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Carbon and nitrogen speciation in nitrogen-rich C–O–H–N fluids at 5.5–7.8 GPa

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ABSTRACT

Carbon and nitrogen speciation has been studied in high-pressure experiments in the C–O–H–N and C–O–H–N–Fe_3C systems at 5.5 to 7.8 GPa and 1100 to 1500 °C using a split-sphere multi-anvil apparatus. Oxygen fugacity in the samples was either buffered by the Mo–MoO_2 (MMO) and Fe–FeO (IW) equilibria using a double-capsule technique or left unbuffered. fO_2 varied from 2 log units below to +4 log units above the iron–wüstite oxygen buffer (IW) depending on water contents in the charges and buffering. Ultra-reduced fluids contained NH_3 as the dominant species, but its concentration was slightly lower, while CH_4 was higher at higher temperatures. As oxygen fugacity and temperature increased to fO_2 0.7 log units above IW and $T \geq 1400\,°C$, N_2 became the predominant nitrogen species; the dominance among carbon species changed from CH_4 and C_2–C_5 alkanes to oxygenated hydrocarbons and higher alkanes. It has been found out for the first time that the N_2-rich fluid lacks methane at fO_2 4 log units above IW but may bear a few percent of C_2H_6, C_3H_8, and C_{15}–C_{18} alkanes and within one percent of alcohols, aldehydes, ketones, carboxylic acids, and furans. Thus, the NH_3 enrichment of fluids and the nitrogen storage capacity of silicates at depths ∼200 km are expected to be the greatest in cold (1100–1200 °C) and reduced continental lithospheric mantle. In a hotter lithosphere of ∼1400 °C, the concentrations of NH_3 and N_2 in fluids are similar, and the nitrogen storage capacity of silicates should be relatively low. The stability of some higher alkanes and oxygenated hydrocarbons in nitrogen-rich fluids near the enstatite–magnesite–olivine–diamond/graphite (EMOG/D) equilibrium suggest that these carbon species, together with N_2, can survive at the redox barrier, where silicate or silicate–carbonate melts capture them and entrain to shallow mantle.

1. Introduction

Deep cycles of carbon and nitrogen have played a critical role in the Earth evolution and were crucial for the origin of its atmosphere and life. Nitrogen from surface reservoirs is progressively transferred and sequestered into the mantle (Dauphas and Marty, 2004; Busigny et al., 2011; Mikhail et al., 2014; Barry and Hilton, 2016). At depths below 250 km and near-adiabatic temperatures, material rich in volatiles and carbonate can become detached from subducted oceanic lithosphere and remixed into the mantle (Rohrbach and Schmidt, 2011; Litasov et al., 2013; Thomson et al., 2016). The ambient mantle below 250 km is currently assumed to be saturated with metals (Frost et al., 2004; Rohrbach and Schmidt, 2011). Therefore, carbonates are unstable in Fe^0-bearing mantle, where oxygen fugacity (fO_2) is controlled by $Fe^0 \leftrightarrow Fe^{2+}$ reactions, and are reduced with the formation of immobile diamond, which is called 'redox freezing' (Rohrbach and Schmidt, 2011; Palyanov et al., 2013). Once the redox freezing has been completed, domains rich in diamond and volatiles (primarily, hydrocarbons, water, and nitrogen) but depleted in Fe^0 can form within the upwelling mantle.

Note that the fO_2 of garnet-bearing mantle increases during upwelling and adiabatic decompression (Frost et al., 2004; Rohrbach and Schmidt, 2011; Stagno et al., 2013) by reduction of Fe^{3+} in silicate minerals. This may lead to oxidation of diamond, hydrocarbons, and N-bearing species at depths between 250 and 150 km in the redox freezing domains. As a result, the carbon and nitrogen speciation in fluids changes and, correspondingly, nitrogen becomes redistributed between the solid, melt and fluid phases (Kadik et al., 2013; Stagno et al., 2013; Li and Keppler, 2014; Mikhail and Sverjensky, 2014; Smith and Kopylova, 2014). In the continental lithosphere, such domains hosting di-

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amond and volatiles can transform into lenses of eclogite with ^{13}C-depleted and nitrogen-rich diamond (Cartigny et al., 2001; Stachel and Luth, 2015). Reduced fluids can undergo similar oxidation during their ascent as separate flows and penetration into more oxidised lithosphere (Foley, 2011; Stachel and Luth, 2015).

There is a consensus that reduced mantle stores nitrogen mainly as ammonia in C–O–H–N fluids and as NH_4^+ which substitutes for alkali cations in phengite, Cr-bearing clinopyroxene and other silicates (Watenphul et al., 2009, 2010; Li et al., 2013; Li and Keppler, 2014; Luth, 2014; Mikhail and Sverjensky, 2014). Nitrogen speciation in mantle C–O–H–N fluids and in their equilibrium solid phases apparently depends on bulk chemistry, fO_2 and pH (Kadik et al., 2013; Li and Keppler, 2014; Luth, 2014; Mikhail and Sverjensky, 2014). Specifically, recent calculations (Mikhail and Sverjensky, 2014) suggest that the silicate environment can influence the pH of deep aqueous fluids and thus the speciation of nitrogen. Ammonia, the dominant nitrogen species in carbon-free fluids, can be entrapped in quartz and olivine at 0.2–3.5 GPa, 600–1400 °C and fO_2 at the IW equilibrium (Li and Keppler, 2014).

The behaviour of N-bearing species in reduced C–O–H–N fluids has never been studied experimentally at pressures above 3.5 GPa. Reduced C–O–H fluids at 2.0 to 6.3 GPa contain C_1–C_4 alkanes in concentrations related as $CH_4 > C_2H_6 > C_3H_8 > C_4H_{10}$, which is consistent with theoretical predictions (Taylor and Green, 1988; Matveev et al., 1997; Kadik, 1997; Woodland and Koch, 2003; Simakov, 2006; Sokol et al., 2004, 2009; Huizenga et al., 2012). Hydrogen was shown (Sokol et al., 2009) to play an important role in ultra reduced fluids at 6.3 GPa. The contents of alkanes higher than C_4 and other organic compounds in C–O–H–N fluids at low fO_2 likewise remain unconstrained.

To bridge the gap, we have performed multi-anvil experiments under P–T–fO_2 conditions typical of the upper mantle. Gas chromatography–mass spectrometry (GC/MS) was applied to study the quenched fluid compositions of the C–O–H–N system at pressures of 5.5, 6.3 and 7.8 GPa, temperatures of 1100–1500 °C, and oxygen fugacities of −2 to +4 $\Delta \log fO_2$ (IW), as well as the C–O–H–N–Fe_3C system at 6.3 GPa and 1400 °C. The revealed NH_3/N_2 variations and P–T–fO_2 dependence of alkanes and oxygenated hydrocarbons in nitrogen-rich C–O–H–N fluids were used to reconstruct the deep cycles of carbon and nitrogen associated with changes of their speciation in fluids ascending to shallower oxidised mantle.

2. Experimental and analytical techniques

2.1. Starting materials

Starting mixtures for generation of nitrogen-bearing fluids consisted of chemical-grade melamine ($C_3H_6N_6$) with added docosane ($C_{22}H_{46}$), stearic acid ($C_{18}H_{36}O_2$), or chemical-grade Fe_3C in some samples (Table 1). Graphite, which made most of the mixture volume, was dried at 110 °C for at least 30 days. The pre-dried graphite contained 700 ppm CO_2 and 700 ppm H_2O determined by chromatography of gases extracted during graphite annealing at 600 °C in a U-shaped quartz cell. Graphite and the materials that release fluids upon thermal decomposition (at a weight ratio of ~10/1) were placed into Pt or Au capsules of 2 or 3 mm outer diameter and a wall thickness of 0.2 mm (Supplementary Fig. 1). The 10/1 ratio of graphite to fluid-generating material provided an amount of C–O–H–N fluid sufficient for GC/MS analysis but did not produce overpressure in the capsule after the runs and during drying before gas analysis (see below for description of the GC/MS method). The capsules with the starting materials were arc-welded using a *Lampert Werktechnik GmbH* PUK-4U impulse microwelding.

Table 1
Experimental conditions, phase composition of samples and main species of fluids synthesised in the C–O–H–N ± Fe_3C system.

Run #	Starting composition (mg)					Capsule	H_2 buffer	P (GPa)	T (°C)	$\log fO_2$[a]	t (h)	Phases	Main species[b] (rel.%)					
	Gr	$C_3H_6N_6$	$C_{22}H_{46}$	$C_{18}H_{36}O_2$	Fe_3C								NH_3	N_2	CH_4	C_2H_6	C_3H_8	H_2O
889_7_2	23.7	1.5	–	–	–	Pt	–	6.3	1400	−6.0	7	Gr + Fl	–	84.3	0.6	0.06	0.01	8.4
1720_2_3	17.7	3.2	1.1	–	–	Pt	–	6.3	1400	−6.0	7	Gr + Fl	–	57.0	–	5.5	1.2	17.9
1875_2_4	6.6	0.3	–	0.3	–	Pt	–	5.5	1400	−6,5	2	Gr + Fl	3.9	44.6	0.1	30.2	2.8	12.5
1761_2_6	20.4	0.9	1.1	–	–	Pt	Mo–MoO_2	6.3	1100	−14.0	0.017	Gr + Fl	92.8	1.4	3.2	2.1	0.3	0.02
947_5_3[c]	23.7	1.5	1.5	–	–	Pt	Mo–MoO_2	6.3	1200	−13.2	7	Gr + Fl	62.0[b]	–	8.3	29.6	–	–
947_5_1	19	3.2	–	–	–	Pt	Mo–MoO_2	6.3	1200	−13.0	7	Gr + Fl	61.2	0.7	15.9	8.0	0.04	1.2
1751_2_1	8	0.7	–	–	–	Au	Mo–MoO_2	6.3	1200	−12.5	7	Gr + Fl	75.2	2.1	8.7	9.3	3.4	0.2
1751_2_4	6.8	0.3	–	0.3	–	Au	Mo–MoO_2	6.3	1200	−11.3	7	Gr + Fl	53.5	0.1	7.8	0.02	0.02	38.5
1746_2_4	8.8	0.3	–	0.3	–	Pt	Mo–MoO_2	6.3	1300	−10.2	2	Gr + Fl	52.9	20.0	14.8	7.0	1.1	3.4
1746_2_1	6.5	0.7	–	–	–	Pt	Mo–MoO_2	6.3	1300	−11.8	2	Gr + Fl	70.9	14.8	10.4	1.8	0.07	1.5
888_7_4	18.9	0.3	1	–	–	Pt	Mo–MoO_2	6.3	1400	−11.1	2	Gr + Fl	70.5	9.0	11.7	7.2	0.6	0.5
1727_2_3	20	1.5	–	1.5	–	Pt	Mo–MoO_2	6.3	1400	−9.1	7	Gr + Fl	37.1	34.1	–	–	0.004	18.9
886_7_5	20.4	0.9	1.1	–	–	Pt	Mo–MoO_2	6.3	1500	−10.6	2	Gr + Fl	51.1	1.6	39.2	6.1	1.0	0.9
894_7_7	6.1	0.4	–	0.4	–	Pt	Mo–MoO_2	6.3	1500	−8.2	1	Gr + Fl	8.1	45.2	11.9	28.4	1.2	4.6
1875_2_1	6.8	0.3	–	0.3	–	Pt	Mo–MoO_2	5.5	1400	−9.4	2	Gr + Fl	12.5	18.3	0.04	4.8	0.2	43.5
1879_2_2	6.6	0.3	–	0.3	–	Pt	Mo–MoO_2	7.8	1400	−8.6	0.3	Gr + Fl	22.4	46.1	0.03	14.3	0.9	12.6
1798_2_4	24	2.4	–	–	12.8	Pt	Fe–FeO	6.3	1400	−9.8	2	Gr + L + Fl	48.3	36.3	2.6	0.4	0.09	10.4

Gr = graphite, Fl = fluid, L = liquid.
[a] fO_2 for oxygen-free charge with 700 ppm H_2O and 700 ppm CO_2 in graphite was calculated.
[b] For more details of fluid composition see Supplementary Table 1.
[c] Analysis aborted due to bursting of the ampoule.

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