

Article

C- and N-Bearing Species in Reduced Fluids in the Simplified C–O–H–N System and in Natural Pelite at Upper Mantle P–T Conditions

Ivan Sokol^{1,*}, Alexander Sokol^{1,2}, Taras Bul'bak¹, Andrey Nefyodov³, Pavel Zaikin³ and Anatoly Tomilenko¹

- ¹ V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences (IGM SB RAS), 3, Koptyug ave., 630090 Novosibirsk, Russia; sokola@igm.nsc.ru (A.S.); taras@igm.nsc.ru (T.B.); tomilen@igm.nsc.ru (A.T.)
- ² Novosibirsk State University, 2, Pirogov str., 630090 Novosibirsk, Russia
- ³ N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 9, Lavrentiev ave., 630090 Novosibirsk, Russia; anefyodov@yandex.ru (A.N.); zaikin@gmail.com (P.Z.)
- * Correspondence: isokol0x5a@gmail.com

Received: 26 September 2019; Accepted: 10 November 2019; Published: 18 November 2019



Abstract: C- and N-bearing species in reduced fluids weree studied experimentally in C-O-H-N and muscovite–C–O–H–N systems and in natural carbonate-bearing samples at mantle *P*–*T* parameters. The experiments reproduced three types of reactions leading to formation of hydrocarbons (HCs) at 3.8–7.8 GPa and 800–1400 °C and at hydrogen fugacity (fH_2) buffered by the Fe–FeO (IW) + H_2O or Mo–MoO₂ (MMO) + H_2O equilibria: (i) Thermal destruction of organic matter during its subduction into the mantle (with an example of docosane), (ii) hydrogenation of graphite upon interaction with H₂-enriched fluids, and (iii) hydrogenation of carbonates and products of their reduction in metamorphic clayey rocks. The obtained quenched fluids analyzed after the runs by gas chromatography-mass spectrometry (GC-MS) and electronic ionization mass-spectrometry (HR-MS) contain CH_4 and C_2H_6 as main carbon species. The concentrations of C_2 - C_4 alkanes in the fluids increase as the pressure and temperature increase from 3.8 to 7.8 GPa and from 800 to 1400 °C, respectively. The fluid equilibrated with the muscovite-garnet-omphacite-kyanite-rutile ± coesite assemblage consists of 50–80 rel.% H₂O and 15–40 rel.% alkanes ($C_1 > C_2 > C_3 > C_4$). Main N-bearing species are ammonia (NH₃) in the C–O–H–N and muscovite–C–O–H–N systems or methanimine (CH₃N) in the fluid derived from the samples of natural pelitic rocks. Nitrogen comes either from air or melamine $(C_3H_6N_6)$ in model systems or from NH_4^+ in the runs with natural samples. The formula CH₃N in the quenched fluid of the C–O–H–N system is confirmed by HR–MS. The impossibility of CH₃N incorporation into K-bearing silicates because of a big CH₃NH⁺ cation may limit the solubility of N in silicates at low fO_2 and hence may substantially influence the mantle cycle of nitrogen. Thus, subduction of slabs containing carbonates, organic matter, and N-bearing minerals into strongly reduced mantle may induce the formation of fluids enriched in H₂O, light alkanes, NH₃, and CH₃N. The presence of these species must be critical for the deep cycles of carbon, nitrogen, and hydrogen.

Keywords: mantle; subduction; pelite; fluid; hydrocarbons; methanimine; deep carbon cycle; deep nitrogen cycle

1. Introduction

Hydrocarbons (HCs) and ammonia have been important agents in the Earth's carbon and nitrogen cycles. Their stability in different tectonic settings in the course of geodynamic evolution has been



responsible for the habitability of the planet, the amounts of carbon and nitrogen migrating in fluids, and the formation of diamonds [1–7].

Much recent progress in experiments at mantle pressures and temperatures allows reconstructing the compositions of hydrocarbon fluids that form in different ways: By thermal decomposition of higher alkanes, aromatic compounds, and fatty carboxylic acids [8–11]; reaction of CO, CO₂, and carbonate with FeO and H₂O; or hydrogenation of carbon [7,12–20]. Thermodynamic calculations and experimental data indicate that organic species, such as light alkanes, acids, and salts, e.g. acetic acid and acetates, can be stable in the silicate mantle under the appropriate redox conditions [4,7,10,12–17,19–22]. Specifically, light alkanes were found out [22] to be stable in a wide range of redox conditions in the presence of a lherzolitic mineral assemblage at 5.5–7.8 GPa and 1150–1350 °C. The discovery of hydrocarbons in diamonds from the mantle and in crustal alkaline rocks [5,17,23–27] supports this conclusion.

Large amounts of volatiles (mainly in carbonates and hydrous minerals) can penetrate into the mantle with sinking slabs that consist of sediments, altered oceanic crust, and partially serpentinized lithospheric mantle [28,29]. Features of HC generation at the account of slab-derived H₂O and iron-bearing carbonates at fO_2 near the FeO–Fe₃O₄ (WM) equilibrium, i.e., in relatively oxidized conditions, were discussed in several publications [7,12,13,16,17]. However, little is known about the formation of HCs with participation of metamorphic mudrocks (pelites) subducted to mantle depths at fO_2 near the Fe–FeO (IW) buffer, where metal phases become stable. The first study of this kind belongs to Kucherov et al. [14]. The importance of the process was highlighted by Smith et al. [5] who discovered sublithospheric diamonds with metal phase inclusions and a thin fluid jacket of CH₄ and H₂. The abundance of CaSi–perovskite and Cr-poor majoritic garnets supports the formation of HC generation by hydrogenation of different carbon sources in the presence of metal phases is another step forward in this field.

Ammonia (NH₃) has received most of attention among N-bearing species in reduced fluids since nitrogen is transported to mantle depths mostly in the form of NH_4^+ that substitutes for K⁺ in silicates from subducted sediments [3,30,31]. The mechanism is maintained by the presence of K-bearing minerals (micas, K-hollandite, K-cymrite) in pelitic slab material [3,32,33] and depends on NH₃/NH₄⁺ ratios in the equilibrated fluid [34]. The possibility for nitrogen to travel with slabs to upper mantle depths is supported by its rather high contents in diamonds, such as those from ultra-high-pressure metamorphic rocks of the Kokchetav complex [35]. The stability of NH_3 in mantle fluids depends on oxygen fugacity. Studies of nitrogen speciation in mantle and crustal N-H-O fluids at 600–1400 °C and 2–35 kbar by Li and Keppler [36] showed that NH_3 can coexist with mantle minerals in aqueous fluids only at strongly reduced conditions close to Fe–FeO buffer, whereas N₂ is the dominant nitrogen specie of the oxidized shallow upper mantle fluids. Yet, Li and Keppler [36] have not analyzed the stability of N- and C-bearing fluid species as nitrogen depots. Later we [10,22,37] investigated the formation and stability of ammonia in fluid phases of C-O-H-N, Fe-C-O-H-N, and lherzolite–C–O–H–N model systems at pressures from 5.5 to 7.8 GPa and temperatures from 1100 to 1400 °C. Ammonia turned out to predominate in quenched fluids synthesized at high fH_2 buffered externally by Fe–FeO (IW) + H_2O or Mo–MoO₂ (MMO) + H_2O equilibria and fO_2 near the IW buffer. However, the $N_2/(N_2 + NH_3)$ ratio exceeded 0.5 at fO_2 values of IW + 0.7 log units and tended to unity in all fluids synthesized at progressively more oxidized conditions, including fluids equilibrated with magnesite-bearing lherzolite. On the other hand, a compound with a mass-to-charge ratio of m/z = 29was the main N-bearing species in quenched N-poor reduced C–O–H–N fluids synthesized at 6.3 GPa and 1100–1400 °C [38]. Judging by the short retention time, this signal represents a low molecular weight compound, namely, methanimine (CH_3N). To exclude a possibility of this signal being an isotope signal of ¹⁴N¹⁵N or a signal of a radical fragment, the identification of CH₃N was supplemented by the measuring of the exact molecular weight of the $[M^+] = 29$ compound and comparing its full mass spectrum with published data.

This study focuses on C- and N-bearing species in reduced fluids synthesized at 3.8–7.8 GPa and 800–1400 °C in the model systems of C–O–H–N and muscovite–C–O–H–N and in charges with natural samples of pelite (Maykop Fm. shale, Russia) and N-bearing mica schist (Polar Ural, Russia) which represented carbonate-bearing slab material subducted to mantle depths. Since methanimine can affect the nitrogen and carbon mantle cycles, it was important to check whether it can exist in hydrocarbon-rich fluids that form during hot subduction. Therefore, special efforts were made to identify methanimine in quenched fluids obtained in the experimental systems at 6.3 GPa and 1000–1200 °C.

2. Materials and Methods

2.1. Materials

The features of C- and N-bearing species in fluids obtained in synthetic systems were studied using pure natural graphite (99.99% C) pre-dried at 110 °C for at least 30 days and chemical grade synthetic diamond (ACM-20/14, 14–20 μ m) pre-annealed in air at 700 °C for 1 h as fluid-generating carbon sources. The starting mixtures also contained at least 99% purity docosane (C₂₂H₄₆), melamine (C₃H₆N₆), distilled water, and silver oxalate (Ag₂C₂O₄) (Table 1). Air was the only N source in melamine-free samples. Pycnometer testing revealed about 39 vol.% of air in the capsules. Pre-dried graphite contained 700 ppm CO₂ and 700 ppm H₂O. Distilled water was added to capsules with a microsyringe to ±0.2 mg accuracy. The capsules were sealed by arc-welding prior to experiments. The capsule assembly details were described in our previous publications [10,19,20,38].

The starting materials used to study C- and N-bearing species in the fluids equilibrated with muscovite (Table 2), natural Maykop Fm. shale (Taman Peninsula, Russia; hereafter referred to as pelite) [39], and N-rich quartz–muscovite–chlorite schist (hereafter referred to as mica schist) (Polar Ural, Russia), as well as melamine or distilled water. The mica schist, with up to 266 ppm NH₄ [40], was metamorphosed at 0.2 GPa and 570 to 580 °C. As shown by the thermogravimetric (TG) analysis, it contained up to 0.91 wt. % carbonate CO₂ and 2.21 wt. % H₂O in total. The pelite sample contained 2.0 wt. % calcite and 1.7 wt. % siderite, according to the quantitative X-ray diffraction (QXRD) data [39] and 1.87 wt. % CO₂, 2.05 wt. % of adsorbed H₂O, and 3.33 wt. % of hydroxyl according to the TG analysis. The content of nitrogen in the pelite sample was not specially analyzed, but it may be from 424 to 2382 ppm [41,42]. The pelite and mica schist samples exposed to the experimental *P*–*T* conditions can be appropriate analogues of metasediments subducted to mantle depths judging by what is known from the literature [6,28,43,44].

D	P (GPa)	T (°C)	Buffer	Capsule	τ (h)	Compositions of Samples, mg								
Kun#						Gr	Ms	Pelite	Mica Schist	$C_3H_6N_6$	H ₂ O	$C_{22}H_{46}$	$Ag_2C_2O_4$	Dm
1668_2_1	5.5	1150	-	Pt	10	10.1	-	-	-	-	-	-	-	-
1906_2_1	6.3	1400	-	Pt	0.33	8.4	-	-	-	-	-	-	-	-
1969_2_1	5.5	1150	MMO	Pt	40	8.5		-	-	-	-	0.8	-	-
996_5_6	5.5	1200	MMO	Pt	10	9.8		-	-	-	-		0.5	-
2107_2_3 *	6.3	1200	MMO	Au	10	9.5		-	-	-	-	0.5	-	-
2107_2_4 *	6.3	1200	MMO	Au	10	10.8	-	-	-	-	-	-	-	-
1942_2_2	7.8	1350	MMO	Pt	10	9.7	-	-	-	-	-	-	-	-
1975_2_1	7.8	1350	IW	Pt	10	16.4	-	-	-	-	-	-	-	-
1670_2_1	7.8	1350	IW	Pt	10	11.4	-	-	-	-	-	-	-	-
1670_2_3	7.8	1350	IW	Pt	10	-		-	-	-	-	-	-	8.1
1695_1_4	3.8	800	MMO	Au	40	-	8.5	-	-	0.5		-	-	-
1981_2_6	5.5	1000	MMO	Au	40	2.1	8.3	-	-	-	0.9	-	-	-
2093_2_1	6.3	1000	MMO	Au	60	-		9.8	-	-	-	-	-	-
2093_2_3	6.3	1000	MMO	Au	60	-		-	10.9	-	-	-	-	-

 Table 1. Compositions of samples and run conditions.

* samples used for high resolution mass-spectrometry. Gr = graphite; Dm = diamond; Ms = muscovite; natural samples are Maykop Fm. shale (Russia) and mica schist (Polar Ural, Russia); $C_{3}H_{6}N_{6}$ is melamine; $C_{22}H_{46}$ is docosane; $Ag_{2}C_{2}O_{4}$ is silver oxalate; IW = Fe–FeO; MMO = Mo–MoO₂.

	Muscovite	Pelite * (Maykop Fm. Russia)	Mica Schist ** (Polar Ural, Russia)
SiO ₂	46.3	53.9	48.4
TiO ₂	0.1	0.8	1.4
Al_2O_3	34.6	16.3	22.4
FeO	1.5	7.3	10.8
MnO	0.1	0.1	0.2
MgO	0.8	3.2	4.3
CaO	-	1.8	0.6
Na ₂ O	0.5	1.3	3.1
K ₂ O	10.8	2.9	3.3
P_2O_5	-	0.1	0.3
BaO	0.4	-	0.1
LOI	-	11.1	4.1
Total	95.1	99.0	99.2

Table 2. Major-element compositions of starting muscovite, pelite and mica schist (wt. %).

* contains 2.0 wt. % calcite and 1.7 wt. % siderite according to QXRD; 1.87 wt. % CO_2 , 2.05 wt. % adsorbed H_2O , and 3.33 wt. % water as OH according to TG; ** contains 0.91 wt. % carbonate CO2 and total 2.21 wt. % H2O according to TG.

2.2. Methods

Experiments at 3.8, 5.5, 6.3, and 7.8 GPa were carried out in a split-sphere multi-anvil high-pressure apparatus [45]. 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 by bracketing the quartz–coesite and the graphite–diamond equilibrium at 3.8, 5.5, 6.3, and 7.8 GPa and high temperatures. The second phase transition of Bi occurring at 7.7 GPa at ambient temperature was not used for calibration since the information obtained from other systems is sufficient. Temperature was monitored in each experiment using a PtRh₆/PtRh₃₀ thermocouple calibrated at 6.3 GPa and 7.8 GPa using the melting points of Al, Ag, Ni and Pt. Pressure and temperature were measured to an accuracy of ± 0.1 GPa and ± 20 °C [45,46]. The charges were quenched under isobaric conditions at a rate of 200 deg/s. As shown by special studies of the effect of cooling rate on fluid compositions [36,38], cooling from 800–1400 °C to room temperature at 200 deg/s can provide quenching and furnish reliable evidence of the fluid compositions at the applied *P*–*T* conditions.

The run durations from 2 to 60 h (Table 1) were chosen because equilibrium fluids rich in hydrocarbons (HC) and N-bearing species in the C–O–H–N experimental system at 6.3 GPa and 1100–1400 °C form in at least two hours [10,38]; one 1400 °C run was as short as 20 min. Long 40–60 h durations were used to bring the fluid-bearing silicate systems close to the equilibrium.

Hydrogen fugacity was buffered by the Fe–FeO (IW) + H₂O and Mo–MoO₂ (MMO) + H₂O equilibria using a modified double-capsule technique, with inner Pt or Au capsules placed inside thick-walled Fe or Mo outer capsules with talc insulation [9]. Our previous experiments at 6.3 GPa and 1150–1400 °C [18,22] showed that fH₂ buffering can maintain invariable compositions of HC and C/H ratios in fluids as the run duration increased from 1 min to >40 h with this technique, thus proving its workability at the applied P–T– τ parameters. For more details of the double-capsule technique, see [47]. As we calculated earlier for quenched C–O–H–N fluids [10], their fO₂ may generally vary from log fO₂ Δ IW – 2.5 to log fO₂ Δ IW + 2.5 (Δ IW is the logarithmic difference between experimental fO₂ and that imposed by the coexistence of iron and wüstite) depending on the initial H₂O contents in the charge and the selected IW or MMO buffers for fH₂. Note that the MMO buffer is slightly more oxidized (log fO₂ Δ IW + 1) [9]. In the absence of an external fH₂ buffer, fO₂ in samples was slightly higher than Δ IW + 2 [10].

2.3. Analytical Techniques

After quenching and retrieval from the high-pressure cells, the Pt 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 pre-heating duration depended on the rate of gas desorption and was analyzed on-line. Blank pre-heating runs showed neither speciation nor concentration changes in volatiles in the capsules at 120–130 °C. The capsules that did not sustain heating were excluded from analysis. The gas mixture extracted from capsules by piercing was analyzed by gas chromatography and mass spectrometry using a Thermo Scientific Focus GS/DSQ II Series single quadrupole gas chromatograph—mass analyzer at the V.S. Sobolev Institute of Geology and Mineralogy. 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. The normalization quality was checked against external standards [10]. 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 <5% in most cases. For details of the GC–MS method, see [10].

Exact masses of methanimine were determined on a Thermo Fisher Scientific *Double Focusing System (DFS) Magnetic Sector* high resolution mass-spectrometer at the N. Vorozhtsov Institute of Organic Chemistry (Novosibirsk). The operation conditions were: 70 eV electron ionization and 200 °C ion source temperature. The capsules with mixtures of volatiles were placed into a specially modified inlet for the mass calibration standard, which allowed capsule opening with a needle inside the volume intended for calibration. The inlet system was maintained at 200 °C. The DFS mass-spectrometer was calibrated with respect to the standard lines of perfluorokerosene (PFK) prior to measurements. The exact masses of methanimine ions were measured relative to the mass lines of known particles (CN⁺, HCN⁺).

In the end of the experiments, the recovered silicate samples were cleaned and mounted in epoxy resin. After the polymerization of resin, the samples were polished under kerosene, without the use of water (final stage 1 µm Al₂O₃) and examined on a Tescan *MIRA 3 LMU* scanning electron microscope (SEM). The solid phase compositions were analyzed using the Tescan *MIRA 3 LMU* scanning electron microscope coupled with an INCA EDS 450 microanalysis system with an Oxford Instruments liquid nitrogen-free Large Area EDS X–Max–80 Silicon Drift Detector. The instruments were operated at an accelerating voltage of 20 keV, a beam current of 1 nA, and a spot size of ~10 nm; the count time for spectra acquisition was 20 s. The EDS spectra were optimized for quantification using the standard XPP procedure built into the INCA Energy 450 software. The TG analyses were accomplished according to the method published by Dementyev et al. [48].

3. Results

The fluid phase was obtained in four runs from charges containing other solid phases besides graphite (see Table 3 for their representative analyses). Recrystallization of muscovite was observed in all runs of muscovite–C–O–H–N systems. The newly formed muscovite gained silica which increased from 3.12 to 3.27 apfu Si upon the temperature and the pressure change from 800 °C to 1000 °C and from 3.8 to 5.5 GPa, respectively, which was associated with growing percentage of the celadionite component (KAl(Mg, Fe²⁺)Si₄O₁₀(OH)₂) and formation of kyanite. The run with pelite and mica schist produced a muscovite–garnet–omphacite–kyanite–coesite–rutile assemblage (Figure 1). Muscovite in the assemblage contained 3.52 apfu Si and thus was more strongly phengitized (had a higher percentage of celadionite) than that obtained in the muscovite–C–O–H–N system. Note that the phengite substitution line implies that Si^{IV} and Mg^{VI} substitute, respectively, for Al^{IV} and Al^{VI} [32,33]. Garnet was mainly almandine or pyrope, and a considerable part was grossular; omphacite had

a high percentage of jadeite. After the 6.3 GPa and 1000 °C run, mica schist consisted of almost the same muscovite–garnet–omphacite–kyanite–rutile assemblage but without coesite. The newly formed muscovite of this assemblage contained 3.49 apfu Si and was compositionally similar to that in the previous run. Garnet was more often almandine and less often grossular varieties; omphacite had a large jadeite component as well.

Table 3. Representative analyses of solid phases obtained in model muscovite–C–O–H–N system and with natural samples (wt. %).

Run#	Phase	SiO_2	TiO ₂	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K ₂ O	BaO	Total
1695_1_4	Ms	45.5	0.6	31.7	2.9	-	1.6	-	0.5	10.7	0.4	93.9
1001 2 6	Ms	47.6	0.2	29.5	3.1	-	1.7	-	-	11.3	0.5	93.8
1981_2_0	Ky	36.6	0.0	63.5	0.3	-		-	-		-	100.4
	Ms	52.5	1.1	23.5	1.6	-	4.6	-	-	11.5	-	94.9
	Grt	40.5	0.6	21.9	20.9	0.7	8.3	6.0	-	-	-	99.7
2002 2 1	Omp	57.6	0.3	21.1	1.4	-	3.1	3.5	11.7	-	-	98.5
2093_2_1	Coe	98.9	-	-	-	-	-	-	-	-	-	98.9
	Ky	38.2	-	59.5	1.2	-	-	-	-	-	-	98.8
	Ru	0.5	95.7	1.6	0.6	-	-	-	-	-	-	98.3
	Ms	52.3	1.1	24.5	2.5	-	4.2	-	-	10.7	-	95.3
	Grt	38.1	0.2	21.2	29.5	0.5	9.4	0.6	-		-	99.6
2093_2_3	Omp	58.7	0.4	23.4	1.7	0.0	1.2	1.2	13.4	0.0	-	100.0
	Ky	36.8	0.0	62.8	0.4	-	-	-	-	-	-	100.0
	Ru	0.5	96.1	1.8	0.9	-	-	-	-	-	-	99.3

Ms = muscovite, Grt = garnet, Omp = omphacite, Ky = kyanite, Coe = coesite, Ru = rutile.



Figure 1. Microphotographs of pelite (**a**) and mica schist (**b**) samples after runs 2093_2_1 and 2093_2_3 at 6.3 GPa and 1000 °C. Abbreviations stand for names of minerals: Ms = muscovite, Grt = garnet, Omp = omphacite, Ky = kyanite, Coe = coesite, Ru = rutile.

According to GC–MS data, the quenched fluids contained light alkanes (Table 4, Figures 2 and 3) which formed by hydrogenation of graphite or diamond in most cases, except for two runs where docosane was used as a source of hydrocarbons (Table 1). Low-N fluids equilibrated in the C–O–H–N system at fH_2 buffered by the IW + H₂O and MMO + H₂O equilibria contained 30 to 70 rel.% alkanes (Table 4). The hydrogenation reaction stopped at H₂O and C⁰ formation in a single run with CO₂ added to the system, and the run products almost lacked light alkanes. The runs without external H₂ buffering produced from 3 to 26 rel.% of alkanes, mainly C₁–C₄ species, with high contents of CH₄ and

 C_2H_6 but less than 10 rel.% C_3H_8 and C_4H_{10} (Figure 2), while C_7-C_{18} were as low as ≤ 1 rel.%. Other species included notable amounts of aldehydes, ketones and carboxylic acids, the latter especially in non-buffered conditions with CO₂ up to 11–43 rel.% (unlike <3.6 rel.% in other runs).



Figure 2. CH_4/C_2H_6 , CH_4/C_3H_8 , and CH_4/C_4H_{10} ratios in quenched fluids obtained in the C–O–H–N and muscovite–C–O–H–N model systems and with natural samples, as a function of H_2O content (**a**), pressure (**b**), and temperature (**c**). See the legend of 2a for 2b and 2c.

Hydrocarbon species appeared for the first time in the quenched fluids formed from the pelite and mica schist samples (Figure 3) at 6.3 GPa, 1000 °C and fH_2 buffered by MMO + H₂O, at the conditions that simulated subduction of these rocks in a slab to ~200 km depths. Carbon in those charges could only come from carbonates which did not exceed a few wt. % (Table 2). Dehydration of mica and

reduction of carbonates led to water enrichment of the fluid, up to 48–81 rel.% H_2O . The fluid contained predominant light HCs, from 15 to 39 rel.%. The fluids synthesized from the charges with natural samples contained lighter alkanes than those obtained in the model C–O–N–H system (Figures 2 and 3).



Figure 3. Speciation of hydrocarbons (HCs) in quenched fluids derived from natural samples, at 6.3 GPa and 1000 °C.

Note that the fluids synthesized in the graphite-bearing muscovite–C–O–H–N system likewise contained mainly light alkanes. As we showed before [18,19], heavier alkanes can form in experimental systems at higher pressures and temperatures, when Pt capsules are used instead of Au ones. Concentrations of heavier alkanes also become lower in fluids with lower H₂O contents in the fluid [19]. Thus, the lighter alkane compositions obtained in the runs with the natural samples may be due to (1) a possible catalytic effect of solid matrix silicates (muscovite–garnet–omphacite–kyanite–rutile \pm coesite; (2) relatively low run temperature (1000 °C); (3) high water content in fluids (Figures 2 and 3), and (4) the use of Au capsules. These factors obviously controlled the composition of alkanes obtained in the muscovite–C–O–H–N system.

According to GC–MS data, N₂, NH₃ and CH₃N are main N-bearing components of quenched fluids (Table 4, Figure 4). Their relative amounts depend on redox conditions, which were varied by either buffering or not the hydrogen fugacity in different runs. In the case of double capsule technique fH_2 buffering, the redox conditions in the inner capsule increases with the water content within [47]. The concentration of CO₂ measured by GC–MS is an informative parameter reflecting the growth of the fluid oxidation degree. N₂ that was captured mainly from the air was a predominant nitrogen specie in the N-poor fluid synthesized in the C–O–H–N system even at CO₂ >1 rel.% (Figure 4a), but ammonia predominated at lower CO₂ levels (Figure 4b). This trend is consistent with the fluid composition of the muscovite–C–O–H–N system in the presence of an additional N source. Importantly, CH₃N (Table 4, Figure 4c) was the main nitrogen specie at low CO₂ levels in the fluids that formed in systems with natural rock samples (nitrogen coming mostly from NH₄⁺ of clay minerals and muscovite), as well as in the model muscovite–C–O–H–N system (ambient air N).



Figure 4. Relative contents of main nitrogen species (N₂, NH₃ and CH₃N) in quenched fluids obtained in the C–O–H–N and muscovite–C–O–H–N model systems and with natural samples, as a function of CO₂ content: N₂/(N₂ + NH₃ + CH₃N) (**a**), NH₃/(N₂ + NH₃ + CH₃N) (**b**), and CH₃N/(N₂ + NH₃ + CH₃N) (**c**). See the legend of 4a for 4b and 4c.

High-resolution mass spectrometry was used to measure the exact molecular weight of the 29 Da compound revealed by GC–MS. The measurements were made for quenched fluids obtained in Au capsules after runs 2007_2_3 and 2007_2_4 with model systems at 6.3 GPa and 1200 °C. The calculated mass for CH₃N [M]⁺ was 29.0260, and the mass/charge ratio was m/z = 26.0250. The closest mass is atmospheric [¹⁵N¹⁴N]⁺ that has m/z = 29.0025. GC–MS data obtained for gas mixtures in runs with high CH₃N contents (pelite and mica schist, Table 4) allowed detecting the mass spectrum more precisely. The mass spectrum we obtained (Figure 5) shows generally the same relative intensities of signals as

the one published by Theule et al. [49], except for the presence of an m/z = 17 signal, which remained cut off in the spectrum of Theule et al. [49], and for the absence of the m/z = 28 signal possibly resulting from N₂ pollution mentioned by the authors. Comparison of the HCN spectrum presented by Theule et al. [49] with the reference one from the NIST library (SRD 69) leads to the same inference since the spectrum by Theule et al. [49] has the heightened m/z = 28 signal.

Run #	Alkanes	Alcohols, Ethers	Aldehydes	Ketones	Carb. Acids	H ₂ O	CO ₂	N_2	CH ₃ N	H ₃ N
1668_2_1	3.9	3.3	15.2	5.3	1.6	4.1	42.9	17.7	0.2	0.0
1906_2_1	26.6	0.4	1.7	0.6	16.9	37.5	10.7	4.3	0.1	0.0
1969_2_1	69.9	1.2	2.5	2.2	1.9	11.7	0.8	0.6	0.9	5.1
996_5_6	25.3	0.8	0.9	0.4	1.7	62.0	0.9	0.2	0.7	6.0
1942_2_2*	30.4	3.6	15.1	9.2	5.7	13.1	3.6	7.2	0.1	0.5
1975_2_1	57.3	1.0	1.2	1.3	2.4	16.9	0.5	10.6	0.3	6.9
1670_2_1	53.1	2.2	3.6	2.3	17.3	9.8	1.7	4.3	0.5	0.4
1670_2_3	52.2	3.6	2.2	2.2	2.2	12.4	1.0	15.2	0.8	5.5
1695_1_4	27.0	0.1	0.2	0.1	0.3	26.4	0.9	13.3	0.5	30.8
1981_2_6	14.7	0.2	0.2	0.0	0.2	81.4	0.3	0.0	1.1	1.2
2093_2_1	15.3	0.0	0.0	0.0	0.0	80.8	0.0	0.3	3.2	0.4
2093_2_3	39.0	0.1	0.1	0.1	0.0	48.0	0.3	0.0	12.4	0.1

 Table 4. Compositions of quenched fluids (rel.%).

* 6.8 rel.% olefins, 0.7 rel.% arenes, and 2.8 rel.% of other N-bearing species.



Figure 5. Mass spectra of the $[M^+] = 29$ compound of pelite (**a**) and mica schist (**b**) samples after runs 2093_2_1 and 2093_2_3 at 6.3 GPa and 1000 °C. The background is subtracted. Relative abundance units are % of the most intensive signal.

4. Discussion

The reported experiments provide new knowledge on the composition of C- and N-bearing species of reduced fluids obtained in the C–O–H–N and muscovite–C–O–H–N systems and from natural rock samples. As shown previously [10], fO_2 may generally vary from log $fO_2 \Delta IW - 2.5$ to log $fO_2 \Delta IW + 2.5$ depending on the initial H₂O contents in the charge and the selected IW or MMO buffers for fH_2 . In the absence of external fH_2 buffering, fO_2 in the samples was slightly above IW + 2.5 log units. The question is whether these redox conditions represent the conditions of slabs and the ambient mantle. Different serpentinization degrees of peridotite, involvement of variable amounts of carbonate in the slab material, and dehydration reactions during subduction can maintain heterogeneous redox conditions within slabs reaching depths of 150–350 km in a range of 6 log units, from log $fO_2 \Delta IW - 1$ to log $fO_2 \Delta IW + 5$, while the surrounding mantle is generally more reduced [50,51]. Thus, the fluids we analyzed can form and remain stable only in the most reduced mantle and slab regions.

4.1. Carbon Species

Carbon species in the quenched fluids from our experiments were mainly light alkanes C_1-C_4 (Table 4; Figure 2); CO₂ reached considerable amounts in two runs with non-buffered fH_2 . In most of the runs, HCs formed by reactions of H_2 –CO₂– H_2 O– N_2 fluids with carbon of graphite, while volatiles included H_2 of the buffer and gases adsorbed on graphite particles of the starting material. The interaction of graphite with H_2 discussed in detail in [19,20] started with reduction of the adsorbed CO₂, which however stopped in few minutes in the absence of other CO₂ sources. No methanation of carbon dioxide can occur at *P*–*T* parameters described. Hydrogenation of graphite produces tens of times more HC-bearing fluids than that of diamond. Graphite exfoliation by the fluid leads to significant increase in its surface area and to acceleration of the reaction [19].

In two runs, HCs formed mainly by thermal destruction of docosane at high pressures and temperatures, most likely by the mechanism of thermal cracking [10]. Decomposition of docosane appears to be the main process involving n-alkanes, including n-docosane and alkyl chains of fatty acids. In principle, the initial thermal formation of radical species of higher hydrocarbons in homolysis and rearrangement reactions leads to further β -scission into alkene and alkyl radicals with shorter chains [10]. Ethylene that forms in β -scission of terminal radicals in excess of H₂ readily reduces to ethane. The radicals resulting from cracking can recombine or react with alkanes or alkenes to form new HC species and radicals.

The speciation of alkanes in quenched fluids (reference to Supplementary Table) is influenced by the experimental conditions. It was previously shown [10,19,20] that in presence of Pt heavier HCs are formed due to the catalytic homologization [52,53] mainly affecting the CH_4/C_2H_6 ratio. This mechanism may also be responsible for the formation of minor amounts of branched or cyclic alkanes. Capsules of pure gold do not show major catalytic effects in the systems investigated, apparently due to the dissociation of hydrogen on the surface of neutral gold having energy barrier [54,55], in contrast to Pt. Theoretical studies also showed that the adsorption of hydrocarbons, alkyl radicals and atomic H to the neutral Au^0 appears to be disadvantageous [56]. On the other hand, the H₂ permeability of Au is substantially lower that of Pt, making the equilibrium to be attained slowly.

The runs with natural samples provided HC generation in strongly reduced conditions at the *P-T* parameters simulating subduction to depths below 200 km. The experiments actually reproduced metamorphic reactions, including partial dehydration of clay minerals and muscovite, which produced a muscovite–garnet–omphacite–kyanite–rutile ± coesite matrix and a fluid, while the latter provided reduction of carbonates at MMO + H_2O -buffered fH_2 . Reactions of this kind were earlier effectuated in simple model systems consisting of carbonate, FeO and H₂O and yielded methane as a main product at high pressures and temperatures [7,12,13,16,17,57]. Methane formation in the reaction of FeO, CaCO₃, and H₂O in experiments of Scott et al. [13] preferably occurred at temperatures below 1000 °C and pressures in a range of 5–11 GPa, and the yield of methane increased continuously as the temperature was elevated from 700 to ~1200 °C at 4 to 5 GPa in the experiments of Kenney et al. [12]. Unlike those results, the quenched fluids we obtained in the runs with the pelite samples at 6.3 GPa and 1000 °C contained commensurate amounts of methane and ethane and notably smaller amounts of other light alkanes (Figure 3). Our experiments differed by high fH_2 which was constrained by oxidation of wüstite at the WM + H_2O equilibrium and exceeded that in the experiments with carbonate, FeO and H_2O . As we calculated [19], fH_2 at the MW + H_2O equilibrium in this range of pressures and temperatures was 1.2–2.1 log units below the IW + H_2O equilibrium. Since fH_2 is the critical parameter governing HCs formation in these reactions [19,57], generation of light alkanes was faster in our case. The pelite sample contained much more carbonates and water than mica schist, and the respective quenched fluid had more water and less light alkanes: 81 rel.% H₂O and 15 rel.% alkanes against 48 rel.% H_2O and 39 rel.% alkanes in the case of mica schist.

Thus, our experiments reproduced three cases of HC generation under the upper mantle PT conditions: Thermal destruction of docosane; hydrogenation of graphite; hydrogenation of carbonates of pelites and products of their reduction. All reactions occurred at buffered fH_2 produced mainly light

alkanes, especially CH₄ and C₂H₆ (Table 4; Figure 2). The muscovite–garnet–omphacite–kyanite–rutile \pm coesite assemblage did not influence much the composition of the generated HCs (Figure 3).

4.2. N-Bearing Species

The fluids synthesized in the N-poor C–O–H–N system changed in predominant nitrogen species from N₂ to NH₃ as they became more reduced and depleted in CO₂, whereas the respective change in the fluids obtained using natural samples was from N₂ to CH₃N (Figure 4c). The identification of CH₃N by the conventional GC–MS routine was supplemented by the HR–MS analysis of a quenched fluid specially synthesized in the C–O–H–N system at 6.3 GPa and 1200 °C. The *m*/*z* = 26.0250 value obtained by HR–MS has provided solid support to the interpretation of the GC–MS data and a reference for detection of this species in fluids from other samples.

The limits of NH₃ and CH₃N redox stability in the analyzed fluids generally coincide (Figure 4b,c), and their contents increase rapidly as CO₂ decreases to <1 rel.%. Taking into account calculations of Stachel and Luth [58], the concentrations of CO_2 about 1 rel.% in the C–O–H fluid can be estimated to represent the ~IW + 1 log unit conditions. The fluids synthesized in our previous study [22] in the lherzolite–C–O–H–N system at 5.5–7.8 GPa and 1150–1350 °C and at fO₂ from strongly reduced conditions (IW – 2.5 log. units) to the EMOD equilibrium contained ammonia as predominant nitrogen specie $(N_2/(NH_3 + N_2) = 0.01-0.17)$ in the presence of metal-saturated lherzolite. However, the $N_2/(NH_3+N_2)$ ratio approached unity in the presence of magnesite-bearing lherzolite, i.e., at more oxidized conditions. In the same way, the reported experiments show the concentration of ammonia decreasing rapidly once CO₂ in the fluid from the lherzolite–C–O–H–N system exceeded 1 rel.% (Figure 4b). The concentration of methanimine (CH_3N) in the reduced fluid is controlled by the ratio of nitrogen to active C-bearing precursors of CH₃N in the system, the content of precursors being substantially higher in the systems containing pelitic rocks. The exact mechanism was not investigated so far. In the presence of melamine in the starting composition, NH₃ predominated over CH₃N over the whole range of applied fO_2 , in the case of both metal- and magnesite-saturated lherzolites. The concentrations of NH₃ and CH₃N remained comparable in N-poor fluids where atmospheric N_2 was the only source of nitrogen. Note that most of nitrogen in the fluids obtained in equilibrium with the pelitic mineral assemblage came from NH4⁺ in clay minerals and micas, and CH3N was the dominant nitrogen species of reduced fluids in that case.

The new experimental results confirm the common trend of NH₃ stability in fluids of the model systems at 3.8 to 7.8 GPa and 800 to 1400 °C, in the upper mantle redox conditions. Therefore, considerable amounts of ammonia may be present in a fluid stable either in a relatively cold reduced lithosphere or in a metal-saturated asthenosphere. This study has provided the first evidence that methanimine (CH₃N) may be an essential N-bearing specie in the reduced fluid obtained from natural pelite samples in the *P*–*T* conditions of 6.3 GPa and 1000 °C corresponding to a hot slab subducted to 200 km. The ammonia concentration controls the solubility of nitrogen in K-bearing silicates since NH₄⁺ can partially replace K⁺ [3,30]. On the other hand, the basicity of CH₃N and the big size of methanimine cation CH₃NH⁺ prevent the replacement of K⁺ in silicates. Thus, the stability of CH₃N in reduced fluids may substantially influence the mantle cycle of nitrogen because methanimine cannot incorporate into silicates (like NH₄⁺ \rightarrow K⁺ substitutions), which limits the solubility of N in silicates at low fO_2 .

5. Conclusions

Our experiments at the upper mantle P-T conditions reproduced three potentially important ways of HC generation: (i) Thermal desctruction of docosane; (ii) hydrogenation of graphite; (iii) hydrogenation of pelitic carbonates or products of their reduction. The aforementioned processes conducted under fH_2 buffering produced mainly light alkanes, especially methane and ethane revealed by the GC–MS analysis of the quenched fluids. The alkanes became heavier upon pressure and temperature increase from 3.8 to 7.8 GPa and from 800 to 1400 °C. The quenched

14 of 17

fluids obtained at unbuffered fH_2 contained >10 rel.% CO₂, lesser amounts of alkanes but more O-bearing organic compounds. The fluids produced by partial dehydration of hydrous minerals or by hydrogenation of carbonates (or their reduction products) in equilibrium with the muscovite–garnet–omphacite–kyanite–rutile ± coesite assemblage consisted of 50–80 rel.% H₂O and 15–40 rel.% alkanes (C₁ > C₂ > C₃ > C₄). Therefore, subduction of H₂O- and carbonate-bearing clayey sediments into strongly reduced mantle below 200 km, where fO_2 is as low as the IW buffer, can be expected to induce generation of light alkanes. The HCs generated in slabs may form a hydrocarbon link in the deep cycles of carbon and hydrogen.

The dominant nitrogen specie in the quenched fluids synthesized in the simplified C–O–H–N system, where nitrogen comes from air or melamine, changes from N₂ to NH₃ as the system becomes more reduced. The respective change in the fluids obtained from natural samples, with NH₄⁺ as the carbon source, is from N₂ to mainly CH₃N. The concentration of CH₃N in the reduced fluid increases at higher ratio of C-bearing precursors to bulk nitrogen in the system. The presence of CH₃N in the quenched fluid derived from the C–O–H–N system has been checked by high resolution mass-spectrometry. The CH₃NH⁺ ion, being much bigger than NH₄⁺, cannot substitute for K⁺ in K-bearing silicates. Therefore, the stability of CH₃N in reduced N-poor fluids may limit the solubility of N in silicates at low fO_2 and thus influence considerably the mantle cycle of nitrogen.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/9/11/712/s1.

Author Contributions: Conceptualization, A.S., I.S. and T.B.; Formal analysis, T.B., A.T. and A.N.; Investigation, I.S., A.S., P.Z. and T.B.; Methodology, A.S., A.T., A.N. and I.S.; Supervision, I.S. and A.S.; Writing—original draft, A.S. and I.S.; Writing—review and editing, A.S. and I.S.

Funding: The study was supported by grant 16-17-10041 from the Russian Science Foundation. Experiments with the muscovite–C–O–H–N system were performed as part of a government assignment to the V.S. Sobolev Institute of Geology and Mineralogy (Novosibirsk).

Acknowledgments: We wish to thank Yuri Palyanov and Yuri Borzdov for their assistance throughout the study.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Etiope, G.; Sherwood Lollar, B. Abiotic methane on Earth. Rev. Geophys. 2013, 51, 276–299. [CrossRef]
- Palyanov, Y.N.; Bataleva, Y.V.; Sokol, A.G.; Borzdov, Y.M.; Kupriyanov, I.N.; Reutsky, V.N.; Sobolev, N.V. Mantle-slab interaction and redox mechanism of diamond formation. *Proc. Natl. Acad. Sci. USA* 2013, 110, 20408–20413. [CrossRef] [PubMed]
- 3. Luth, R.W. Volatiles in Earth's mantle. In *Treatise on Geochemistry*, 2nd ed.; Elsevier: Oxford, UK, 2014; Volume 3, pp. 355–391.
- 4. Sverjensky, D.A.; Stagno, V.; Huang, F. Important role for organic carbon in subduction-zone fluids in the deep carbon cycle. *Nat. Geosci.* **2014**, *7*, 909. [CrossRef]
- 5. Smith, E.M.; Shirey, S.B.; Nestola, F.; Bullock, E.S.; Wang, J.; Richardson, S.H.; Wang, W. Large gem diamonds from metallic liquid in Earth's deep mantle. *Science* **2016**, *354*, 1403–1405. [CrossRef]
- 6. Bebout, G.E.; Lazzeri, K.E.; Geiger, C.A. Pathways for nitrogen cycling in Earth's crust and upper mantle: A review and new results for microporous beryl and cordierite. *Am. Mineral.* **2016**, *101*, 7–24. [CrossRef]
- 7. Kolesnikov, A.Y.; Saul, J.M.; Kutcherov, V.G. Chemistry of hydrocarbons under extreme thermobaric conditions. *ChemistrySelect* 2017, 2, 1336–1352. [CrossRef]
- 8. Matveev, S.; Ballhaus, C.; Fricke, K.; Truckenbrodt, J.; Ziegenben, D. Volatiles in the Earth's mantle: I. Synthesis of CHO fluids at 1273 K and 2.4 GPa. *Geochim. Cosmochim. Acta* **1997**, *61*, 3081–3088. [CrossRef]
- Sokol, A.G.; Palyanova, G.A.; Palyanov, Y.N.; Tomilenko, A.A.; Melenevsky, V.N. Fluid regime and diamond formation in the reduced mantle: Experimental constraints. *Geochim. Cosmochim. Acta* 2009, 73, 5820–5834. [CrossRef]
- 10. Sokol, A.G.; Tomilenko, A.A.; Bul'bak, T.A.; Palyanova, G.A.; Sokol, I.A.; Palyanov, Y.N. Carbon and Nitrogen Speciation in N-poor C–O–H–N Fluids at 6.3 GPa and 1100–1400 °C. *Sci. Rep.* **2017**, *7*, 706. [CrossRef]

- 11. Matjuschkin, V.; Woodland, A.B.; Yaxley, G.M. Methane-bearing fluids in the upper mantle: An experimental approach. *Contrib. Mineral. Petrol.* **2019**, *174*, 1. [CrossRef]
- 12. Kenney, J.F.; Kutcherov, V.A.; Bendeliani, N.A.; Alekseev, V.A. The evolution of multicomponent systems at high pressures: The thermodynamic stability of the hydrogen-carbon system: The genesis of hydrocarbons and the origin of petroleum. *Proc. Nat. Acad. Sci. USA* **2002**, *99*, 10976–10981. [CrossRef] [PubMed]
- Scott, H.P.; Hemley, R.J.; Mao, H.; Herschbach, D.R.; Fried, L.E.; Howard, W.M.; Bastea, S. Generation of methane in the Earth's mantle: In situ high pressure–temperature measurements of carbonate reduction. *Proc. Nat. Acad. Sci. USA* 2004, 101, 14023–14026. [CrossRef] [PubMed]
- Kutcherov, V.G.; Kolesnikov, A.Y.; Dyuzheva, T.I.; Kulikova, L.F.; Nikolaev, N.N.; Sazanova, O.A.; Braghkin, V.V. Synthesis of Complex Hydrocarbon Systems at Temperatures and Pressures Corresponding to the Earth's Upper Mantle Conditions. *Dokl. Phys. Chem.* 2010, 433, 132–135. [CrossRef]
- 15. Palyanov, Y.N.; Borzdov, Y.M.; Kupriyanov, I.N.; Khokhryakov, A.F. Effect of H₂O on diamond crystal growth in metal–carbon systems. *Cryst. Growth Des.* **2010**, *12*, 5571–5578. [CrossRef]
- 16. Mukhina, E.; Kolesnikov, A.; Kutcherov, V. The lower pT limit of deep hydrocarbon synthesis by CaCO₃ aqueous reduction. *Sci. Rep.* **2017**, *7*, 5749. [CrossRef] [PubMed]
- 17. Tao, R.; Zhang, L.; Tian, M.; Zhu, J.; Liu, X.; Liu, J.; Höfer, H.E.; Stagno, V.; Fei, Y. Formation of abiotic hydrocarbon from reduction of carbonate in subduction zones: Constraints from petrological observation and experimental simulation. *Geochim. Cosmochim. Acta* **2018**, *239*, 390–408. [CrossRef]
- Sokol, A.G.; Tomilenko, A.A.; Bul'bak, T.A.; Sokol, I.A.; Persikov, E.S.; Bukhtiyarov, P.G.; Palyanov, Y.N. Distribution of light alkanes in the reaction of graphite hydrogenation at pressure of 0.1–7.8 GPa and temperatures of 1000–1350 °C. *High Press. Res.* 2018, *38*, 468–481. [CrossRef]
- Sokol, A.G.; Tomilenko, A.A.; Bul'bak, T.A.; Sokol, I.A.; Zaikin, P.A.; Palyanova, G.A.; Palyanov, Y.N. Hydrogenation of carbon at 5.5–7.8 GPa and 1100–1400 °C: Implications to formation of hydrocarbons in reduced mantles of terrestrial planets. *Phys. Earth Planet. Inter.* 2019, 291, 12–23. [CrossRef]
- 20. Sokol, A.; Tomilenko, A.; Sokol, I.; Zaikin, P.; Bul'bak, T. Formation of Hydrocarbons in the Presence of Native Iron at Upper Mantle Conditions: Experimental Constraints. *Minerals* **2019**, in press.
- 21. Mikhail, S.; Sverjensky, D.A. Nitrogen speciation in upper mantle fluids and the origin of Earth's nitrogen-rich atmosphere. *Nat. Geosci.* 2014, *7*, 816–819. [CrossRef]
- Sokol, A.G.; Tomilenko, A.A.; Bul'bak, T.A.; Kruk, A.N.; Sokol, I.A.; Palyanov, Y.N. Fate of fluids at the base of subcratonic lithosphere: Experimental constraints at 5.5–7.8 GPa and 1150–1350 deg C. *Lithos* 2018, *318*, 419–433. [CrossRef]
- 23. Chukanov, N.V.; Pekov, I.V.; Sokolov, S.V.; Nekrasov, A.N.; Chukanova, V.N.; Naumova, I.S. On the problem of the formation and geochemical role of bituminous matter in pegmatites of the Khibiny and Lovozero alkaline massifs, Kola Peninsula, Russia. *Geochem. Int.* **2006**, *44*, 715–728. [CrossRef]
- 24. Smith, E.M.; Shirey, S.B.; Richardson, S.H.; Nestola, F.; Bullock, E.S.; Wang, J.; Wang, W. Blue boron-bearing diamonds from Earth's lower mantle. *Nature* **2018**, *560*, 84. [CrossRef] [PubMed]
- Sobolev, N.V.; Sobolev, A.V.; Tomilenko, A.A.; Kuz'min, D.V.; Grakhanov, S.A.; Batanova, V.G.; Logvinova, A.M.; Bul'bak, T.A.; Kostrovitskii, S.I.; Yakovlev, D.A.; et al. Prospects of search for diamondiferous kimberlites in the northeastern Siberian. Platform. *Russ. Geol. Geophys.* 2018, 59, 1365–1379. [CrossRef]
- Sobolev, N.V.; Tomilenko, A.A.; Bul'bak, T.A.; Logvinova, A.M. Composition of volatile components in the diamonds, associated garnet and olivine from diamondiferous peridotites from the Udachnaya pipe, Yakutia, Russia (by coupled gas chromatographic-mass spectrometric analysis). *Engineering* 2019, *5*, 471–478. [CrossRef]
- Sobolev, N.V.; Logvinova, A.M.; Tomilenko, A.A.; Wirth, R.; Bul'bak, T.A.; Luk'yanova, L.I.; Fedorova, E.N.; Reutsky, V.N.; Efimova, E.S. Mineral and fluid inclusions in diamonds from the Urals placers, Russia: Evidence for solid molecular N₂ and hydrocarbons in fluid inclusions. *Geochim. Cosmochim. Acta* 2019, 266, 197–219. [CrossRef]
- 28. Plank, T.; Langmuir, C.H. The chemical composition of subducting sediment and its consequences for the crust and mantle. *Chem. Geol.* **1998**, *145*, 325–394. [CrossRef]
- 29. Schmidt, M.; Poli, S. Devolatilization during subduction. In *Treatise on Geochemistry*, 2nd ed.; Elsevier: Oxford, UK, 2014; pp. 669–701.
- 30. Watenphul, A.; Wunder, B.; Heinrich, W. High-pressure ammonium-bearing silicates: Implications for nitrogen and hydrogen storage in the Earth's mantle. *Am. Mineral.* **2009**, *94*, 283–292. [CrossRef]

- 31. Watenphul, A.; Wunder, B.; Wirth, R.; Heinrich, W. Ammonium-bearing clinopyroxene: A potential nitrogen reservoir in the Earth's mantle. *Chem. Geol.* **2010**, 270, 240–248. [CrossRef]
- 32. Domanik, K.J.; Holloway, J.R. The stability and composition of phengitic muscovite and associated phases from 5.5 to 11 GPa: Implications for deeply subducted sediments. *Geochim. Cosmochim. Acta* **1996**, *60*, 4133–4150. [CrossRef]
- 33. Schmidt, M.W.; Vielzeuf, D.; Auzanneau, E. Melting and dissolution of subducting crust at high pressurfufes: The key role of white mica. *Earth Planet. Sci. Lett.* **2004**, *228*, 65–84. [CrossRef]
- 34. Busigny, V.; Cartigny, P.; Philippot, P.; Ader, M.; Javoy, M. Massive recycling of nitrogen and other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: Evidence from HP to UHP oceanic metasediments of the Schistes Lustrés nappe (western Alps, Europe). *Earth Planet. Sci. Lett.* **2003**, *215*, 27–42. [CrossRef]
- 35. Cartigny, P.; Harris, J.W.; Javoy, M. Diamond genesis, mantle fractionations and mantle nitrogen content: A study of δ¹³C–N concentrations in diamonds. *Earth Planet. Sci. Lett.* **2001**, *185*, 85–98. [CrossRef]
- 36. Li, Y.; Keppler, H. Nitrogen speciation in mantle and crustal fluids. *Geochim. Cosmochim. Acta* **2014**, 129, 13–32. [CrossRef]
- 37. Sokol, A.G.; Tomilenko, A.A.; Bul'bak, T.A.; Kruk, A.N.; Zaikin, P.A.; Sokol, I.A.; Seryotkin, Y.V.; Palyanov, Y.N. The Fe–C–O–H–N system at 6.3–7.8 GPa and 1200–1400 °C: Implications for deep carbon and nitrogen cycles. *Contrib. Mineral. Petrol.* **2018**, *173*, 47. [CrossRef]
- 38. Sokol, A.G.; Palyanov, Y.N.; Tomilenko, A.A.; Bul'bak, T.A.; Palyanova, G.A. Carbon and nitrogen speciation in nitrogen-rich C–O–H–N fluids at 5.5–7.8 GPa. *Earth Planet. Sci. Lett.* **2017**, *460*, 234–243. [CrossRef]
- Sokol, E.; Kokh, S.; Kozmenko, O.; Novikova, S.; Khvorov, P.; Nigmatulina, E.; Belogub, E.; Kirillov, M. Mineralogy and Geochemistry of Mud Volcanic Ejecta: A New Look at Old Issues (A Case Study from the Bulganak Field, Northern Black Sea). *Minerals* 2018, *8*, 344. [CrossRef]
- Karpenko, V.Y.; Pautov, L.A.; Agakhanov, A.A.; Khvorov, P.V. On Nitrogen Content in the Schist of the Mun'-Khambo Ridge (N. Ural); The Ural Mineralogical Collected Papers #11. Scientific Edition; Institute of Mineralogy, Ural Branch of Russian Academy of Sciences: Miass, Russia, 2001; p. 330.
- 41. Li, L.; Bebout, G.E. Carbon and nitrogen geochemistry of sediments in the Central American convergent margin: Insights regarding subduction input fluxes, diagenesis, and paleoproductivity. *J. Geophys. Res. Solid Earth* **2005**, *110*, B11202. [CrossRef]
- 42. Busigny, V.; Cartigny, P.; Philippot, P. Nitrogen isotopes in ophiolitic metagabbros: A re-evaluation of modern nitrogen fluxes in subduction zones and implication for the early Earth atmosphere. *Geochim. Cosmochim. Acta* **2011**, *75*, 7502–7521. [CrossRef]
- Bebout, G.E.; Agard, P.; Kobayashi, K.; Moriguti, T.; Nakamura, E. Devolatilization history and trace element mobility in deeply subducted sedimentary rocks: Evidence from Western Alps HP/UHP suites. *Chem. Geol.* 2013, 342, 1–20. [CrossRef]
- 44. Busigny, V.; Bebout, G.E. Nitrogen in the silicate Earth: Speciation and isotopic behavior during mineral–fluid interactions. *Elements* **2013**, *9*, 353–358. [CrossRef]
- 45. Palyanov, Y.N.; Borzdov, Y.M.; Khokhryakov, A.F.; Kupriyanov, I.N.; Sokol, A.G. Effect of nitrogen impurity on diamond crystal growth processes. *Cryst. Growth Des.* **2010**, *10*, 3169–3175. [CrossRef]
- 46. Sokol, A.G.; Borzdov, Y.M.; Palyanov, Y.N.; Khokhryakov, A.F. High-temperature calibration of a multi-anvil high-pressure apparatus. *High Press. Res.* **2015**, *35*, 139–147. [CrossRef]
- 47. Luth, R.W. Natural versus experimental control of oxidation state: Effects on the composition and speciation of C–O–H fluids. *Am. Mineral.* **1989**, *74*, 50–57.
- 48. Dementyev, S.N.; Drebushchak, V.A. Zeolites' dehydration under dynamic regime. *Geochem. Int.* **1992**, *9*, 1361–1367.
- Theule, P.; Borget, F.; Mispelaer, F.; Danger, G.; Duvernay, F.; Guillemin, J.C.; Chiavassa, T. Hydrogenation of solid hydrogen cyanide HCN and methanimine CH₂NH at low temperature. *Astron. Astrophys.* 2011, 534, A64. [CrossRef]
- 50. Foley, S. A reappraisal of redox melting in the Earth's mantle as a function of tectonic setting and time. *J. Petrol.* **2011**, *52*, 1363–1391. [CrossRef]
- 51. Stagno, V.; Ojwang, D.O.; McCammon, C.A.; Frost, D.J. The oxidation state of the mantle and the extraction of carbon from Earth's interior. *Nature* **2013**, *493*, 84. [CrossRef]
- 52. Robertson, A.J.B. The Pyrolysis of Methane, Ethane and n-butane on a Platinum Filament. *Proc. R. Soc. Lond. A Math. Phys. Eng. Sci.* **1949**, 199, 394.

- 53. Belgued, M.; Amariglio, A.; Paréja, P.; Amariglio, H. Oxygen-Free conversion of methane to higher alkanes through an isothermal two-step reaction on platinum (EUROPT-1): II. hydrogenation of the adspecies resulting from the chemisorption of methane. *J. Catal.* **1996**, *159*, 449–457. [CrossRef]
- 54. Hammer, B.; Nørskov, J. Why gold is the noblest of all the metals. *Nature* 1995, 376, 238. [CrossRef]
- 55. McEwan, L.; Julius, M.; Roberts, S.; Fletcher, J.C.Q. A review of the use of gold catalysts in selective hydrogenation reactions. *Gold Bull.* **2010**, *43*, 298.
- 56. Mowbray, D.J.; Migani, A.; Walther, G.; Cardamone, D.M.; Rubio, A. Gold and methane: A noble combination for delicate oxidation. *J. Phys. Chem. Lett.* **2013**, *4*, 3006–3012. [CrossRef]
- 57. Sharma, A.; Cody, G.D.; Hemley, R.J. In situ diamond-anvil cell observations of methanogenesis at high pressures and temperatures. *Energy Fuels* **2009**, *23*, 5571–5579. [CrossRef]
- 58. Stachel, T.; Luth, R.W. Diamond formation—Where, when and how? Lithos 2015, 220, 200–220. [CrossRef]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).