1987), by poisoning (loss of activity due to impurities) or by coking, that is, the formation of carbonaceous residues which cover the active surface. The latter is a common process when hydrocarbons are involved in the reaction (Forzatti & Lietti 1999). At all temperatures, the catalyst supported by titania was less productive than that with alumina, likely because of higher initial poisoning, or because titania is more sensitive to air contamination that may oxidize and deactivate the catalyst (Jacquemin *et al.* 2010). In some bottles, the residual CO₂ and H₂ appear unbalanced respect to CH₄ production. This is typically due to the fact that there are always some CO₂ and CH₄ that may be sorbed on the catalyst surface and thus are not observable in the gas phase (Thampi *et al.* 1988). It must be noted that the catalyst was not pretreated but was subject to random exposure to ambient air with normal relative humidity (in Rome typically ranging from 67% in summer to 79% in winter). Thus, the amount of these sorbed gases may vary from a catalyst sample to another, and samples that experienced longer exposure to air may have led to different CO₂ adsorption/CH₄ production ratios and isotope fractionation. However, differential leakage during sample manipulation for analyses cannot be excluded.

The CH₄ production rates are lower than those measured by Thampi *et al.* (1987) using pretreated Ru (under H₂ flow in the absence of any contact with air; approximately 14 and 880 mgCH₄/g_{Ru} at 25°C, and 90°C, respectively). The catalytic power of air-contaminated Ru has been inadequately investigated in the past because the objective of laboratory methanation for industrial applications was to maximize efficiency using only pretreated catalysts. Our work indicates that Ru is effective even after adsorption of humidity from ambient air.

Carbon and hydrogen isotopes

We measured for the first time the isotopic composition of CH₄ abiotically generated below 100°C. At all temperatures, CH₄ was initially extremely ¹³C depleted with δ¹³C up to 102‰ lower than initial CO₂. Using a CO₂ with δ¹³C: -40‰ at the lowest temperatures (20–25°C), we obtained CH₄ with δ¹³C: -142‰. Although artificially generated and based on quite ¹³C-depleted CO₂, this is the most ¹³C depleted abiotic CH₄ reported in the literature. We observed that the lower the temperature, the less CH₄ produced and the longer the time until δ¹³C_{CH₄} values matched the initial CO₂, consistent with kinetic isotope fractionation over the surface of the catalyst, where

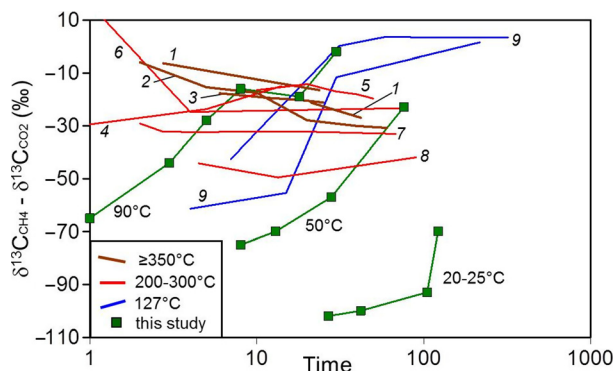


Fig. 5. The carbon isotopic separation observed in different FTFT experiments, at several temperatures. Time axis is in hours for experiments n. 2, 3, 5, 6, 7 and 9; and days for experiments n. 1, 4, 8 and for the present study. Data from: 1. Fu *et al.* (2007), 400°C; 2. Zhang *et al.* (2013), 400°C; 3. Taran *et al.* (2010), 350°C; 4. Horita & Berndt (1999), 300°C; 5. Taran *et al.* (2007), 296°C; 6. Hu *et al.* (1998), 280°C; 7. McCollom *et al.* (2010), 250°C; 8. Horita & Berndt (1999), 200°C; 9. Lancet & Anders (1970), 127°C. The isotopic fractionation from CO₂ to CH₄ increases over time or does not significantly change, in experiments at high temperatures (>200°C); it decreases over time in lower temperature experiments; the lower the temperature, the higher the isotopic fractionation.

¹²CO₂ molecules due to their weaker bond energies are first involved in the adsorption–desorption process (Hu *et al.* 1998; McCollom *et al.* 2010). As the reaction proceeds, increasingly more ¹³CO₂ molecules are involved, thereby producing ¹³C enriched CH₄. Similar observations were reported by Lancet & Anders (1970) with cobalt-catalysed CO hydrogenation at 127°C. The opposite (i.e. an increase in isotope fractionation with time) was instead observed in all experiments at temperatures >200°C (Fig. 5). As suggested by Fu *et al.* (2007), high temperatures may promote back reactions of higher hydrocarbons to CH₄, that is, depolymerization resulting in a progressive ¹³C depletion in CH₄.

In our experiments, only three δ²H_{CH₄ and three δ²H_{H₂ values were measured. Our measurements indicate that the CH₄ produced after approximately 1 week at 90°C was strongly depleted in deuterium (δ²H_{CH₄ up to −465‰) relative to the H₂ precursor (δ²H_{H₂: −226.7‰). Residual H₂ is then isotopically depleted in ²H relative to the initial H₂ as reported by Fu *et al.* (2007) and Taran *et al.* (2010) due to deuterium enrichment in the produced water. Our hydrogen isotope result is different from that reported by McCollom *et al.* (2010) for aqueous solutions at 250°C, where δ²H_{H₂ and δ²H_{CH₄ had similar values. Our data indicate that ²H increased over time, consistent with kinetic isotopic fractionation on the catalyst surface analogous to carbon. In accordance with isotope effect, we also expect that hydrogen isotopic fractionation will decrease with increasing temperature. At approximately 250°C, the difference between δ²H_{H₂ and δ²H_{CH₄ could potentially}}}}}}}}

be small or negligible, as observed by McCollom *et al.* (2010).

Production of C₂–C₆ hydrocarbons and carbon monoxide

For a smaller set of samples, we determined the generation of C₂–C₆ hydrocarbons (ethane, propane, butanes, pentanes, hexanes and benzene) and carbon monoxide. The latter is an intermediate product of the Sabatier reaction. Most of the analyses are semiquantitative with a relatively high analytical error (up to 20%, see the Methods section), so the present discussion should be considered preliminary. More analyses are required to understand hydrocarbon production mechanisms by low-temperature FTFT synthesis. Important to note, however, is that methane is not the only hydrocarbon produced and that more complex reactions, in addition to simple CO₂ hydrogenation, likely occurred on the ruthenium catalyst. Abiotic C₂₊ hydrocarbons are generally assumed to be produced following methane polymerization on the catalyst surface (McCollom 2013), whereas the molecular concentration of various alkanes is typically characterized by the Schulz–Flory distribution (Sherwood Lollar *et al.* 2008; McCollom 2013). The 10–20% error in most hydrocarbon analyses did not permit us to make a reliable test of such a distribution. However, the C₁/(C₂+C₃) ratio is generally <100, which is typical of the dominantly abiotic gas observed in geothermal fluids (McCollom & Seewald 2007), igneous rocks (Sherwood Lollar *et al.* 2008) and low-temperature serpentinization systems (Etiope *et al.* 2011, 2013a,b; Etiope & Sherwood Lollar 2013; Szponar *et al.* 2013) (Figure S2a).

CO production differed in relation to the temperature and type of support, titania or alumina. Elucidating the reason for this phenomenon was not the aim of this work, but future experiments may help us to understand why CO has never been observed in the gases seeping from continental serpentinized rocks (Etiope *et al.* 2011, 2013a, b; Boschetti *et al.* 2013). The structural and chemical properties of the support and, in particular, the surface specific area and the acidity are known to influence catalyst behaviour (Wang *et al.* 2011). In laboratory experiments where methanation is studied on very short timescales (hours or a few days), CO is not observed in the gas phase and remains adsorbed as an intermediate product on the catalyst surface. Over longer time periods, and in the presence of the water produced by the Sabatier reaction (as in our closed system), the chemical differences in the supports (principally acid–base strength and distribution) may modify the nature of the sites of dissociation and adsorption of CO₂ on the surface and the stability of adsorbed intermediates such as CO. The lack of significant amounts of CO in natural abiotic gas may suggest that the catalyst in the rocks is not deactivated for the final reaction step,

converting CO to CH₄, leading to a complete Sabatier reaction.

Low-temperature abiotic CH₄ isotopic composition, laboratory vs. natural settings

The observed C-H isotope fractionations between CO₂ and CH₄ and between H₂ and CH₄ depend on both the reaction temperature and the degree of reaction completeness. When the carbon precursor is ¹³C-depleted (as the CO₂ we used), abiotic CH₄ can resemble a microbial gas. However, within natural geological environments, CO₂ hydrogenation may evolve over very long timescales if the catalyst is abundant, widespread, and is not rapidly deactivated. Under such closed systems with quantitative conversion (as postulated by Proskurowski *et al.* (2008) for the Lost City hydrothermal system), the δ¹³C_{CH₄} will approach the original δ¹³C_{CO₂}. If, for any reason, the available catalyst ceases to operate, it is likely that the CH₄ produced will be more ¹³C depleted compared with the initial CO₂. Open systems are likely to produce different results. The determination as to whether or not natural Sabatier reaction systems in deep rocks are open or closed is an important area for further investigation. Natural δ¹³C_{CH₄} values measured in seeps and springs in continental ultramafic rocks with present-day serpentinization range from -6 to -37‰ (Etioppe & Sherwood Lollar 2013). Such variability may be due to the different origins of carbon feedstock (original δ¹³C_{CO₂}) but, as shown in our experiments, it is also dependent on the temperature and the degree of the reaction. The types of catalysts and the surrounding minerals that can act as a support may also play a role. Assuming an initial ¹³C enriched CO₂ of magmatic or limestone origin (δ¹³C: 0 to -10‰), and the smallest isotopic separation, we observed at the highest CH₄ concentrations, above 10 000 ppmv (δ¹³C_{CO₂} - δ¹³C_{CH₄} = 1-38‰), CH₄ could have a range of δ¹³C_{CH₄} values similar to those observed in land-based serpentinized rocks (Figure S2b).

The potential of ruthenium as a methanation catalyst in chromitites

The catalytic effect of Ru is not only due to the chemical properties of the metal, but also due to the particle sizes and their dispersion on the support, which includes the method of preparing the catalyst. How the catalytic performance of naturally occurring Ru in chromitites compares to that of artificially prepared catalysts is unknown and should be investigated with specific and integrated mineralogical and catalytic competences. Radiocarbon analyses of methane issuing from the land-based serpentinization system of Chimaera, in Turkey, indicated that the gas is fossil (per cent of modern carbon approximately 0), that is, older

than 50 000 years (Etioppe & Schoell 2014). If this is valid in general for land-based serpentinization systems, low-temperature methane could have been generated over long timescales, analogous to thermogenic gas generation. In this case, the rate of natural methane production in chromitites is not particularly important, except for the relation to the rates of mineralogical changes (e.g. precipitation of secondary minerals) that may modify Ru catalysis. Critical are the conditions necessary for abiotic methane production. Even with extremely slow production rates, it is acceptable to consider Ru-bearing chromitites as inorganic gas source rocks, analogous to thermogenic gas organic source rocks. However, we may assume that (i) the Ru concentration, (ii) the particle size and distribution, (iii) the mineralogical form (type of oxide, mineral or alloy), (iv) the particle surface exposure to gas in fractures and (v) the actual content of H₂O also in unsaturated rocks can all be key factors for determining the potential of chromitite as gas source rock.

The Ru concentrations in chromitites, as reported in the literature, range from a few ppb to several ppm for samples collected in chromite mines at depths up to 450 m (Mosier *et al.* 2012). Higher Ru concentrations are possible in deeper chromitites and are also found in veins enriched with Cr-spinels (Economou-Eliopoulos, 1996). Our experiments used Ru amounts within these natural ranges.

The Ru particles observed in chromitites can either be micrometric (Garuti & Zaccarini 1997) or nanometric (Wirth *et al.* 2013) and dispersed, similar to the grain size of the catalyst we used. Primary particles on the alumina support had dimensions of 10–20 angstroms (1–2 nm; Thampi *et al.* 1987) and micrometric particle aggregates, comparable in size to laurite minerals (Economou-Eliopoulos 1996; Garuti & Zaccarini 1997), were observed by field emission scanning electron microscopy (Figure S3).

The catalyst support is known to influence the catalytic activity of metals (Wang *et al.* 2011). In industrial applications, supports are used to control the size of metal particles and the surface area of the metal exposed to reagent gases, to develop particular crystallographic faces and to promote the adsorption of particular species, etc. Therefore, several natural forms of Ru in chromitites (laurite, Ru-Ir-Os alloy, ruthenian pentlandite and Ru oxides), due to their various chemistry, particle size and distribution, may have variable catalytic activity. Our experiments used a Ru oxide similar to that observed in chromitites (Garuti & Zaccarini 1997), but the effect of incorporating the oxide into actual mineralogic matrix is unknown.

In all cases, the exposure of Ru minerals to gas (H₂ + CO₂) in fractures is essential and can be determined by secondary permeability, that is, the occurrence of microcracks and fissures produced by serpentinization, chromite alteration and/or by tectonic stress (Garuti *et al.* 2007; Etioppe *et al.* 2013c). In weathered chromitites, Ru minerals

have been observed close to microcracks and can be altered at low temperatures by serpentinization fluids including molecular hydrogen (Garuti & Zaccarini 1997). An indication that Ru and H₂ can be in contact is given by the transformation of laurite into pentlandite, as typically observed close to serpentine-filled cracks due to the reducing conditions caused by the release of H₂ during the hydration of olivine (Garuti & Zaccarini 1997; Garuti *et al.* 2007). Considering the evidence, it is reasonable to hypothesize that PGE-enriched veins in altered chromitites are the good *loci* for methane generation in land-based serpentinized rocks.

The role of H₂O in natural rock conditions needs to be investigated. As discussed in Introduction, Sabatier reaction in aqueous hyperalkaline solution and at low temperature is improbable, mainly because of the lack of dissolved CO₂ at pH > 9. The reaction could, however, occur in a nonalkaline saturated system, and for this possibility, the Ru catalysis needs to be studied through specific aqueous FTT experiments. In unsaturated rocks, then, H₂O may be present in low amounts that can affect the catalytic performance of Ru. Our experiments used non-pretreated Ru, with random adsorption of humidity from air, to better simulate actual conditions in the rocks.

A simple model is proposed (Fig. 6) where unsaturated and PGE-rich chromitites in ophiolites or ultramafic batholiths can be considered as methane generating source rocks. This model assumes Sabatier reaction in gas phase (unsaturated rock). In general, methane can also be produced by other FTT reactions in aqueous solutions and, perhaps, directly from H₂O (without H₂ mediation) via specific serpentinization reactions (Oze & Sharma 2005;

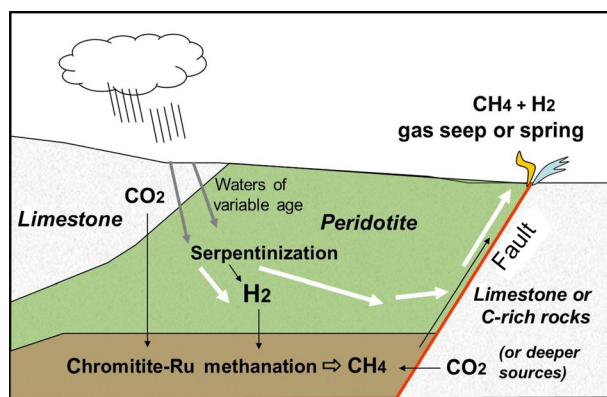


Fig. 6. A schematic representation of methane production at a land-based ultramafic serpentinization site. H₂ is produced by serpentinization and CO₂ may derive from limestone, the atmosphere or other sources. When the two gases mix and permeate ruthenium-bearing, unsaturated chromitites in ophiolitic sequences or igneous intrusions, methane can be generated. The gas may then migrate to the surface, eventually transported by hyperalkaline water (the white arrows) derived from serpentinization. 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.

Suda *et al.* 2014). Different models shall describe these mechanisms.

In our unsaturated rock model, it is assumed that H₂ and CH₄ are produced in different rocks: H₂ via serpentinization of peridotites and CH₄ via CO₂ hydrogenation in chromitites. Then, CH₄ can migrate into surrounding mafic and ultramafic rocks and can eventually enter groundwater. This could explain the CH₄-bearing hyperalkaline water observed in several countries (Fritz *et al.*, 1992; Boschetti *et al.* 2013; Etiope *et al.* 2013a,b; Szponar *et al.* 2013). It is important to remark again what was anticipated in the Introduction, that is, in many land-based serpentinization sites methane reaches the surface along faults also without hyperalkaline groundwater. Even at the hyperalkaline spring sites, gas frequently ascends as separate gas phase, via bubbles or invisible seepage from the surrounding soil. This suggests that the hyperalkaline water may only serve as the transport medium of the gas to the surface, and it is not the site of gas generation. We should also remember that CO₂ does not exist in hyperalkaline water, and the only available carbon form, CO₃²⁻, does not significantly react with hydrogen at low temperatures. The model can be tested in future studies by analysing the gas contained in several rock types, including chromitites. However, other transition metal catalysts (e.g. Fe, Ni, Cr and Co) might also support methanation at low temperature over longer timescales (years and centuries), so they cannot be excluded. Such slow methanation is theoretically possible, but it has not been demonstrated experimentally.

CONCLUSIONS

Our experiments demonstrated that abiotic methane can actually be produced at temperatures below 100°C from ruthenium that has not been artificially pretreated and is at concentrations equivalent to geological conditions occurring in chromitites in ophiolites or in igneous complexes. Under the same experimental conditions, Fe and Ni oxide catalysts do not generate methane. The CO₂-CH₄ isotope separation decreases over time and by increasing the temperature; the final δ¹³C_{CH₄} values approached that of initial δ¹³C_{CO₂}. The presence of minor amounts of C₂-C₆ hydrocarbons is consistent with observations in natural settings.

Additional studies are necessary to demonstrate that Ru minerals are actually effective catalysts in natural geological conditions, under different Ru chemical forms (e.g. sulphides) and water saturation conditions.

Our findings complement the recent discovery of abiotic molecular H₂ generated at temperatures down to 55°C from alteration of igneous rocks (Mayhew *et al.* 2013; Neubeck *et al.* 2014). The fact that abiotic gases, in particular hydrocarbons, may form at very low temperatures has relevant implications in petroleum geology, astrobiology and studies related to the origins of life. Atypical petro-

leum systems characterized by igneous reservoir rocks with ruthenium minerals could host minor amounts of abiotic methane. As this abiotic methane may have large carbon isotope separations from the precursor CO₂, its $\delta^{13}\text{C}$ values could be similar to those of biotic gases. The interpretation of gas-geochemical data for these atypical systems may require re-examination. Ruthenium-based methanation could explain, at least in part, the presence of methane in low-temperature environments on other planets such as Mars, because ruthenium has been documented in Martian meteorites (Jones *et al.* 2003). The abiotic transition from inorganic to organic chemistry (i.e. the Sabatier reaction) may have occurred at temperatures lower than those of the hydrothermal systems traditionally considered in some theories on the origin of life (Russell *et al.* 2010). Then, low-temperature originated methane, for example in submarine chromitites or Ru-bearing Archaean komatiites (Locmelis *et al.* 2011), may have migrated and provided metabolic energy for microbial life in a chemically suitable system (Schrenk *et al.* 2013). In general, the environments that can host methane and methane-fuelled microbial life could be more widespread and commonplace than generally thought.

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CONFLICT OF INTEREST

The authors have no conflict of interest to declare.

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SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Figure S1. A schematic plot of temperature and time scales considered in FTT experiments in geology and industrial catalysis.

Figure S2. Ru-based abiotic methane in genetic diagrams, compared with natural gas.

Figure S3. Field Emission Scanning Electron Microscopy (FESEM) images of Ru/alumina catalyst.

Figure S4. CH₄ concentrations observed with Ni and Fe catalyst at 90°C.

Table S1. Comparative tests with Fe and Ni catalysts

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