Formation of Hydrocarbons in the Presence of Native Iron under Upper Mantle Conditions: Experimental Constraints

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Abstract: The formation of hydrocarbons (HCs) upon interaction of metal and metal–carbon phases (solid Fe, Fe3C, Fe7C3, Ni, and liquid Fe–Ni alloys) with or without additional sources of carbon (graphite, diamond, carbonate, and H2O–CO2 fluids) was investigated in quenching experiments at 6.3 GPa and 1000–1400 °C, wherein hydrogen fugacity (fH2) was controlled by the Fe–FeO + H2O or Mo–MoO2 + H2O equilibria. The aim of the study was to investigate abiotic generation of hydrocarbons and to characterize the diversity of HC species that form in the presence of Fe/Ni metal phases at P–T–fH2 conditions typical of the upper mantle. The carbon donors were not fully depleted at experimental conditions. The ratio of H2 ingress and consumption rates depended on hydrogen permeability of the capsule material: runs with low-permeable Au capsules and/or high hydrogenation rates (H2O–CO2 fluid) yielded fluids equilibrated with the final assemblage of solid phases at fH2sample ≤ fH2buffer. The synthesized quenched fluids contained diverse HC species, predominantly light alkanes. The relative percentages of light alkane species were greater in higher temperature runs. At 1200 °C, light alkanes (C1 ≈ C2 > C3 > C4) formed either by direct hydrogenation of Fe3C or Fe7C3, or by hydrogenation of graphite/diamond in the presence of Fe3C, Fe7C3, and a liquid Fe–Ni alloy. The CH4/C2H6 ratio in the fluids decreased from 5 to 0.5 with decreasing iron activity and the C fraction increased in the series: Fe–Fe3C → Fe3C–Fe7C3 → Fe7C3–graphite → graphite. Fe3C–magnesite and Fe3C–H2O–CO2 systems at 1200 °C yielded magnesiowüstite and wüstite, respectively, and both produced C-enriched carbide Fe7C3 and mainly light alkanes (C1 ≈ C2 > C3 > C4). Thus, reactions of metal phases that simulate the composition of native iron with various carbon donors (graphite, diamond, carbonate, or H2O–CO2 fluid) at the upper mantle P–T conditions and enhanced fH2 can provide abiotic generation of complex hydrocarbon systems that predominantly contain light alkanes. The conditions favorable for HC formation exist in mantle zones, where slab-derived H2O-, CO2- and carbonate-bearing fluids interact with metal-saturated mantle.

Keywords: mantle; fluid; hydrocarbons; subduction; experiment; native iron; gas chromatography–mass spectrometry

1. Introduction

Abiotic hydrocarbons (HCs) have been found in Earth’s seafloor hydrothermal systems [1,2], crustal crystalline rocks [3], inclusions of mantle-derived diamonds [4–7], and meteorites [8], as well
as on other planets [9]. Abiotic hydrocarbon production on the global scale is minor compared to hydrocarbon production by microbial processes or thermogenic degradation of organic matter in sedimentary rocks [10]. Yet, HCs that form in reduced mantle may play a key role in the deep cycles of carbon and hydrogen, and facilitate the transport of volatiles to shallow oxidized mantle [11,12]. On the other hand, oxidation of HCs at depths ranging from 150 km to 200 km with the formation of H2O, C0, and CO2 is favorable for magma generation [11–13] and crystallization of lithospheric diamonds [14,15].

Hydrocarbon genesis in the mantle may potentially occur by hydrolysis or hydrogenation of iron carbides and graphite or diamond, or by reduction of CO, CO2, and carbonates upon reactions with iron compounds and H2O [10,16–25]. The formation of HCs in the presence of FeO-bearing carbonates and H2O has received the most exhaustive experimental constraints [16,17,21–23]. The synthesis of HCs under the mantle P–T conditions was inferred [21] to require a donor of carbon (of any type), a donor of hydrogen, and a reducing environment. Specific P–T conditions in the pressure range of 1–11 GPa and temperatures ≤1600 °C determine the predominant HC species: methane and ethane or natural gas-like mixtures [16,21]. Only at pressures greater than 2.5 GPa, methane transforms into heavier alkanes, and the transformation processes are enhanced at higher temperatures [16]. Heavy hydrocarbon species commonly form in the C–H system at lower mantle pressures and temperatures [26]. Direct hydrogenation of graphite at high fH2 yields larger amounts of methane than the reaction of FeO, CaCO3, and H2O at low fH2 [18]. In a previous study [25], we reproduced the formation of HCs at 5.5–7.8 GPa and 1100–1400 °C by reacting hydrogen-bearing fluids with 13C soot-like carbon, graphite, or diamond as carbon sources. 13C carbon reacted with hydrogen to yield isotopically pure 13C light alkanes; the reaction with graphite at 6.3 GPa progressively accelerated and became avalanche-like in runs longer than 1 h; and the use of diamond as a carbon source resulted in HC formation, but at the slowest rate.

Currently, there is a wealth of evidence [11,12,27–31] on settings favorable for abiotic HC generation in the mantle in the presence of carbon and hydrogen donors and a reducing environment. Large amounts of C- and H-bearing species are delivered to the mantle by subducted slabs, which can carry and release H2O, CO2, and carbonates as far as the lower mantle [29–32]. The redox conditions in the slab are variable, but generally more oxidized than in the ambient mantle [11,33]. The total amount of water transported to the mantle is estimated to be 8.7 × 1011 kg/year [29], and the subducted mass of H2O in most slabs is much larger than that of CO2 [32,34]. At pressures greater than 5 GPa, the carbonate-bearing sediments yield an H2O-bearing carbonated melt [35]. Carbonated melts are expected to travel into the mantle due to their low viscosity and good wetting properties [35,36]. The present-day annual subduction input of carbon reaches 5.4–8.8 × 1013 g [31]. Slab-derived fluids are known to interact with the ambient mantle and cause its metasomatic alteration [37,38].

The decrease in oxygen fugacity with depth is maintained by progressive disproportionation by the reaction 3Fe2+ → 2Fe3+ + Fe0 resulting from a pressure-dependent increase of Fe3+ stability in silicate phases [28,39], whereby the mantle becomes saturated with native iron [27,28,39,40]. The presence of a metal phase in the upper mantle is evident from inclusions in diamonds that store iron, widespread cognite (Fe3C), and Fe–Ni or Fe–Ni–S alloys [7,41–44]. The metal phase of inclusions in eclogitic diamond commonly contains 0.1–0.5% Ni [42–44], and that in equilibrium with peridotite can contain up to XNi > 0.5 [28,39,40,45]. Specifically, at 10 GPa, the contents of Fe-based alloys in peridotite can vary from 50 to 700 ppm, with XNi between 0.34 and 0.58 [40]. Judging by phase relations in the Fe–Ni–C and Fe–Fe3C–Fe3N systems at 7.8–10 GPa and 1350–1475 °C, the dissolution of C and N in amounts typical of the upper mantle can produce assemblages of Fe3C or FeC carbides (with Ni impurity) ± metal melt ± diamond [40,46]. At greater depths of 600 km, the metal concentration may reach 5000 ppm [39] and carbide Fe3C may gain more importance [40,47].

The penetration of slab-derived fluids or melts into the metal-saturated mantle can induce the Fe + H2O → FeO + H2 reaction [29,48,49] which buffers fH2 at the IW + H2O (Fe–FeO + H2O) equilibrium. This provides a constant source of hydrogen and controls strongly reduced conditions, while the melting of silicates is impeded by “redox freezing” [11,40]. Carbon may come from iron carbides, graphite, or diamond produced by reactions of Fe-based alloys with carbonate or CO2:
Thus, necessary and sufficient conditions for HC generation may arise in the zones of interaction between slab-derived H2O–CO2 fluids or H2O-bearing carbonated melts and reduced iron-saturated mantle. The process of abiotic generation of HCs at the mantle P–T–fH2 conditions upon interaction of iron carbides and an Fe–Ni melt with graphite, diamond, carbonate, and fluids, as well as the speciation of the resulting hydrocarbons, can be investigated in laboratory experiments. For this, we have performed quenching experiments at 6.3 GPa and 1000–1400 °C, which generally reproduce the conditions that typically occur in zones of mantle–slab interaction. Iron carbides, graphite, diamond, magnesite, and CO2 in fluids were used as carbon donors, while the presence of metal phases maintained strongly reduced conditions in the samples. Hydrogen fugacity was buffered using the double-capsule technique [52] by the IW + H2O or MMO + H2O (Mo–MoO2 + H2O) equilibria [53]. Thus, more insights were gained into the formation mechanism and speciation of HCs which may originate abiotically upon mantle–slab interaction, and into their fate in the lithospheric mantle.

2. Materials and Methods

2.1. Materials

Some experiments were prepared by mixing Fe, Ni, or Fe3C with graphite (all >99.99% pure; Table 1). The starting iron and nickel powders (10–50 μm) were cleaned from oxygen by annealing for 1 h in a stream of hydrogen at 600 °C. Some amounts of oxides may have formed on metal particles even after cleaning. Graphite pre-dried at 110 °C for at least 30 days contained 700 ppm of CO2 and 700 ppm of H2O. In other experiments, the starting materials included Fe3C, natural magnesite (Mg0.9Ca0.1) CO3 (Satka, Ural region), chemical-grade oxalic acid (C2H2O4), and synthetic diamond (ACM-20/14, 14–20 μm). Initial Fe3C (X-ray tested) was synthesized at 6.3 GPa and 1400 °C from iron and graphite (both >99.99% pure). Samples with low carbon contents were placed in an Al2O3 container with a 0.5 mm inner diameter, which prevented Pt or Au capsules from fusion with iron and/or carbides and thus kept them tight. The use of a graphite container (0.5 mm inner diameter) in the runs with graphite-saturated samples impeded reactions of the capsule material with the metal phases. The Al2O3 and graphite containers, in turn, were placed in Pt or Au capsules with a 2 mm outer diameter and a wall thickness of 0.2 mm and then were arc-welded using a PUK-4U impulse micro welding device (Lampert Werktechnik GmbH, Germany).

Unlike Pt, Au does not show obvious catalytic activity with respect to the HC fluid, but Pt is more permeable to hydrogen than Au and thus can provide the required rate of fH2 equilibration during buffering. Therefore, Pt capsules were used preferably in most of the runs.

### Table 1. Starting compositions and conditions of 6.3 GPa runs and phase compositions of run products (according to X-ray diffraction analysis and EDS microanalysis).

| Run #     | Starting Composition (mg) | C (wt.%) | T (°C) | t (hrs) | fH2 Buffer | Capsule | Phase Composition (XRD + EDS) | TIC (Arbitrary Units) |
|-----------|--------------------------|----------|--------|---------|------------|---------|--------------------------------|----------------------|
|           | Gr | Dm | Fe | Ni | Fe3C | Mgs | OA |                            |                      |
| 2095_2_2* | 0.3 | - | 4 | - | - | - | 7 | 1200 | 10 | IW | Pt | Fe + FeC | 1.23 × 10^10 |
| 2095_2_4* | 0.3 | - | - | 4.2 | - | - | 13 | 1200 | 10 | IW | Pt | Fe3C + FeC3 | 1.16 × 10^10 |
| 688_6_2*  | - | - | - | 3.6 | 1.0 | - | 11 | 1200 | 10 | IW | Au | Fe3C + Mgs + Mws | 3.39 × 10^9 |
| 688_6_3*  | - | - | - | 2.4 | - | 0.4 | 10 | 1200 | 10 | IW | Au | Fe3C + FeO | 3.93 × 10^9 |
| 1079_5_1  | 7.3 | - | - | - | - | - | 100 | 800 | 10 | MMO | Pt | Gr | 5.65 × 10^8 |
| 1079_5_2  | 10 | 2.4 | - | - | - | - | 81 | 800 | 10 | MMO | Pt | Gr + FeC | 6.28 × 10^8 |
| 1001_4_3* | 10 | 2.3 | - | - | - | - | 81 | 1000 | 10 | MMO | Pt | Gr + Ni | 4.79 × 10^10 |
| 1001_4_4* | 10 | 2.1 | - | - | - | - | 83 | 1000 | 10 | MMO | Pt | Gr + FeC | 5.24 × 10^10 |
| 2095_2_3* | 1.6 | - | - | 4.2 | - | - | 67 | 1200 | 10 | IW | Pt | Gr + Fe3C | - |
| 600_8_2   | 10 | 3.3 | 1.7 | - | - | - | 67 | 1200 | 15 | IW | Pt | Gr + L | 6.63 × 10^10 |
| 600_8_4   | 6.9 | - | 4.5 | - | - | - | 61 | 1200 | 15 | IW | Pt | Gr + Ni | 4.43 × 10^10 |
| 2100_2_2* | 8.5 | - | 8.8 | - | - | - | 53 | 1200 | 10 | IW | Pt | Gr + Fe3C | 7.52 × 10^10 |
| 2100_2_3* | 10.4 | - | 1.5 | 9.4 | - | - | 52 | 1200 | 10 | IW | Pt | Gr + L | 3.95 × 10^10 |
2.2. High-Pressure Apparatus

Experiments at 6.3 GPa were carried out in a split-sphere multi-anvil high-pressure apparatus [54]. The size of pressure cells was 21.1 × 21.1 × 25.4 mm; graphite heaters in the high pressure runs had an inner diameter of 12 mm and a height of 18.5 mm. Pressure was calibrated by recording the change in the resistance of Bi at 2.55 GPa and PbSe at 4.0 and 6.8 GPa at room temperature and at 1350 °C by bracketing the graphite–diamond equilibrium in the Ni_{0.7}–Fe_{0.3}–C system. Temperature was monitored in each experiment with a PtRh6/PtRh30 thermocouple calibrated at 6.3 GPa using the melting points of Al and Ag [55]. See Supplementary Figure S1a,b for the cell layout and the temperature pattern. Pressure and temperature were measured to an accuracy of ±0.1 GPa and ±20 °C, respectively [54,55]; no significant pressure gradients were observed. The run duration of 10–15 h was chosen from our earlier experimental studies [56], in which a system consisting mainly of light alkanes (formed by thermal destruction of docosane and stearic acid) reached equilibrium in 2 h at 6.3 GPa and 1200–1400 °C. The obtained fluids were quenched at 200 deg/s.

The presence of Fe and iron carbides buffered \( f_{O_2} \) in the samples within IW (\( \Delta \log f_{O_2} \) FMQ-5). Hydrogen fugacity was controlled by the IW + H₂O (Fe–FeO + H₂O) and slightly more oxidized MMO + H₂O (Mo–MoO₂ + H₂O) buffers (MMO = \( \Delta \log f_{O_2} \) IW + 1 [53]). A double-capsule technique was used: inner Pt capsules were placed inside thick-walled Fe or Mo outer capsules with talc as a source of water and low-melting CsCl insulation which maintained quasi-hydrostatic pressure transfer (Supplementary Figure S1). The precipitation of FeO and MoO₂ on the inner walls of the outer capsules after the experiments was confirmed by X-ray analysis. The procedure was previously described in detail in [25,53,56].

2.3. Analytical Methods

After retrieval from the high-pressure cells, the Pt and Au capsules were placed into a crush cell connected on-line to a gas chromatograph before the analytical column. They were heated at 120–130 °C in a stream of carrier gas (99.9999% pure He) for 90 min to clean the surface from adsorbed gases and to evaporate water for further analysis of the released gases. The duration of pre-heating depended on the rate of gas desorption and was analyzed on-line. The blank pre-heating runs showed neither speciation nor concentration changes of volatiles in the capsules at 120–130 °C. The capsules that did not sustain heating were excluded from the analysis. The gas mixture extracted from the capsules by piercing was analyzed by gas chromatography and mass spectrometry using a Focus GS/DSQ II Series Single Quadrupole MS analyzer (Thermo Fischer Scientific, Waltham, MA, USA) [56]. Gas samples were not pyrolized and the analysis was thus applied to an almost in situ gas mixture. Trace amounts of poorly volatile components of the quenched fluids, especially heavy hydrocarbons (>C₁₈), remained in the capsules.

According to our estimates [25], HC formation by hydrogenation of graphite and diamond in the 5.5–7.8 GPa and 1100–1400 °C runs increased the fluid in the capsules by 3 to 100 times relative to the amount prior to experiments. In this study, total ion count (TIC) was used to semi-quantitatively characterize the amount of fluid in the capsule after the run. The relative concentrations (rel.%) of volatile components in the studied mixture were obtained by normalization: the total area of all chromatographic peaks was normalized to 100% and the area of an individual
component defined its proportion in the mixture (Supplementary Figures S2 and S3). The normalization quality was checked against external standards [56]. The concentration ranges of alkanes during the calibration were the same as in the run products. Analytical uncertainty was below 5% for C1–C4 alkanes and less than 10% for H2O, NH3, and CO2 (determined in the range from 12.5 pptv to 12.5 ppbv and expressed as precision), or even less than 5% in most cases.

The samples retrieved from the capsules were mounted in an epoxy resin by vacuum impregnation. After resin polymerization, the samples were polished under kerosene, without the use of water (final stage: 1 μm Al2O3) and examined on a MIRA 3 LMU scanning electron microscope (SEM) (Tescan, Brno, Czech Republic). For quantitative determination, metal phases were analyzed on the Tescan MIRA 3 LMU scanning electron microscope coupled with an INCA EDS 450 microanalysis system with a liquid nitrogen-free large area EDS X-Max-80 Silicon Drift Detector (Oxford Instruments Nanoanalysis Ltd, Oxford, UK). The instruments were operated at an accelerating voltage of 20 kV, a beam current of 1 nA, and a spot diameter of ~10 nm; and the counting time was 20 s.

The phases were identified by X-ray powder diffraction on an IPDS-2T diffractometer (Stoe & Cie GmbH, Darmstadt, Germany) in the Gandolfi mode (MoKα radiation, graphite monochromator). Two-dimensional X-ray patterns were radially integrated using the XArea software package. The diffraction profiles were processed in WinXPow (Stoe & Cie GmbH, Darmstadt, Germany). The database of PDF-4 Minerals (Powder Diffraction File PDF-4+, 2006) was used for phase analysis.

3. Results

3.1. Phase Relations

The phase composition of run products was reconstructed using scanning electron microscopy coupled with EDS microanalysis and X-ray powder diffraction (Tables 1 and 2; Figure 1; Supplementary Figure S4). In the course of the experiment, the samples became either saturated or unsaturated with respect to graphite/diamond (Table 1). The C-unsaturated samples contained ≤13 wt % C, while graphite from the starting mixture disappeared, as it was confirmed by X-ray and SEM data. Most likely it was dissolved in metal phases early during the runs and formed iron carbides which underwent hydrogenation to produce HCs. At 1200 °C, the carbon-deficient run (2095_2_2) yielded FeC (93.0 wt % Fe) and Fe (Tables 1 and 2; Figure 1a; Supplementary Figure S4c), but the carbides FeC (92.4 wt % Fe) and Fe7C3 (90.4 wt % Fe) formed at higher C contents in runs 2095_2_4 (Tables 1 and 2; Figure 1b). The run 688_6_1 was likely unequilibrated, judging by the association of diamond with two carbides, FeC and Fe7C3.

In other 1200 °C runs with graphite/diamond-unsaturated samples (688_6_2 and 688_6_3), reactions of FeC with magnesite or oxalic acid yielded assemblages of FeC3 (90.3 wt % Fe) with magnesiowüstite (18–20 wt % MgO) or wüstite (Figure 1c,d). As indicated by the sample texture, a large part of magnesiowüstite was molten, but the EDS microanalysis showed almost identical compositions of solid and quenched magnesiowüstite (Table 2). The carbon-saturated systems produced graphite and FeC with 91.1–92.7 wt % Fe at 800 °C and 1000 °C (Tables 1 and 2; Supplementary Figure S4b), but a higher-C carbide FeC3 with 90.4–90.6 wt % Fe at 1200 °C (Supplementary Figure S4d). The 1000 °C and 1200 °C runs with Ni-bearing and C-saturated samples yielded nickel and graphite (Supplementary Figure S4a).
Figure 1. Backscattered electron (BSE) images of quenched samples after 6.3 GPa and 1200 °C runs. (a) run 2095_2_2 (Pt capsule); (b) run 2095_2_4 (Pt capsule); (c) run 688_2_2 (Au capsule); (d) run 688_2_3 (Au capsule).

Table 2. Chemistry of metal phases according to EDS microanalysis (wt.%).

| Run #   | n | Phase | Fe   | $\sigma$ | Ni | $\sigma$ | O  | $\sigma$ | Mg | $\sigma$ | Pt | $\sigma$ | Total |
|---------|---|-------|------|---------|----|---------|----|---------|----|---------|----|---------|-------|
| 2095_2_2 | 5 | Fe    | 99.0 | 0.4     | -  | -       | -  | -       | -  | -       | -  | -       | 99.0  |
| 2095_2_2 | 5 | FeC   | 93.0 | 0.4     | -  | -       | -  | -       | -  | -       | -  | -       | 93.0  |
| 2095_2_4 | 15 | FeC  | 92.4 | 0.4     | -  | -       | -  | -       | -  | -       | -  | -       | 92.4  |
| 2095_2_4 | 6  | FeC3 | 90.4 | 0.4     | -  | -       | -  | -       | -  | -       | -  | -       | 90.4  |
| 688_6_2  | 8  | FeC3 | 90.3 | 0.4     | -  | -       | -  | -       | -  | -       | -  | -       | 90.3  |
| 688_6_2  | 8  | Mws  | 62.6 | 0.6     | -  | -       | -  | -       | 24.7| 0.5     | 11.7| 0.3     | 99.0  |
| 688_6_2  | 9  | MwsL | 63.8 | 2.7     | -  | -       | -  | -       | 26.0| 1.5     | 11.2| 1.1     | 101.0 |
| 1079_5_2 | 7  | FeC  | 92.5 | 0.4     | -  | -       | -  | -       | -  | -       | -  | -       | 92.5  |
| 1001_4_3 | 7  | Ni   | -    | -       | 99.7| 0.2     | -  | -       | -  | -       | -  | -       | 99.7  |
| 1001_4_4 | 8  | FeC  | 92.7 | 0.5     | -  | -       | -  | -       | -  | -       | -  | -       | 92.7  |
| 1001_4_4 | 6  | FeO  | 78.9 | 0.6     | -  | -       | -  | -       | 22.1| 0.5     | -  | -       | 100.9 |
| 2095_2_3 | 6  | FeC3 | 90.6 | 0.4     | -  | -       | -  | -       | -  | -       | -  | -       | 90.6  |
| 600_8_2  | 7  | L    | 65.8 | 0.8     | 29.1| 0.6     | -  | -       | -  | -       | 1.8| 0.5     | 96.7  |
| 600_8_4  | 5  | Ni   | -    | -       | 99.3| 0.7     | -  | -       | -  | -       | -  | -       | 99.3  |
| 2100_2_2 | 8  | FeC  | 91.1 | 0.1     | -  | -       | -  | -       | -  | -       | -  | -       | 91.1  |
| 2100_2_3 | 6  | L    | 73.1 | 0.2     | 15.4| 0.5     | -  | -       | -  | -       | 7.2| 0.4     | 95.7  |
| 2100_2_4 | 6  | FeC3 | 90.6 | 0.4     | -  | -       | -  | -       | -  | -       | -  | -       | 90.6  |
| 688_6_1  | 8  | FeC  | 92.7 | 0.3     | -  | -       | -  | -       | -  | -       | -  | -       | 92.7  |
| 688_6_1  | 7  | FeC3 | 90.2 | 0.4     | -  | -       | -  | -       | -  | -       | -  | -       | 90.2  |
| 688_6_3  | 7  | FeC3 | 90.3 | 0.3     | -  | -       | -  | -       | -  | -       | -  | -       | 90.3  |
| 688_6_3  | 9  | FeO  | 77.8 | 0.3     | -  | -       | -  | -       | 23.2| 0.3     | -  | -       | 101.0 |
| 605_8_5  | 7  | L    | 79.4 | 0.2     | -  | -       | -  | -       | -  | -       | 16.3| 0.8     | 95.6  |
| 605_8_5  | 8  | FeO  | 76.6 | 0.2     | -  | -       | -  | -       | 21.9| 0.5     | -  | -       | 98.5  |
The metal phases (some obtained at 1200 °C and all from 1400 °C runs; Table 1) had particular textures due to dendritic crystals. These crystals may be produced by melt quenching, as evidenced by published experimental results for Fe–Ni–C–N systems at mantle P–T conditions [40,47,57]. Melting was observed in a 1200 °C run with the graphite-Fe–Ni system (Fe/(Fe + Ni) weight ratios of 0.5 and 0.75) and in 1400 °C runs with the graphite-Fe, graphite-Ni, and graphite-Fe–Ni (Fe/(Fe + Ni) = 0.2) systems (Table 1). The EDS microanalysis revealed Pt contamination of the molten metal, which increased with temperature (1.8–7 wt % Pt at 1200 °C and 16–50 wt % Pt at 1400 °C). The graphite-Fe, graphite-Fe3C, and graphite-Ni samples were free from Pt in the 800 °C to 1200 °C runs, when no melting occurred.

3.2. Species in Quenched Fluids

Fluids equilibrated with solid or liquid metal phases were present in the run products at all T–fH2 conditions, and their compositions were analyzed by the GC-MS method. The fluid phase was distributed along grain boundaries within the crystalline matrix. The fluids appeared quenched upon capsule opening and consisted of species that are gaseous or liquid under normal conditions. Our previous results [56,58,59], along with published data [16,21,48], confirmed that the applied 200 deg/s quenching rate prevents any inverse reaction and ensures preservation of species till the GC-MS analysis.

As we showed previously [25], the fluid with high contents of N2, CO2, and H2O formed a few minutes after the graphite-rich system had achieved the target pressure and temperature, on account of species adsorbed on graphite or air entrapped in the welded capsules. The fluid composition did not change in long runs in the absence of external fH2 buffering [25]. The quenched fluid that formed in 10-h 800 °C runs was rich in nitrogen and carbon dioxide despite the MMO + H2O buffering of fH2: 32–63 rel.% N2, 15–20 rel.% CO2, and 14–16 rel.% H2O (Supplementary Table S1; Figure 2). Therefore, the double-capsule technique for fH2 buffering failed at 6.3 GPa and 800 °C. Judging by the high N2 in quenched fluid after the run at 6.3 GPa and 800 °C with the graphite + Fe system, the nitrogen entrapped from air dissolved neither in the Fe0 phase nor in graphite.

The quenched fluids obtained at a higher temperature of 1000 °C had markedly different compositions (Supplementary Table S1; Figures 2–6), with N2 and CO2 < 5 rel.%. This could be attributed to the almost complete reduction of CO2 adsorbed on graphite by hydrogen at buffered fH2, N2: dilution with newly formed HCs, and the formation of other N-bearing species [25,56,59]. Thus, the fH2 buffering technique worked well at 1000 °C; at higher temperatures, the contents of N2 and CO2 increased slightly and exceeded 5 rel.% only at 1400 °C (Figure 2). The CO2 increase was due to the temperature-dependent decrease in the oxygen affinity of Mo and Fe and the corresponding decrease of buffered fH2. As calculated previously [25], the MMO + H2O-buffered fH2 became 0.4 log unit lower at 6.3 GPa as the temperature increased from 1100 °C to 1400 °C. To balance the fH2 decrease, a slightly more reduced IW + H2O buffer was used instead of MMO + H2O. The fluids obtained in the 800 °C runs appeared to be equilibrated under unbuffered conditions because the buffer did not work properly at this temperature. The quenched fluids that formed in C-saturated systems at 1000 °C consisted mainly of light alkanes (C2 > C3 > C4 > C1), predominantly those heavier than methane (Supplementary Table S1; Figure 4); C5H12 was no more than a few percent, while heavier alkanes were vanishing. The graphite–Fe-C and graphite–Ni systems produced almost identical species at 1000 °C.
The quenched fluids obtained at 1200 °C in Pt capsules consisted mainly of C1–C4 alkanes, but their relative contents differed from the respective values of lower temperature runs (Figures 3–6; Supplementary Table S1; Supplementary Figure S2). The systems including an Fe–Fe3C mixture or an Fe–Ni melt yielded fluids with up to 80 rel.% CH4, <20 rel.% C2H6, less than a few percent of other alkanes, and up to 0.1 rel.% of O-bearing species (runs 2095_2_2 and 2100_2_3, respectively; Figures 5 and 6). Similar alkane species, but with 35–50 rel.% CH4 and 20–40 rel.% C2H6, formed from the systems with graphite plus Fe3C, FeC, and FeC3 or only FeC3. The fluid synthesized from the graphite–Ni system predominantly contained C2H6 (C2 > C1 > C3 > C4) and was compositionally similar to that obtained earlier by hydrogenation of metal-free graphite at the same P–T conditions [25].
Figure 4. Speciation of minor organic components in quenched fluids obtained in 1000 °C runs in the presence of Ni and Fe₃C.

The quenched fluids from the non-equilibrium assemblage Dm + Fe₃C + Fe₇C₃ obtained at 1200 °C in Au capsules predominantly contained C₆H₆ (C₆ > C₅ > C₄ ≈ C₃) and, especially, quite a large amount (0.1–1.0 rel.%) of O-bearing species (run 688_8_1; Figure 6). A similar fluid composition containing predominantly C₆H₆ and high contents of O-bearing species resulted from Fe₃C interaction with magnesite in an Au capsule (run 688_8_2; Figure 6). The reaction of Fe₃C with an H₂O–CO₂ fluid in an Au capsule (run 688_8_3; Figure 6) yielded quite a different composition: predominantly H₂O, no more than 10 rel.% of alkanes, and CH₄ exceeding C₆H₆. The quenched fluids produced by reactions with oxidized magnesite and a H₂O–CO₂ fluid contained 1.3 and 0.01 rel.% CO₂, respectively (Supplementary Table S1).
Figure 5. (a) Contents of light alkanes C1–C4 and CH4/C2H6 ratio in quenched fluids obtained at 1200 °C in samples with buffered Fe and C activity in Pt capsules. Data on run 1905_2_3 are from [25]. CH4 and C2H6 contents calculated with GFluid [60] on the right are shown for comparison. (b) TIC (total ion count) values obtained by GC-MS on the right characterize semi-quantitatively the amount of fluid in the capsule after the run.

Figure 6. Speciation of minor organic components in quenched fluids obtained in the presence of metal phases at 1200 °C. (a) Pt capsules; (b) Au capsules.

The fluids that resulted from 1400 °C runs were in equilibrium with Pt-bearing melts and showed the same speciation trends as revealed in the 1200 °C runs. The HC species included predominant light alkanes (Supplementary Table S1; Figure 4), with CH4 decreasing as C2H6 increased, while the melt composition changed successively as Fe(–Pt) → Ni–Fe(–Pt) → Ni(–Pt). The quenched fluids obtained at 1000–1400 °C contained from tenth fractions of percent to 2 rel.% CH3N and NH3 as main nitrogen species (Supplementary Table S1). In our previous study [25], the amounts of HCs in quenched fluids were inferred from the degree of atmospheric N dilution with newly formed species. Yet, the approach is inapplicable to this study as nitrogen in Fe-bearing systems can bind efficiently with both Fe0 and iron carbides by the reaction Fe3C + N fl → Fe3N + C gr,dm, at the applied P–T conditions [58].

4. Discussion

4.1. Formation of Hydrocarbons in the Presence of a Metal Phase

The results of experiments at 6.3 GPa and 1000–1400 °C with buffered fH2 highlighted the speciation of HCs produced by hydrogenation of Fe + Fe3C and FeC + FeC3 in systems unsaturated with respect to graphite/diamond and in C-saturated systems of graphite with FeC, FeC6, and an Fe–Ni alloy.

Hydrogen fugacity in Pt and Au capsules was controlled by the reactions:
The obtained data have implications for the mechanism of HC generation in the mantle upon interaction between native iron and carbon-bearing phases (graphite, diamond, carbonate, and fluids) at buffered $f$H$_2$. With the diverse samples used in the experiments, it was possible to reproduce the initial HC formation via hydrogenation:

\[
\text{Fe} + \text{H}_2\text{O} \rightarrow \text{FeO} + \text{H}_2 \quad (1)
\]

\[
\text{Mo} + 2\text{H}_2\text{O} \rightarrow \text{MoO}_2 + 2\text{H}_2 \quad (2)
\]

\[
\text{C}_{Gr} + \text{H}_2 \rightarrow \text{HC}s \quad (3)
\]

\[
\text{Fe}_3\text{C} + \text{H}_2 \rightarrow \text{Fe} + \text{HC}s \quad (4)
\]

\[
\text{Fe}_3\text{C} + \text{C}_{Gr,Dm} + \text{H}_2 \rightarrow \text{Fe}_7\text{C}_3 + \text{HC}s \quad (5)
\]

\[
\text{Fe}_3\text{C} + \text{MgCO}_3 + \text{H}_2 \rightarrow \text{Fe}_7\text{C}_3 + (\text{Fe},\text{Mg})\text{O} + \text{HC}s \quad (6)
\]

\[
\text{Fe}_3\text{C} + \text{H}_2\text{O} + \text{CO}_2 + \text{H}_2 \rightarrow \text{Fe}_7\text{C}_3 + \text{FeO} + \text{HC}s \quad (7)
\]

At the applied P–T conditions, the fluid compositions in the capsules became readily equilibrated due to high rates of the reactions [24]. Several non-catalytic [25] and catalytic processes led to redistribution of the HCs, vide infra.

Note that, according to the TIC values obtained by GC-MS (Supplementary Table S1), the amount of fluid synthesized in Pt capsules from graphite was greater than in the case of Au capsules and C-poor systems like Fe-carbide, due to lower hydrogen permeability of gold and lower activity of carbon in C-poor systems (e.g., 2095_2_2). Low contents of light hydrocarbons <$C_5$ in the gas mixture allowed the detection of all minor species with higher relative abundances (Figure 6). The gold capsules, which are less permeable for hydrogen than the platinum ones, may keep $f$H$_2$ below the buffered value at high rates of H$_2$ consumption. Therefore, the Au capsule runs typically yielded fluids equilibrated with $f$H$_2$\text{sample} < $f$H$_2$\text{buffer}$, and their amount was substantially smaller than that in the Pt capsules. The systems producing little fluid (Au capsules, Fe + Fe$_3$C) contained the background composition of minor organic compounds (Figure 6).

In all runs, HCs formed from the available carbon sources: graphite/diamond, carbides, CO$_2$, carbonate, or any combination thereof. As FeC converted to C-enriched Fe$_7$C$_3$, most of carbon came from magnesite, which reduced to magnesiowüstite either by H$_2$ or by partial FeC oxidation, while FeC oxidation provided additional C inputs to the system. The run products obtained with the FeC and MgCO$_3$ proportion used in the study were free from graphite/diamond, possibly, because all excess carbon was reduced at buffered $f$H$_2$. The formation of graphite and diamond by FeC oxidation and by FeC reactions with carbonate was reproduced in previous experiments [50,61,62]. Excess carbon required for HC formation and FeC-to-Fe$_7$C$_3$ conversion appeared in reaction 7 on account of FeC oxidation and CO$_2$ reduction by hydrogen. The hydrogenation of FeC–Fe$_7$C$_3$ or FeC–graphite systems at 6.3 GPa and 1200 °C in Pt capsules (reactions 4 and 5) produced fluids with the $C_1 > C_2 > C_3 > C_4$ distribution of alkanes. The CH$_4$/C$_2$H$_6$ ratio in the fluids decreased from 5 to 0.5 as the iron activity decreased and the C fraction increased in the series: Fe–FeC $\rightarrow$ FeC–FeC$_3$ $\rightarrow$ FeC–graphite $\rightarrow$ graphite (Figure 5). In the presence of iron and carbides, $f$O$_2$ was about the IW buffer and thus caused no influence on speciation of HCs in the fluid. The fluid obtained by hydrogenation of graphite in the presence of solid Ni had strongly predominant C$_2$H$_6$ ($C_2 > C_1 > C_3 > C_4$), but the one synthesized in the presence of an Fe–Ni melt (reaction 3) was rich in CH$_4$, while the fraction of Ni was minor. The fluid that formed at 1200 °C in an Au capsule in the system with diamond, FeC, and FeC$_3$ (reaction 5) contained commensurate amounts of CH$_4$ and C$_2$H$_6$ (Figure 6). A similar fluid composition was obtained in an Au capsule by the interaction of FeC with magnesite (reaction 6). The interaction of FeC with a H$_2$O–CO$_2$ fluid (reaction 7) in an Au capsule produced an aqueous fluid predominantly containing CH$_4$. The relative amounts of alkane species from lower temperature 1000 °C runs with FeC and Ni were different from those at 1200 °C: $C_2 > C_3 > C_4 > C_1$. In general, as
the temperature increased from 1000 °C to 1400 °C, the overall alkane composition became lighter (Figure 3).

Previously, we reported that HC fluids obtained by hydrogenation of graphite at high pressures and temperatures in Pt capsules had low methane/ethane ratios [25]; a similar observation was also reported for HC fluids synthesized from graphite with docosane and/or stearic acid [56]. We tentatively attributed the shift toward lower CH₄/C₂H₆ ratios to Pt-promoted radical methane condensation [62]. Similar processes may occur in the presence of supported metal Pt catalysts of alkane homologization, which was described in detail in [63]. The 6.3 GPa and 1200 °C runs in Pt capsules in the presence of Fe-C and/or Fe-C₃ produced lighter alkanes (C₁ > C₂ > C₃ > C₄), while a methane-enriched alkane mixture (up to 80 rel.% CH₄) was obtained in the C-unsaturated Fe–Fe₃C system, with iron carbide being the only carbon source. The hydrogenation of graphite in the presence of an Ni-poor Fe–Ni melt also yielded a lighter HC composition. At the same time, alkanes formed by hydrogenation of graphite were similar, despite the presence of solid Ni, and showed typical Pt-related distribution (C₁ > C₂ > C₃ > C₄), i.e., solid Ni appeared not to influence the speciation of alkanes. Similar distribution was obtained in the presence of an Ni-poor Fe–Ni melt.

The CH₄/C₂H₆ ratios in the experimental Fe-rich systems approached those in C–O–H fluids estimated using the GFluid model [60] for 6.3 GPa and 1200 °C (Figure 5): CH₄ in the latter was either close to or slightly higher than the experimental values, while C₂H₆ was most often lower. Some other models, e.g., Deep Earth Water (DEW) [64], may be applicable to further research as they allow calculating the compositions of fluids equilibrated with solid phases.

Right after the H₂ buffer starts working, the Pt surface rapidly saturates with adsorbed hydrogen. Methane generated by carbon hydrogenation adsorbs dissociatively onto the inner surface of the Pt capsule, with the formation of methyl species. As their surface concentration increases, the methyl species recombines to produce ethane that desorbs to the fluid. Since the capsule surface is covered with adsorbed hydrogen at the applied run conditions, methane adsorption may require quite a high methane fugacity to compete with the hydrogen. An increase in Fe loading decreased the available amount of carbon and, hence, the volume of fluid generated by carbon hydrogenation (Figure 5). Low methane fugacity may lead to a shift in the methane adsorption equilibrium and a lower surface concentration of methyl species and related ethane production. The methane/ethane ratio was substantially high at low amounts of fluid produced in runs 2095_2_2 and 2095_2_4, due to a pronounced effect of metallic Fe. It was also relatively high in run 600_8_2, which yielded a high-methane fluid and an Fe–Ni melt, while the amount of fluid was greater than that in 2095_2_4 (6.6 × 10¹⁰ against 1.23 × 10¹⁰, according to TIC). Thus, metal phases having high Fe contents increase the methane/ethane ratio of equilibrated fluids. The mechanism may be similar to that reported by Cimino et al. [65] and involves catalytic hydrogenation-cracking. While the distribution of CH₄/C₂H₆ shifted from that predicted by GFluid toward ethane in the absence of Fe-rich metal phases, fluids contained light hydrocarbons in a ratio close to thermodynamically predicted in the presence of Fe-rich metal phases.

4.2. Interaction of Slab-Derived Fluids with Metal-Saturated Mantle

The most advanced of the existing models explains the origin of hydrocarbons in the upper mantle by interaction between FeO-bearing carbonates and H₂O under moderately reduced conditions of fO₂ near the WM (FeO–Fe₃O₄) equilibrium [16,17,21–23]. We suggest a new model which provides insights into the formation of HCs during the interaction of slab-derived fluids with metal-saturated mantle and into their fate in the shallow mantle. With this model, it became possible, for the first time, to evaluate the volume and duration of mantle HC generation in the context of global geodynamic evolution.

The available geochemical, petrological, and experimental data provide solid proof that downgoing slabs transport aqueous fluids with variable amounts of CO₂ and carbonate into the transition zone and lower mantle [29,31,32,34]. Therefore, slab-derived fluids may penetrate into reduced metal-saturated mantle regions and induce reaction 1 which buffers fH₂ at the IW + H₂O equilibrium in the zones of mantle–slab interaction [29,48,49]. CO₂ in these zones may result from the
reaction of Fe-based alloys with carbonate or CO₂ [40,50] or reactions 6 and 7 of our study. Thus, slab-derived fluids interact with the mantle under conditions that are necessary and sufficient for HC generation as reproduced in our experiments: the presence of iron (Fe, Fe₃C, Fe₇C₃, and Fe–Ni alloy) and carbon donors (iron carbides, graphite, diamond, carbonate, or H₂O–CO₂ fluids), as well as enhanced hydrogen fugacity (Figure 7). Heat flux in subcratonic mantle ranges commonly from 35 to 40 mW/m² [66,67] and corresponds to temperatures of −1200 to −1450 °C at a depth of 300 km, while the slab temperatures about this depth may be below 1000 °C [67]. Thus, the temperatures in the mantle–slab interaction zones may range from −1000 to −1400 °C.

**Figure 7.** Formation of light alkanes in the zone of interaction between slab-derived oxidized volatiles and Fe⁰-bearing mantle. Black arrows show paths and relative magnitudes of volatile fluxes [29,31]. IW (Fe–FeO buffer), IW + 2.5 log units, and IW + 4.5 log units are fO₂ values according to [13]. Metasomatic vein network is according to [68]. Blue rhombs are mark diamonds.

Summing up the experimentally reproduced reactions 1 and 3–7, we infer that HCs can form in the zones of mantle–slab interaction by the simplified reaction:

$$4Fe + 2H_2O + CO_2 \rightarrow 4FeO + CH_4$$

(8)

If all Fe⁰ becomes consumed, the input of the following H₂O and CO₂ batches from the subduction zone can provide fO₂ increase in the zone of mantle–slab interaction. Wüstite or magnesiwüstite resulting from this interaction may become dissolved in silicate minerals. In a short time, fO₂ may reach values within the so-called water maximum (carbon-saturated maximum H₂O content for C–O–H fluids, CW) at an oxidation degree of IW + 2.5 to IW + 4 log units (the limit of C⁰ stability) [11]. Rapid fO₂ increase and fH₂ decrease under the effect of slab-derived fluids in this zone can reduce the yield of HCs, but their generation will hardly stop completely [16,17,21,23].

Thus, the suggested scenario of large-scale HC generation during mantle–slab interaction obviously could work in the very beginning of subduction, when oceanic crust and lithosphere reached the depths of metal-saturated mantle and could be brief on the scale of geological processes. Irreversible binding of oxygen associated with fO₂ increase in the interaction zone could lead to a brief oxygen decrease in the Earth’s atmosphere of that time.

### 4.3. Fate of HCs in Shallow Mantle

Hydrocarbons, being poorly soluble in silicates, can ascend to shallow mantle with other fluid components, including Mg-, Si-, and Na-bearing organic species [30]. While ascending, such fluids can interact with the ambient peridotite, a typical mantle rock at these depths. The available data on xenoliths indicate a gradual fO₂ increase from −220 km to the crustal base [11,13,28]. According to experimental results and thermodynamic calculations, rapid oxidation of HCs should occur at <200 km where fO₂ is near the CW level, and the forming water-rich fluids can bear some HC species.
The effect of H2O- and HC-bearing fluids on subcratonic lithosphere can induce its metasomatism with the liberation of quite abundant C0 as diamond or graphite [71–73]. For instance, the effect of H2O–CH4 fluids may be responsible for the formation of MARID-type veins within the lower reaches of the North Atlantic cratonic lithosphere before approximately 1400 Ma (presumably during the Paleoproterozoic era) [68]. A later redox change, shortly prior and subsequently to approximately 610 Ma, may have led to the injection of oxidized low-degree CO2-rich convective mantle-derived melts into the pre-existing, more reduced, cratonic vein network. The isotope fractionation factor of carbon (ΔC\text{diamond-fluid}) indicates that partial oxidation of methane-bearing fluids and release of C0 can maintain the crystallization of diamond [14,71].

The reactions of fluids with lithospheric peridotite at depths of 150–200 km at f\text{O2} corresponding to the EMOD (enstatite-magnesite-olivine-diamond) equilibrium produce CO2-rich fluids/melts [13], which can contain minor amounts of alkanes, alkenes, and O-bearing organic species [70]. Thus, migration of deep HCs should mainly lead to their complete oxidation within the lithospheric mantle. The amount of HCs that the lithospheric mantle can oxidize remains unknown. According to the estimates of Stachel and Luth [14], depleted lithospheric peridotites have quite low buffer capacity, and the f\text{O2} change from IW to EMOD on account of bulk Fe3+/ΣFe would require fluid transport of <5 mg O2 per 100 g of rock.

5. Conclusions

Thus, we have demonstrated that HCs, predominantly light alkanes (C1 ≈ C2 > C3 > C4), can form upon interaction of metal and metal–carbon phases (solid Fe, Fe3C, Fe7C3, Ni, and liquid Fe–Ni alloys) with or without additional sources of carbon (graphite, diamond, carbonate, and H2O–CO2 fluids) at 6.3 GPa and 1000–1400 °C and relatively high f\text{H2}. This is experimental proof that the HC generation mechanism can work in the zones of interaction between metal-saturated mantle and slab-derived fluids/melts. The amount of metal phases available for the reaction with volatiles in these zones is small relative to those of water and carbon subducted annually to the mantle. The oxidation of all Fe0 to FeO by slab-derived fluids and cessation of large-scale HC generation may occur within a geologically short time span. The existence of a highly oxidized mantle at depths of 150–200 km indicates that HCs generated in reduced mantle can be oxidized completely in the lithosphere.

Supplementary Materials: The following are available online at www.mdpi.com/2075-163X/10/2/88/s1, Table S1: Compositions of quenched fluid. Figure S1: (a) The high-pressure cell; (b) temperature patterns in furnace assembly predicted using the software of Hernlund et al. [74]; (c) the double-capsule technique used to constrain the f\text{H2} conditions by the assemblage Fe + FeO + H2O buffer. Figure S2: Results of GC-MS analysis of quenched fluid extracted by mechanical shock destruction from run 2095_2_4. Figure S3: Results of GC-MS analysis of of quenched fluid extracted by mechanical shock destruction from run 2095_2_4. Figure S4: Phases identified by X-ray powder diffraction in the Gandolfi mode.

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