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Carbon isotope effects in the open-system Fischer–Tropsch synthesis

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Abstract

Carbon isotopic composition was measured for products of the Fischer–Tropsch synthesis: catalytic reaction between CO and H_2 to produce CO, CO_2, light hydrocarbons C1–C4 and "oil" fraction. Hydrogen isotopes were also measured in the oil fraction and the produced water. Experimental runs were conducted in the flow-through reactor at 260–310 °C and 30 bar using the synthesis gas composed of $5N_2 + 3H_2 + 2CO$, on Fe-catalyst mixed with ZSM-5 synthetic zeolite. In the two of seven runs a Fe + Co-catalyst was used that gives a lower yield of unsaturated hydrocarbons in reaction products. The isotopic effects depended on the conversion of the carbon monoxide. Under steady-state conditions (CO conversion more than 90%) a strong kinetic fractionation was observed between CO and CO_2 ($\sim -10‰$) and CO and hydrocarbons ($\sim +38‰$). At low conversion a clear "inverse" isotopic trend of the depletion in ^{13}C of longer hydrocarbon chains was observed. On average, $\Delta_{12} = \delta^{13}C(CH_4) - \delta^{13}C(C_2H_6)$ correlates well with the CO conversion: the C_2H_6 is $\sim 6‰$ isotopically lighter than CH_4 at low conversion and $\sim 2‰$ heavier at steady-state regime. Under steady-state conditions there almost no difference was observed in the isotopic composition of methane and ethane and higher hydrocarbons. The chemical composition of light hydrocarbons in the products of flow-through, dynamic FTS is different from that found in the static FTS-type experiments with Fe-catalyst, but isotopic effects are similar. Our results suggest that the isotopic distribution of carbon found in so-called "abiogenic" hydrocarbons from some natural gases ($\delta^{13}C1 > \delta^{13}C2 > \delta^{13}C3 > \cdots$) is somewhat similar to that at low conversion of CO, but do not resemble the distribution characteristic for the high conversion products, at least, on Fe-catalyst. Other processes (a simple mixing of two or more endmembers) or other P–T conditions of the carbon reduction could be responsible for the "inverse" isotopic trend found in meteorites and some natural gases.

1. INTRODUCTION

The Fischer–Tropsch synthesis (FTS), which generally can be defined as the heterogeneous catalytic reduction of oxidized carbon compounds by molecular hydrogen, is widely accepted as a process potentially responsible for the presence of organic compounds in meteorites, submarine hydrothermal systems and igneous rocks (e.g. Lancet and Anders, 1970; Shock, 1990; Salvi and Williams-Jones, 1997; Yuen et al., 1984; Foustoukos and Seyfried, 2004; Horita, 2005). This "inorganic", "abiotic" synthesis has also been considered to be important in global geologic processes including production of methane and petroleum and finally, as a source of prebiotic compounds on the early Earth (Szatmari, 1989; Charlou et al., 2002; Sherwood Lollar et al., 2002; Horita, 2005, among others).

However, despite this apparent agreement about the importance and existence of the abiotic synthesis on the early and modern Earth, there are still no rules how to distinguish abiogenic and biogenic organic compounds, especially, methane and light hydrocarbons which are common species in any natural gas manifestation, even in

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high-temperature hydrothermal systems and fumaroles of active volcanoes (Capaccioni et al., 1995; Giggenbach, 1997; Taran and Giggenbach, 2003).

Usually, light natural (oil–gas fields, thermal springs, volcanic fumaroles, etc.) hydrocarbons (alkanes, C_nH_{2n+2}) and alkenes (C_nH_{2n}) are characterized by a monotonic decrease of concentrations against carbon number and by the enrichment in ^{13}C of longer chains (Jenden et al., 1993a,b; Capaccioni et al., 1995; Taran and Giggenbach, 2003). Such distributions are also characteristic for the products of experiments on thermal decomposition of complex organics or biologically derived organic matter (Des Marais et al., 1981; Tannenbaum and Kaplan, 1985; Mango and Elrod, 1999). After determination of the isotopic composition of hydrocarbons occluded in alkaline rocks of Kola peninsula (Galimov and Petersilie, 1967), in the Murchison meteorite (Yuen et al., 1984) and experimental works by Lancet and Anders (1970) and Des Marais et al. (1981), it has been proposed that the "inverse" isotopic distribution, i.e. decreasing ^{13}C content in longer chains, may be a distinct isotopic signature for abiogenically derived hydrocarbons which, in turn, may be produced by FTS-type natural reactions (Jenden et al., 1993b; Sherwood Lollar et al., 2002, 2006; Potter et al., 2004).

Developments of the new GC-IRMS techniques have provoked appearance during the last decade of several experimental works (synthesis, decomposition and transformations of hydrocarbons under hydrothermal and dry conditions) with measuring isotopic composition of methane and heavier hydrocarbons (Hu et al., 1998; Horita and Berndt, 1999; Du et al., 2003; McCollom and Seewald, 2006; Pan et al., 2006; Fu et al., 2007). The FTS-type experiments by Hu et al. (1998) and McCollom and Seewald (2006) were conducted to address the problem of isotopic fractionation between hydrocarbons in closed reactors at 250–300 °C and pressure from 7 to 325 bar using Fe and other transition metal catalysts and different starting material of the oxidized carbon. No clear isotope fractionation trends between hydrocarbons have been observed. Yuen et al. (1990) have experimented with static and dynamic FTS over the 150–500 °C temperature range with a Fe-bearing catalyst. They made a similar conclusion but a description of the experimental methods and detailed analyses were not provided. Fu et al. (2007) have found a significant enrichment in ^{13}C of C2, C3 and C4 relatively CH_4 and almost no difference in δD in their hydrothermal experiment at 400 °C and 500 bar with magnetite as a catalyst.

Closed-system hydrothermal experiments are adequate for achieving equilibration between species for measuring equilibrium properties (e.g. Horita, 2001 for the CO_2/CH_4 equilibration). In many cases the closed-system conditions can model real geochemical processes, but closed systems are specific in terms of the mass conservation (e.g. exhausting of a reactant) and resulting "compensation" effects. Another problem of closed-system experiments is the background amount of the reduced carbon in minerals used as a buffer and/or a catalyst (e.g. McCollom and Seewald, 2001; Fu et al., 2007). A steady-state open system (flow-through reactor) with stationary supply of reactants and output of products is another limiting case, supposedly applicable for the fast-flow geochemical processes (e.g. spreading center submarine hydrothermal systems). This type of experiments, as a rule, requires bigger volumes of apparatus and high flow rates of reactants, on the level of mol/h. In that case the effect of a few milligrams of the initial background reduced carbon is negligible.

The objective of this study is to measure carbon isotope composition in light hydrocarbons, CO and CO_2 produced in a classical Fischer–Tropsch synthesis in a flow-through reactor on Fe-catalyst at 250–310 °C and 30 bar pressure. Here, we describe results of the experiment, and discuss the significance of isotopic indicators for biogenic and abiogenic hydrocarbons in natural gases.

2. FISCHER–TROPSCH SYNTHESIS

Strictly (chemically) speaking, the Fischer–Tropsch synthesis (FTS) is the heterogeneous catalytic reductive oligomerization of carbon monoxide (Anderson, 1984; Steynberg and Dry, 2004):

$$nCO + mH_2 \rightarrow C_xH_yO_z. \quad (1)$$

As a rule, the process is conducted in the flow-through reactors at 100–300 °C and elevated pressure in presence of catalysts which are native transition metals (Fe, Co, Ni, Ru). The final products of the FTS are alkanes (C_nH_{2n+2}), alkenes (C_nH_{2n}) and oxygen-bearing compounds (oxygenates). The accessory reactions include methane formation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2)$$

disproportionation of CO (Bell–Boudouard reaction):

$$2CO \rightarrow CO_2 + C \quad (3)$$

and so-called water–gas shift reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2. \quad (4)$$

Despite the fact that the first studies of the FTS started in the beginning of the 20th century, the mechanisms of the hydrocarbon formation from CO and H_2 are still the object of debates, because the whole process is a very complex combination of chain, simultaneous and consecutive reactions upon the changing metal–oxide–carbide surface (e.g. Raje and Davis, 1996; Van der Laan et al., 1999; Steynberg and Dry, 2004). The composition of FTS products differs essentially from equilibrium composition (Anderson, 1984; Glebov and Kliger, 1994; Shi and Davis, 2004). The FTS is a kinetically controlled process, and the product distribution depends on the nature of a catalyst and conditions of the synthesis. The main initial step is adsorption of H_2 and CO on the metal surface. The activity and selectivity of a catalyst both depend mainly on the character of the adsorption–desorption–dissociation of CO, which in contrast to H_2 can be adsorbed on both, metal and oxide surfaces (Lapidus and Krylova, 2000). Simple rules of the FTS declare that on the Fe-catalyst more alkenes and CO_2 are formed, but Ni- and Co-catalyst give a higher yield of alkanes and H_2O (Anderson, 1984).

The formation of long hydrocarbon chains in FTS occurs by a combination of polymerization and polycondensation. That is why the chain growth probability factor

Table 1
Average temperature of experiments, CO conversion (%), chemical composition (mol/mol of CH_4 for hydrocarbons C2–C8 and mol/mol of N_2 for CO, CO_2, H_2 and CH_4)

# Run and catalyst	*t* (°C)	CO conversion	Time (h)	CO	CO_2	H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	1-C_4H_8	2-C_4H_8	*i*-C_4H_{10}	*n*-C_4H_{10}	C5	C6	C7	C8
10-216	263	6.9	8	0.39	0.0006	0.56	0												
Fe + Z		42.5	20	0.23	0.11	0.51	0.0037	0.200	0.086	0.105	0.046	0.025	0.022	0.003	0.060	0.11	0.05	0.04	0.02
		97.6	32	0.0094	0.17	0.21	0.030	0.204	0.092	0.100	0.056	0.028	0.026	0.003	0.058	0.09	0.06	0.03	0.02
		97.9	50	0.0084	0.18	0.23	0.034	0.191	0.096	0.099	0.045	0.030	0.025	0.004	0.062	0.11	0.05	0.04	0.02
10-217	296	35	10	0.26	0.06	0.47	0.019	0.230	0.082	0.110	0.040	0.023	0.031	0.004	0.058	0.12	0.05	0.03	0.02
Fe + Z		72	20	0.11	0.12	0.40	0.031	0.199	0.091	0.116	0.034	0.029	0.024	0.003	0.064	0.11	0.06	0.03	0.02
		81	30	0.076	0.14	0.38	0.028	0.229	0.087	0.115	0.042	0.032	0.022	0.004	0.065	0.14	0.05	0.03	0.02
		95.1	40	0.019	0.15	0.29	0.040	0.227	0.094	0.108	0.035	0.026	0.034	0.003	0.066	0.14	0.04	0.03	0.02
		96.9	50	0.013	0.14	0.29	0.034	0.224	0.092	0.115	0.036	0.028	0.032	0.004	0.064	0.12	0.05	0.03	0.02
10-219	293	93.9	30	0.024	0.13	0.32	0.031	0.224	0.092	0.115	0.036	0.049	0.02	0.004	0.070	0.10	0.05	0.03	0.02
Fe + Z		95.9	40	0.017	0.13	0.32	0.029	0.224	0.092	0.115	0.036	0.048	b.d.	0.004	0.064	0.12	0.04	0.04	0.02
		95.8	50	0.016	0.13	0.35	0.031	0.144	0.144	0.158	0.154	0.050	b.d.	0.030	0.060	0.11	0.04	0.03	0.02
9-137 Fe + Z	255	98.7	50	0.005	0.14	0.31	0.025	0.218	0.231	0.298	0.048	0.042	0.054	b.d.	0.101	0.14	0.07	0.05	0.03
9-138	293	75	20	0.10	0.10	0.33	0.025	0.224	0.092	0.115	0.036	0.041	0.032	0.004	0.079	0.13	0.08	0.08	0.03
Fe + Z		93.5	40	0.026	0.14	0.34	0.031	0.224	0.092	0.115	0.036	0.034	0.032	0.004	0.078	0.12	0.06	0.05	0.02
		95.5	50	0.018	0.13	0.26	0.029	0.305	0.117	0.260	0.084	0.039	0.045	0.006	0.083	0.14	0.07	0.06	0.03
9-136	279	84.8	38	0.061	0.12	0.35	0.041	0.012	0.263	0.005	0.253	0.018	0.002	0.004	0.065	0.12	0.05	0.03	0.02
Fe + Co + Z		84.8	56	0.061	0.13	0.32	0.047	0.024	0.268	0.004	0.272	0.012	0.008	0.020	0.067	0.09	0.05	0.04	0.03
10-218 Fe + Co + Z	308	94.8	90	0.021	0.13	0.32	0.023	0.032	0.301	0.006	0.336	0.006	0.003	0.051	0.076	0.14	0.06	0.04	0.02

Conversion of CO is computed as $c\% = (1 - (CO/N_2)/0.4) \times 100$, because the initial $(CO/N_2)_o = 0.4$. A mixture of Fe + Co was used in runs 9-136 and 10-218 for the suppression of the unsaturated hydrocarbon fraction. Z—synthetic zeolite; b.d.—below detection limit.

(α) for the products of the FTS ($\alpha = Cn + 1/Cn \approx$ const., where Cn is concentration in mole units) is similar to that applied in the macromolecular chemistry (Flory–Schultz distribution, or Anderson–Schultz–Flory, ASF-distribution, Anderson, 1984; Glebov and Kliger, 1994; Shi and Davis, 2004). One of the numerous expressions for the molecular-mass distribution of polycondensation products may be given as:

$$\log m_n = \log[(1-\alpha)/\alpha] + n \log \alpha \qquad (5)$$

where m_n is the mole fraction of a hydrocarbon with the carbon number n. This distribution on a semi-log plot is a decreasing linear function of the carbon number. However, often, the distribution of FTS light products obtained on Fe- and Co-catalysts has a sharp bend (local minimum) on C2 and a maximum at C3–C4 (Anderson, 1984; Glebov and Kliger, 1994). The monotonic distribution (5) cannot be an identification of abiogenic FTS of hydrocarbons in nature, because the same distribution appears for the polymer destruction including aging and thermal decomposition (Flory, 1936; Giggenbach, 1997).

To our knowledge, the first attempt to use natural magmatic rock samples as a catalyst in the FTS has been realized by Taran et al. (1981). After reduction by H_2 at 450 °C and 50 atm, basalts and dacites became active catalysts in flow-through reactor at 350° and 50 atm, with an average CO conversion of 85% and the whole spectrum of typical products. Gelpi et al. (1970) have used iron of meteoritic origin. Natural Fe-bearing minerals as redox-buffers and potential catalysts have been used later for the experimental modeling of C–H–O system (Berndt et al., 1996; McCollom and Seewald, 2001, 2006, among others). The Ni alloy as a catalyst was successfully applied for the isotopic and chemical equilibration of the CO_2–CH_4 system (Horita, 2001).

3. EXPERIMENTAL

All experiments were conducted at the Bashkirov Laboratory of the Institute of Petrochemical Synthesis, Moscow. For many years this laboratory has been testing catalysts for industrial use in FTS and petroleum chemistry. Reactions were carried out in a 100 ml stainless steel fixed bed reaction vessel filled with a mixture of the reduced magnetite catalyst (15 g) and an approximately equal amount of an alumosilicate promoter (ZSM-5 synthetic zeolite). The zeolite, as a catalyst for the cracking processes, was added for compositional changes in the liquid fraction ("diesel", C11+) of products in order to increase the "gasoline" fraction (C6–C9) and it practically did not affect the composition of light (C1–C5) products (less than 4 mol% of the total C in the gas phase, Vytnova et al., 2006). One of the roles of zeolite (or kaolinite, or a mixture of Al_2O_3 and SiO_2) is to provide a longer life-time of a catalyst liberating the surface of long, immobile hydrocarbon chains. The iron-catalyst was prepared of a natural commercial magnetite from the Olenegorsk mine by reduction in a flow of pure hydrogen at 450 °C and 50 atm during 12 h. The initial product is almost pure magnetite (in wt%: Fe_3O_4—99.3; SiO_2—0.1; TiO_2—0.02; Al_2O_3—0.17; MnO—0.05; CaO—0.1; MgO—0.06; $Na_2O + K_2O$—0.1; P_2O_5—0.07; C—0.03; S—0.02). Very low initial background content of carbon (<3 mg in 15 g of the prepared Fe-catalyst, probably as graphite, if it is not released almost completely during reduction) can not affect the composition of FTS products, because those production rate in our experiment is higher than 10 g/h (see below).

The inflow rate of the mixture of $5N_2 + 3H_2 + 2CO$ was 40 ± 2 L STP/h, that corresponds to ~10 cc STP/s or ~0.1 volume of the reactor per second (STP—standard T–P conditions: 0 °C, 1 atm pressure). Composition of the initial gas mixture models a synthetic gas obtained by wet reforming of a CH_4-rich natural gas or products of the coal gasification. The ammoniac synthesis is inhibited by a fast and strong adsorption of CO on the metal surface, preventing any chemical interaction between N_2 and hydrogen. Seven 56-to-96-h runs were conducted at temperatures from 254 to 316 °C and pressure 30 atm using slightly different proportions between the catalyst and synthetic zeolite (ZSM-5) promoter. In two runs a mixed Fe + Co-catalyst was used to minimize fraction of unsaturated hydrocarbons. Temperature inside reactor usually varies in a range of ±10 °C due to complex heat transfer and heat production processes of this heterogeneous reaction.

Gaseous products of the reaction were sampled periodically from the output line in vacuntainers (Labco-Exetainer) with an excess pressure of about 0.4 atm and pre-analyzed by a conventional gas chromatography using

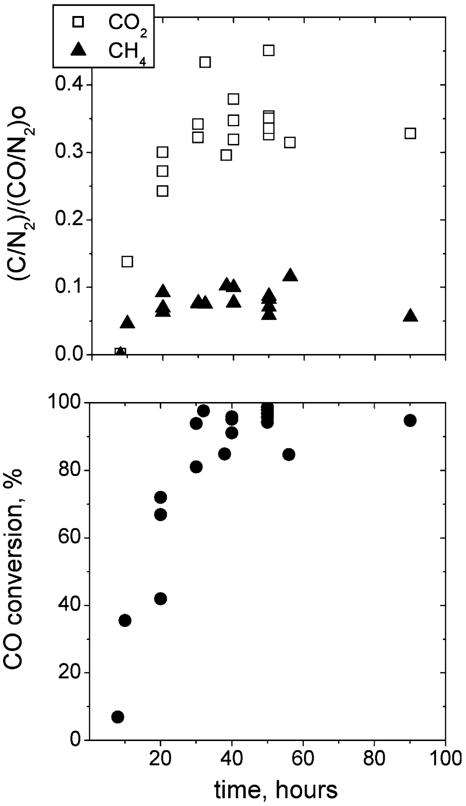

Fig. 1. The CO_2 and CH_4 concentrations and conversion of CO as functions of duration of the experiment for all runs. The concentrations are expressed as mole fractions of the initial CO.

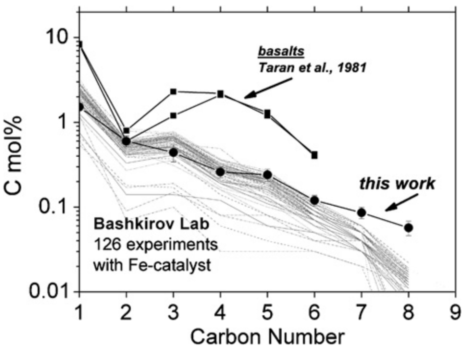

Fig. 2. The average concentration distribution of C1–C8 products in our experiment compared with the data of Bashkirov Laboratory and distributions obtained on reduced basalts by Taran et al. (1981).

flame ionization detector (FID) on a packed Porapak Q column. The vacuntainers were sealed by silicon rubber septa and ''blank'' samples of pure CO and H_2 in same vacuntainers show no traces of hydrocarbons. Gas products were analyzed for carbon isotopes by the GC-CI-IRMS method using continuous flow gas chromatograph (Varian 3400) connected to the Delta PLUS mass spectrometer. GC separation of CO_2 and hydrocarbons was performed on a Paraplot column (30 m, 0.32 mm i.d.). For the separation of CO and CH_4 a molecular sieves 5A column was used. The cumulative samples of the oil fraction and water were sampled after each run (56 or 96 h). Oil samples were analyzed for carbon and hydrogen isotopes by on-line combustion with CuO and then analyzed on a Finnigan Delta S instrument. All carbon isotope values are expressed relative to V-PDB standard. Analytical uncertainty was approximately ±1‰ as was indicated by analysis of duplicate samples. Hydrogen isotope values are expressed relative to V-SMOW standard with analytical uncertainty ∼ ± 5‰.

4. RESULTS

4.1. Reaction dynamics, chemistry of products and mass balance estimations

It is a known experience that iron-based FTS catalysts require 20–40 h on stream before its activity and sensitivity approach steady-state conditions. During this time the bulk catalyst, initially α-Fe, is converted to a mixture of α-Fe and iron carbides, as determined by Mössbauer spectroscopy, (e.g. Setterfield et al., 1985; Davis, 2003) and the CO conversion increases. The transition period was reported also for static experiments (Lancet and Anders, 1970; Horita and Berndt, 1999). Taking into account that N_2 is an inert component of the synthesis gas and therefore has the same input and output flow rates, the conversion of CO can be expressed as:

$$c\% = [1 - (\mathrm{CO}/\mathrm{N}_2)/(\mathrm{CO}/\mathrm{N}_2)_o] \times 100\%, \qquad (6)$$

where the subscript ''o'' refers to the initial CO/N_2 mole ratio of 0.4 in our experiments. Table 1 shows average temperature of the experiment, time of sampling, conversion of CO and chemical composition of products in all runs. Concentrations of macro-species (H_2, CO, CO_2 and CH_4) are normalized to N_2 concentration: $X_i = C_i/N_2$. For the initial mixture $CO/N_2 = 0.4$ and $H_2/N_2 = 0.6$. Concentrations of gaseous hydrocarbons C2–C8 are normalized to CH_4 concentrations. Conversion of CO and the production of CO_2 and CH_4 over time of experiments for all runs are shown in Fig. 1. The steady-state is attained after about 30 h of the transitional, non-stationary period. Note that during this period the composition of C2–C8 components and the CH_4/C_{2+} ratio in gaseous products do not change significantly in all runs (Table 1).

Hydrocarbon gaseous products of FTS are dominated by methane (Table 1), though the CH_4/C_{2+} mole ratio is low (1–2), which is typical for Fe- and Co-catalyst (Anderson, 1984; Glebov and Kliger, 1994). Similar low ratios were reported by Hu et al. (1998) and McCollom and Seewald (2006) for static, closed-system experiments with Fe-bearing catalysts, in contrast to Fu et al. (2007) who, using magnetite as a catalyst in similar to the McCollom and Seewald (2006) hydrothermal experiment, found CH_4/C_{2+} ratios close to 10. Low-alkene runs (9-136 and 10-218, with Fe + Co-catalyst) are characterized by alkane/alkene mole ratios close to 10, while the high-alkene runs gave alkane/alkene ∼0.5. The average distribution of C1–C8 in the gas phase is shown in Fig. 2. It is close to the average distribution of light products (C1–C5) of the FTS on Fe-catalysts obtained at the Bashkirov laboratory during the last two decades. Note that a common characteristic of FTS—local minimum

Table 2
The total yield of water and condensed hydrocarbon fraction (''oil'') in grams and calculated outflow rates of products in terms of C and H_2 (mmol/h) for all runs in the steady-state regime

# Run	Time (h)	Oil (g)	Water (g)	C-gas	C-oil	C-total	C IN–OUT	H_2-gas	H_2-oil	H_2-water	H_2-total	H_2 IN–OUT
10-216	56	37.35	52.20	311	48	359	−3	414	48	63	525	+11
10-217	56	43.69	67.31	256	68	314	+42	433	68	67	568	−32
10-218	96	76.11	107.34	264	63	327	+29	453	63	65	591	−55
10-219	56	39.69	51.21	248	62	310	+46	475	62	51	588	−52
9-136	56	18.3	48.51	357	28	385	−29	458	28	48	534	+2
9-137	56	36.81	56.84	255	57	312	+45	444	57	56	557	−21
9-138	56	34.74	50.60	271	54	328	+28	413	54	50	517	+19

The input flow rate for CO is 356 mmol/h and for H_2 is 536 mmol/h for all runs. IN–OUT is the misbalance for C and H_2 in mmol/h. C-gas contains CO_2, CO and C1–C8 gases. H_2-gas fraction contains H_2 and C1–C8 hydrocarbons. See text for explanations.

Table 3
Carbon isotopic composition of C1–C4 hydrocarbons and "oil" fraction and of δD of the produced water and oil

# Run and catalyst	CO conversion %	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	1-C_4H_8	2-C_4H_8	*i*-C_4H_{10}	*n*-C_4H_{10}	Oil	Balance $\Delta^{13}C$‰	δD water	δD oil
10-216	6.9	−23.6														
Fe + Z	42.5	−20.4	−21.1	−41.6	−44.6	−47.6	−44.7	−46.1	−42.6	−47.1		−49.0				
	97.6	−8.9	0.38	−46.9	−40.2	−46.3	−42.4	−44.9	−46.8	−45.5		−45.8				
	97.9	−9.2	1.47	−47.1	−38.9	−45.8	−41.8	−44.7	−42.5	−45.1		−48.7	−44.5	2.5	−103	−238
10-217	35	−20.2	−19.8	−41.6	−43.2	−46.8	−41.1	−46.3	−44.5	−47.2		−48.4				
Fe + Z	72	−18.4	−11.1	−39.4	−42.7	−44.7	−41.3	−46.1	−46.3	−47.0		−48.7				
	81	−12.8	−11.7	−42.2	−38.5	−44.7	−44.5	−44.6	−44.5	−44.0		−46.4				
	95.1	−10	−1.3	−43.3	−35.2	−42.6	−40.7	−44.4	−42.1			−44.6				
	96.9	−11.7	1.1	−44.9	−40.1	−46.0	−41.7	−43.6	−44.9	−44.1		−44.7	−46.2	5.2	−102	−241
10-219	93.9	−12.2	−5.1	−48.0	−35.3	−45.8	−41.1	−48.0	−44.5		−49.8	−46.2				
Fe + Z	95.9	−8.2	−3.4	−49.7	−37.8	−46.7	−42.0	−48.4	−45.7		−52.1	−46.5				
	95.8	−9.9	−1.0	−51.0	−40.7	−48.4	−43.4	−48.1	−45.7		−49.3	−46.9	−45.8	1.2	−109	−268
9-137	98.7	−11.8	0.1	−47.2	−47.7	−49.2	−47.5	−48.3	−46.3	−46.1		−46.7	−46.1	2.9	−107	−238
Fe + Z																
9-138	75	−13.1	−14.3	−43.1	−40.4	−49.6	−44.2	−48.9	−44.4	−46.5		−47.6	−45.6			
Fe + Z	93.5	−9.2	−3.5	−48.3	−41.2	−46.5	−43.2	−47.5	−44.6	−45.1		−46.6				
	95.5	−9.3	−2	−47.6	−42.3	−47.5	−42.4	−46.4	−44.0	−45.3		−46.3		2.0	−96	−240
9-136	84.8	−13.3	−4.3	−43.6		−43.8		−44.7			−45.5	−44.7				
Fe + Co + Z	84.8	−13.0	−5.3	−43.7		−43.3		−45.9			−46.2	−45.0	−45.9	−2.3	−111	−259
10-218	94.8	−7.9	−0.6	−49.6	−36.5	−42.0		−45.3			−44.8	−46.4	−45.5	1.5	−106	−246
Fe + Co + Z																

The $\delta^{13}C$ of species with low concentrations are not shown. The isotope imbalance was calculated for the initial $\delta^{13}C$–CO = −25.2‰ and assuming that the "oil" production rate is constant and does not depend on the CO conversion. The initial δD of H_2 was −440‰.

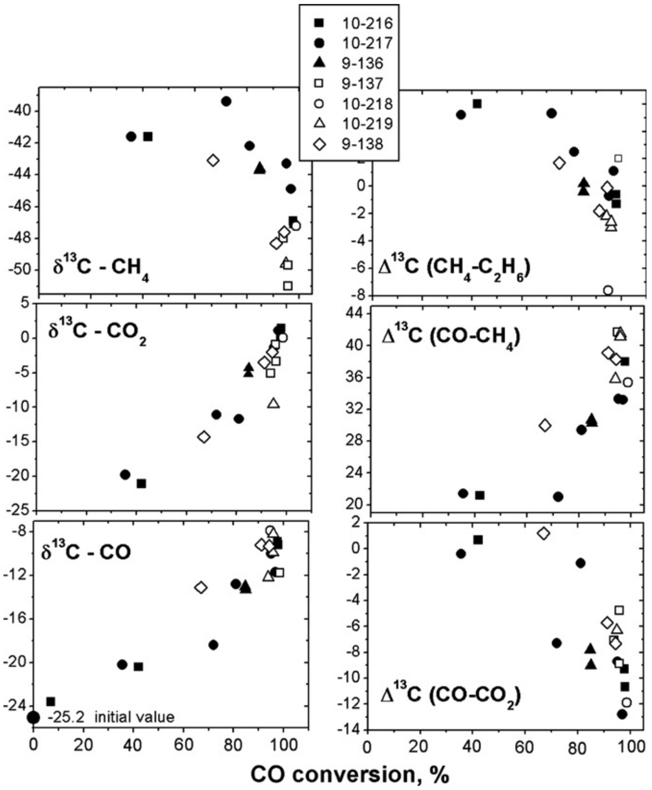

Fig. 3. The isotopic compositions of CO, CO_2 and CH_4 and the isotopic fractionation factors $\Delta^{13}C$ (CO–CO_2), (CO–CH_4), (CO–CH_4) and (CO–C_2H_6) (‰ vs V-PDB) as functions of the CO conversion.

at C2—is well expressed in the Bashkirov Laboratory data, but not observed in our experiments. Higher concentrations of C6–C8 in our experiments could be the result of the "cracking" of the higher molecular weight hydrocarbons on zeolite. Basaltic catalysts (Taran et al., 1981) give a high maximum at C3–C4 as it is also shown in Fig. 2.

In the steady-state regime the outflow rate in our experiment was ~30 L STP/h of the gaseous products, N_2 and non-reacted and secondary H_2 indicating that ~10 L STP/h of the initial gas mixture was converted to water and liquid organic products ("oil"). Water/oil weight ratio in all runs was close to 1.5. Usually, water fraction contained up to 2 wt% of dissolved alcohols and other soluble organics. For example, water fraction of the run #219 contained (in wt%): acetone—0.7, methanol—0.45, ethanol—0.41 and (C3+)OH—0.2. "Oil" products are essentially saturated hydrocarbons with an average fraction of "gasoline" (C5–C10) of ~80 wt% and "diesel" (C11+) of ~20 wt% (see also Anderson, 1984; Glebov and Kliger, 1994). The final, steady-state CO conversions reached values from 84.3 to 97.8%. Table 2 shows estimations of the carbon and hydrogen mass balance in steady-state products for each run assuming that gas/oil ratio does not depend on time, oil and water outflow rates are constant and all liquid hydrocarbons are considered as $(–CH_2–)_n$. Calculated by this manner very approximate mass misbalance is ~ ± 10% relative to both H_2 and CO input rates (Table 2).

4.2. Isotopic composition of products

Isotopic compositions of CO, CO_2 CH_4 and hydrocarbons C2–C4 are shown in Table 3. The transition period of the FTS experiments may be characterized by plots showing correlations between isotopic compositions of CO_2, CO and CH_4 and the CO conversion, as well as the fractionation factors $\Delta^{13}C$ (CO–CO_2), $\Delta^{13}C$ (CO–CH_4) and $\Delta^{13}C$ (CH_4–C_2H_6) vs conversion of CO (Fig. 3). Starting from the initial value of −25.2‰, CO becomes more and more enriched in ^{13}C until a steady-state value of ~−10 ± 2‰ at more than 90% of conversion. The CO_2 isotopic composition stabilizes at $\delta^{13}C$ close to 0‰ with increasing the CO conversion. Methane is isotopically heavier at low CO conversions starting from ~−40‰ and approaching a steady-state value of −48 ± 3‰. The steady-state fractionation between CO and CO_2 is ~−10 ± 2‰, between CO and CH_4 is ~38 ± 4‰ and between CH_4 and C_2H_6 is ~0 ± 2‰. Though with a considerable scattering, points for different runs on these plots form uniform monotonic trends (Fig. 3) including runs with the Fe + Co-catalyst (a low yield of unsaturated hydrocarbons). Isotopic compositions of C2–C4 hydrocarbons do not show correlations with the CO conversion (Fig. 4).

In isotopic equilibrium at 300 °C, CO is isotopically lighter than methane ($\Delta^{13}C$ (CO–CH_4) ~ −5‰, Bottinga, 1969) and correspondingly, lighter than CO_2 ($\Delta^{13}C$ (CO–CO_2) ~ −30‰). It should be noted that the final isotopic fractionation between CO_2 and CH_4 at 250 °C in the static hydrothermal experiment of McCollom and Seewald (2006) was about +36‰, almost same value as in our dynamic experiment, but in our case, between CO and CH_4. Yuen et al. (1990) reported maximum fractionation between CO and hydrocarbons of 35‰, close to our value. In the static experiment of Hu et al. (1998) the isotopic composition of CO almost did not change with the conversion, (from −28‰ to −22‰ with the initial value of −26‰). Fractionation between CO and CH_4 in their experiments at a high conversion of CO was close to +20‰ and −15‰ at a low CO conversion.

The carbon isotope balance in steady-state runs shown in Table 3 was calculated from the chemical and isotopic composition of the gas phase and data from the yield of the "oil" fraction (Table 2) assuming that "oil" is a mixture of $(–CH_2–)_n$ fragments.

Fig. 5 shows the carbon isotopic composition of Cn in intermediate products for run #217. A clear negative trend for the first three non-stationary steps for saturated C1–C4 becomes flat at a high conversion of CO. It looks like the enrichment of CH_4 in ^{13}C at low CO conversion is the main factor responsible for this inverse isotopic trend during the transition period of the catalytic reaction.

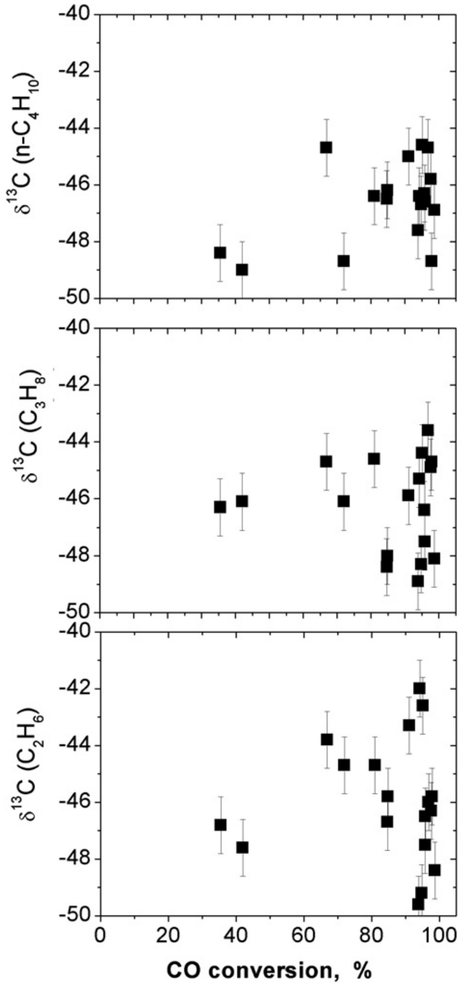

Fig. 4. Carbon isotopic compositions of ethane, propane and *n*-butane as functions of the CO conversion.

Unsaturated C1–C4 ($\delta^{13}C$ of C4 is a mean value for 1-C_4H_8 and 2-C_4H_8) show a stable inverse trend but in a narrow range of $\delta^{13}C$. It should be noted that unsaturated hydrocarbons in general are enriched in heavy isotope in all runs. In isotopic equilibrium unsaturated hydrocarbons are always slightly isotopically lighter than their saturated analogues (Galimov, 1985). We did not find literature data on the carbon isotopic composition of unsaturated hydrocarbons in natural gases. The observed relative ^{13}C enrichment of unsaturated chains may be an evidence for a strong kinetic isotopic effect related to a specific role of olefins in the chain growth mechanism in FTS (so-called, vinyl mechanism for FTS, Anderson, 1984; Shi and Davis, 2005). It could be due to a higher adsorption–desorption rate for ^{13}C-depleted ethylene molecule. On the other hand, the reason could be the metastable equilibrium between alkanes and alkenes in the reactor that already has been reported for hydrothermal experiment by Seewald (1994). Taran and Giggenbach (2003, 2004) found that equilibrium concentration ratios between C2–C3 alkanes and alkenes in volcanic fumaroles correspond to the vent temperature in a wide range of temperatures (100–800 °C). This may mean in our case that hydrogen easily reduces the double bond in the gas phase off the catalyst surface preferring to bind with ^{12}C.

The C1–C4 isotopic distributions for all runs at high conversion of CO are shown in Fig. 6. Two runs with a low yield of alkenes (#9-136 and #10-218) give a slightly negative trend for saturated C1–C4 under steady-state conditions. Note that ethane in these runs is isotopically slightly heavier than methane. Unsaturated C1–C4 show a inverse trend almost in all runs.

All data on $\delta^{13}C_n$ in the steady-state products for saturated and unsaturated hydrocarbons are shown in Fig. 7 in form of fractionation factors between CH_4 and a corresponding molecule: $\Delta^{13}C_n = \delta\ ^{13}C_n - \delta^{13}C_{CH4}$. It can be seen that the only feature of this distribution is the enrichment in ^{13}C of unsaturated hydrocarbons, which decreases with increasing carbon number from almost 12‰ for C2 to almost zero for C4 (see above). The only run #9-137 that produced $C1/C_{2+} < 1$ and was conducted at the lowest temperature (255 °C) did not show a large isotopic shift between saturated and unsaturated hydrocarbons. There is no any specific trend of enrichment or depletion in ^{13}C of longer chains up to C4.

5. DISCUSSION

5.1. Comparison between closed- and open-system Fischer–Tropsch synthesis

All published studies on closed-system FT-type reactions to date for modeling natural processes are different in many aspects, particularly, in the choice of catalysts. Therefore, results of these experiments are difficult to compare. Studies in FTS during the past century have shown that even small modifications in chemical and physical properties of catalysts may drastically change the chemical composition of products

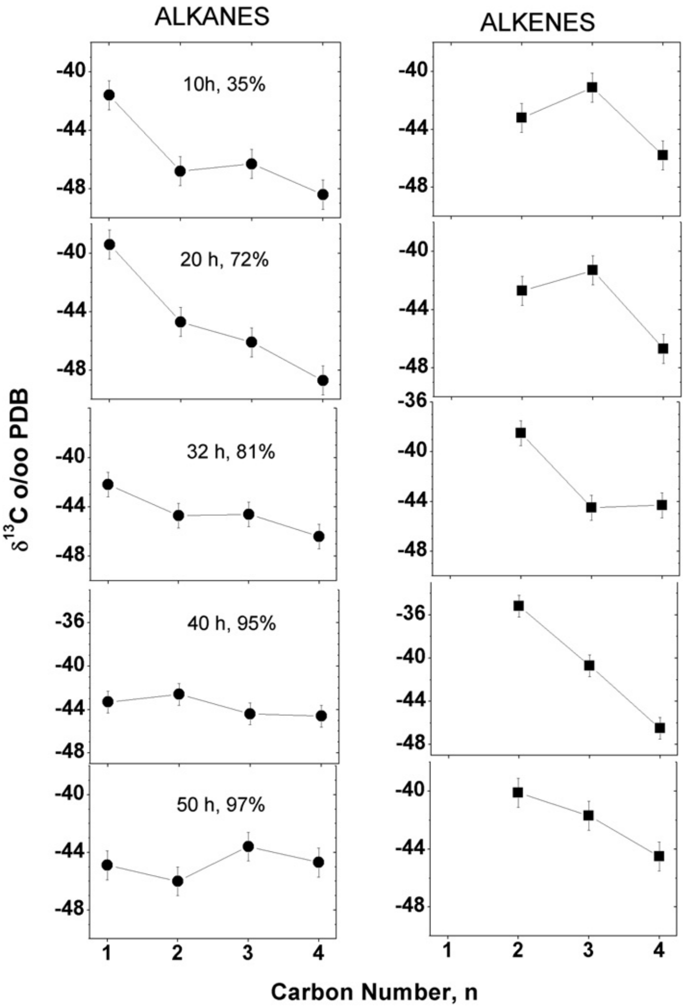

Fig. 5. Variations in the carbon isotopic composition of alkanes and alkenes for run #10-217 as a function of carbon number, time and conversion of CO.

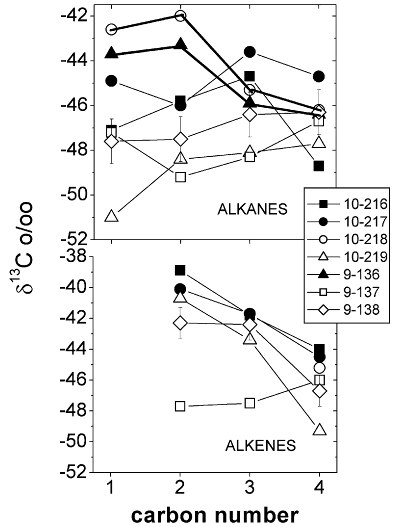

Fig. 6. Steady-state carbon isotopic compositions of C1–C4 alkanes and alkenes as functions of carbon number. Two bold lines correspond to runs with a low yield of alkenes.

(e.g. Steynberg and Dry, 2004). The FTS-rules are mostly empirical, because too many parameters control the process and it is still difficult, even for a simplest catalyst like native iron, to build a strict theory.

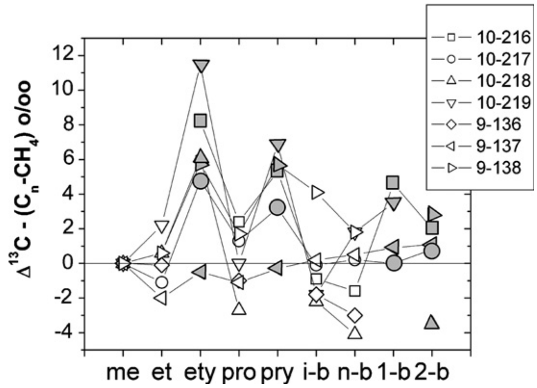

Fig. 7. "Fractionation factors", $\Delta^{13}C$ (C_n–CH_4) for all C2–C4 hydrocarbons in steady-state regime. Dark symbols mark unsaturated hydrocarbons.

To date, only a few works have addressed the isotopic composition of carbon in FT-type reactions in closed systems. They used different catalysts, different P–T conditions and different sources of C and H (Table 4). The isotopic composition of products, as well as their chemical composition, were different in these experiments, with trends sometimes in opposite directions.

For example, Lancet and Anders (1970) conducted their "classical" FTS from CO and H_2 on Co-catalyst, at 1 atm pressure and 127 °C. They reported a high CO conversion (>90%) after 300 h of experiment, a low yield of CO_2 and high ratios of $C1/C_{2+}$ ($\sim$30). In other words, almost all CO was converted to CH_4 and the fraction of $CO_2 +$ hydrocarbons was <2%. In the course of the reaction, $\delta^{13}C$ of CH_4 was approaching $\delta^{13}C$ of the initial CO (~-39‰). Hydrocarbons C_{2+} almost did not change their isotopic composition (~-60‰); however, the isotopic composition of CH_4 changed significantly from -100‰ at a low CO conversion to -39‰ at a high conversion. Therefore, C_{2+} at a low CO conversion were isotopically heavier than CH_4 and became lighter after 20% of conversion, until about 25‰ of the difference. Thus, it was shown that the CH_4 changes its isotopic composition with consumption of CO but C_{2+} is practically stable. In other words, Δ_{12} is a function of CO conversion.

The experiments of Hu et al. (1998) were conducted with a mixture $2CO + 3H_2$ on different catalysts at 280–300 °C and 7–10 atm. Unfortunately, no details about the experimental design were reported. They obtained high conversions of CO on the reduced magnetite catalyst, high yields of CO_2 and $CO_2/CH_4 \sim 4$. This means that more than 70% of the initial CO was converted to CO_2 but not to CH_4 as in the experiments of Lancet and Anders (1970). The isotopic composition of products was measured only in five sets of products. An apparent depletion of CH_4 in ^{13}C with conversion was obtained (in contrast to the Lancet and Anders results) and C_{2+} were isotopically heavier than CH_4 at a high conversion of CO.

The experiment of McCollom and Seewald (2006) modeled P–T conditions of spreading ridge hydrothermal system (325 °C and 325 bar pressure) using iron powder as a catalyst and water solution of HCOOH as a source of CO_2. They realized only one run with a duration of 86 h during which only one intermediate sampling and analysis of products was done after 44 h. About 65% of the initial carbon was converted to CH_4 and higher hydrocarbons with $C1/C_{2+} < 1$. They found an exponential concentration distribution of C1–C6 and a quite uniform isotopic composition for all analyzed hydrocarbon products, without a notable fractionation.

Lastly, in a recent study Fu et al. (2007) conducted hydrothermal experiments similar to those of McCollom and Seewald (2006) but in a slightly acidic 0.5 M solution of NaCl, at 400 °C and 500 bar. They used magnetite as a catalyst and either HCOOH as the initial source of CO_2 and H_2 or a direct injection of a mixture of these gases. Even after 1000 h of the experiment the CO_2 conversion and the yield of CH_4 and hydrocarbons were low. A stable "positive" trend of the enrichment in ^{13}C of longer chains was reported with $\Delta_{12} > 10$‰.

Our seven open-system experimental runs with two different catalysts, under slightly different P–T conditions, but with the strictly controlled input flow rates of synthesis gas of the same composition and chemical and isotopic control of products showed uniform transition and steady-state variations, both in the isotopic and the chemical composition of products. The apparent inverse trend for alkanes (Fig. 5) found in our experiments is caused only by the systematic depletion in ^{13}C of methane with increasing CO conversion, and thus, may be a specific characteristics the $CO + H_2$ catalytic reaction with a high production of CO_2.

The fractionation pattern for CO and CO_2 also differs drastically in the published experiments. First at all, in the both static FT experiments (Lancet and Anders, 1970; Hu et al., 1998), the isotopic composition of CO did not change notably during the experimental runs, independently on the CO conversion (Table 4). McCollom and Seewald (2006) reported a slight enrichment in ^{13}C of the total dissolved CO_2 in comparison with the initial HCOOH (-14‰ vs ~-20‰, estimated from the isotopic balance). In our experiments, the isotopic composition of carbon in CO is the conversion-dependent process, and the steady-state CO is $\sim$15‰ heavier than the initial value (-10‰ vs -25.2‰, Fig. 3).

As a summary to this section, all averaged fractionation factors in terms of $\Delta^{13}C$ (CH_4–C_x) obtained in our experiment at high CO conversion and other FTS or FT-type synthesis are shown in Fig. 8 together with the calculated equilibrium fractionation factors (Galimov, 1985) and the data obtained by Du et al. (2003) by high-temperature (500–600 °C) and high-pressure (10–30 kbar) pyrolysis of lignite, where clear negative isotopic trends have been observed. This plot demonstrates that it is difficult (rather impossible) to distinguish between synthesis and degradation of hydrocarbons based on their isotopic composition, as it was already suggested by McCollom and Seewald (2006).

5.2. Isotopic indicators of "abiogenic" hydrocarbons

Based on our experiments and other published works on the isotopic fractionation in hydrocarbon synthesis by the FTS-type processes, it is not clear, how and why some $\delta^{13}C_n$ isotopic distributions observed in natural fluids have been attributed to have abiogenic origin. The presently available data including this work suggest that FTS may not generate the type of inverse isotopic trends that have been observed in natural samples (Galimov and Petersilie, 1967; Potter et al., 2004; Sherwood Lollar et al., 2002, 2006). Other reaction conditions and reaction pathways and/or a simple mixing can be responsible for the observed natural trends. The ^{13}C depletion could be the result of (radical?) recombination of C_n fragments in homogeneous media because the ^{12}C–^{12}C bond is formed easier than the ^{12}C–^{13}C bond (e.g.. Roginskii, 1956). This is also the reason for the enrichment in ^{13}C of the longer chains as the result of thermo-degradation of organic matter. The Fischer–Tropsch synthesis is essentially heterogeneous process with strong limitations on the mobility of adsorbed molecules

Table 4
Comparison of the parameters, isotopic and chemical compositions of products of the open-system flow-through FTS experiment (this work) and the published data for the closed-system FTS and hydrothermal experiments

	This work	Lancet and Anders (1970)	Hu et al. (1998)	McCollom and Seewald (2006)	Fu et al. (2007)
t (°C)	260–316	130	270–300	250	400
P (atm)	30	1	7–20	320	500
H_2:CO	3:2	1:1	3:2	CO_2:H_2 = 1:1 as 125 mm/l of HCOOH	CO_2:H_2 = 1:1 as 170 mm/l of HCOOH or direct injection
Duration (h)	8–90	4–320	1–105	44 and 86	Up to 1017
Catalyst	Fe	Co	Co, Fe, Ru	Fe	Fe_3O_4
Conversion of CO (%)	5–98	10–90	5–99	0.65 mmol of products/ 4.2 mmol of the initial HCOOH	~0.03 mmol of hydrocarbons/6.4 mmol of the initial CO_2
CH_4/C_{2+}	0.8–2.5	2–30	0.2–2.2	1.8	7–15
Alkanes/alkenes	0.5–10	—	0.2–2.5	18	No alkenes reported
$\Delta^{13}C$ (CO–CO_2)[a]	+7.8 to −10.6‰	−37‰	−21.2 to −45.7‰	—	−17 to −22
$\Delta^{13}C$ (CO_2–CH_4)[a]	+31 to +47‰	+25‰	+5.6 to + 68.9‰	+ 36‰	+5 to +27
Δ13C (CO–CH_4)[a]	−13.4 to −20‰	−10‰	−3.6 to +1.8‰	—	0 to −8
$\Delta^{13}C$ (C1–C2)[b]	−5.9 to +0.9‰ ⟨−1.1⟩	−50‰ after 7 h and +26‰ after 320 h	−18 to +38‰ ⟨+0.9⟩	−5.9	−5 to −16
$\Delta^{13}C$ (C2–C3)[b]	−0.6 to +3.6‰ ⟨+1.0⟩	—	+12 to +16‰ ⟨+14⟩	+2.7	−1.5
$\Delta^{13}C$ (C3–C4)[b]	−1.2 to +3.1‰ ⟨+1.4⟩	—	+1.2 to +2.6‰ ⟨+1.7⟩	−3.2	−4.4
Oil/gas	~1	"wax" 1.5% of total C	—	~0.01	0.1–0.7[c]
$\Delta^{13}C$ (oil–CH_4)[a]	~0‰	−35‰	—	~0‰	+0.8 to +25[d]

[a] Only for stationary products.

[b] For all products. Average fractionation in brackets.

[c] Mole ratio of hydrocarbons in solution and a condensed C-material on mineral surface.

[d] Isotopic composition of C of condensed hydrocarbons.

and radicals, with the rate-controlling stage being adsorption–desorption that provides smaller isotope effects at high temperatures (e.g. Ozaki, 1977; Raje and Davis, 1996; Shi and Davis, 2005).

The Murchison meteorite (Yuen et al., 1984) and gases in alkaline rocks of Kola Peninsula (Galimov and Petersilie, 1967; Potter et al., 2004) could have undergone a high-temperature (meteorite) and a high P–T (rocks) post-genetic influence with the following destruction, radicalization and recombination of light molecules like in experiments of Des Marais et al. (1981) (low pressure) and Du et al. (2003) (high pressure) with the resulting inverse isotopic trend in light hydrocarbons. It is worth to note here that the Kola Peninsula isotopic data should be revised—they had been obtained by an old methodology. For natural gases showing a inverse "abiogenic" isotope distribution pattern like some gases from Appalachian Basin (Jenden et al., 1993b) or from oil fields in China (Huang et al., 2001) and Siberia, hot springs of Chukotka peninsula (Prasolov, 1990), a mixture of two or more endmembers have been suggested, with each endmember characterized by a positive, "thermogenic" $\delta^{13}C_n$ trend and a different C1/C_{2+} ratio (see also Prinzhofer and Huc (1995) with another explanation based on a "leakage" model with kinetic fractionation due to diffusion of a gas through a caprock).

Recently, Sherwood Lollar et al. (2002, 2006) have formulated new criterion for abiogenic hydrocarbons: "*an inverse correlation of* ^{13}*C-depletion and* ^{2}*H-enrichment between* CH_4 *and ethane*" (Sherwood Lollar et al., 2006).

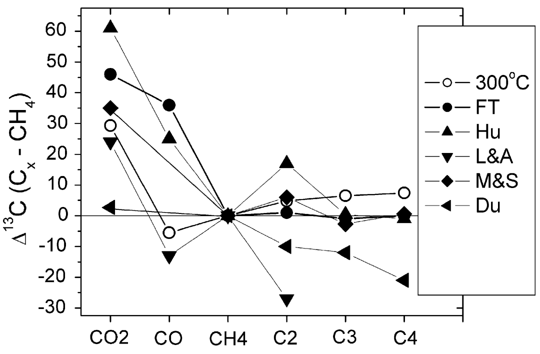

Fig. 8. Carbon isotopic shift relative methane for CO_2, CO and C2–C4 in equilibrium at 300 °C, in FTS experiments (FT—this work, run 10-217), Hu—Hu et al., 1998; L&A—Lancet and Anders (1970), M&S—hydrothermal experiment by McCollom and Seewald, and Du—Du et al. (2003), high P–T pyrolysis of lignite.

Some samples of gases from several Precambrian Shields (Canada, Finland, South Africa) with a positive $\Delta_{12} = \delta^{13}C(CH_4)–\delta^{13}C(C_2H_6)$ were named as "abiogenic" because of the apparent impossibility to explain how their carbon and hydrogen isotopic composition could be formed (Sherwood Lollar et al., 2006). For the inverse Δ_{12} a "polymerization of CH_4" has been suggested as a proved effect based on Des Marais et al. (1981) spark experiments. It should be noted that the overall tendency to have isotopically heavier hydrogen in longer hydrocarbons is the same for usual thermogenic and Precambrian exotic gases (e.g. Prinzhofer and Huc, 1995). The characteristic carbon isotopic pattern attributed by Sherwood Lollar et al. (2002, 2006) to abiogenic hydrocarbon synthesis ($\Delta_{12} > 0$) may be obtained by a simple mixing of two endmembers, each one with a "right", positive $\delta^{13}C_n$ trend but with a large difference in $C1/C_{2+}$ ratios (Prasolov, 1990; Jenden et al., 1993b; Prinzhofer and Huc, 1995; Huang et al., 2001). Only one condition should be fulfilled: the $\delta^{13}C$ of ethane in one of endmembers should be lower than $\delta^{13}C$ of methane in another endmember. A simple example presented in Fig. 9 shows that "abiogenic" pattern on the $\delta^{13}C$ between C1 and C2 could be reproduced by a simple mixing of two endmembers: a high-temperature and high-maturity thermogenic gas, typical for active hydrothermal systems (Taran, 1988) and a typical lower maturity gas (e.g. Jenden et al., 1993b; Prinzhofer and Huc, 1995). The latter has an overall carbon isotopic composition lighter than that of the first endmember and with ethane lighter than methane in the first endmember.

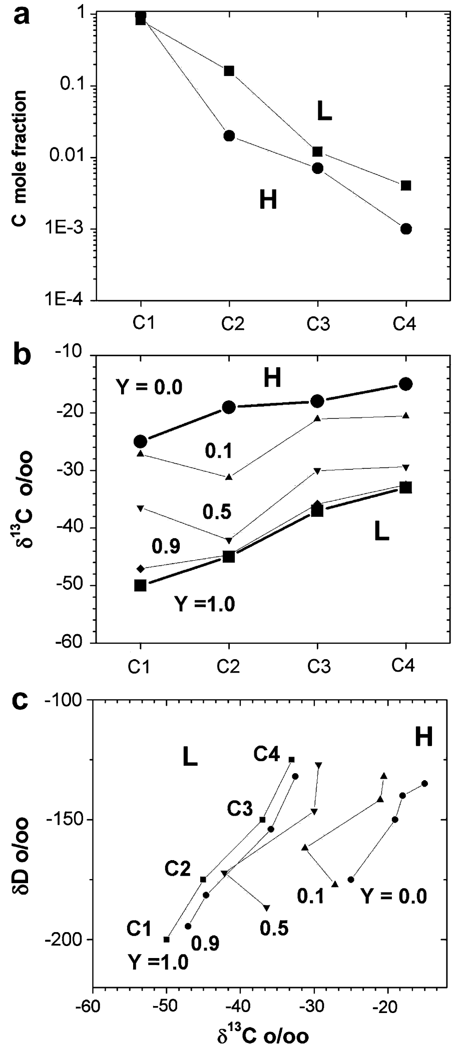

Fig. 9. Mixing of L (low maturity) and H (high maturity) C1–C4 hydrocarbons of a typical chemical composition (a), carbon isotope (b) and hydrogen isotope (c) "thermogenic" pattern. Mixtures with low fraction of H component (0.1–0.5) show both the inverse Δ13C ($CH_4–C_2H_6$) (b) and the inversed correlation between Δ12 and ΔD ($CH_4–C_2H_6$) (c) as for some Precambrian shield gases reported by Sherwood Lollar et al. (2002, 2006).

6. CONCLUSIONS

Neither static, closed-system, nor dynamic, open-system FTS show an unambiguous inverse distribution of $\delta^{13}C$ for light hydrocarbons. Light hydrocarbons, products of flow-through dynamic FTS show inverse C isotope trend only at low conversion of CO. This means that there are no carbon isotopic data presently available to distinguish the isotopic composition of terrestrial hydrocarbons produced by abiotic synthesis from the simplest C–O–H constituents from those formed by the degradation of the already existed bio-organic matter. Other isotopic systems (D/H, $^{18}O/^{16}O$, $^{15}N/^{14}N$) may become more successful in future. On the other hand, there are no doubts that the abiogenic synthesis of organic matter on the modern and early Earth does and did exist and in a large extent is and was realized by the FTS-type processes in crustal environment (moderate temperatures and pressures and local or regional appropriate redox conditions).

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