Reduced methane-bearing fluids as a source for diamond

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Supplementary information

**Experimental procedures.** High-pressure experiments were carried out using a belt-apparatus at the Goethe-Universität Frankfurt and a large volume multi-anvil press at the Universität Bayreuth. The experimental assembly follows the design of Matjuschkin et al. \cite{33} and consists of (i) an outer Au capsule containing the mineral starting material (Table S1), (ii) a reduced fluid source (e.g. stearic acid), (iii) an inner capsule containing a reduced metal buffer assemblage (Fe-FeO or Mo-MoO\textsubscript{2}) plus H\textsubscript{2}O, as well as (iv) an outer pressure cell made of a material (CaF\textsubscript{2}) to provide a hydrostatic environment and to minimize H\textsubscript{2}-loss from the capsule. The $f$O\textsubscript{2} inside the outer capsule was determined using the Ir-Fe redox sensor technique \cite{34} as is reported in Table S2. Part of the starting material was packed into a single-crystal capsule of San Carlos Olivine that was initially anhydrous (~0 ppm H\textsubscript{2}O, see Figure S2). This capsule was used to trap fluid inclusions that could be investigated ex situ by Raman spectroscopy. Details are provided in a separate manuscript by Matjuschkin et al. \cite{33}. The buffer assemblage was always detected by microprobe investigation after the experiment. An example of such an image is provided in Matjuschkin et al. \cite{33}.

Amount of fluid added was calculated from the decomposition reaction of stearic acid: C\textsubscript{18}H\textsubscript{36}O\textsubscript{2} = 8 CH\textsubscript{4} + 2 H\textsubscript{2}O + 10 C \cite{32, 43}. (In practice, a small amount of C\textsubscript{6}H\textsubscript{6} may also form \cite{31}). The amount of CH\textsubscript{4} and H\textsubscript{2}O is 58 wt\% of the total mass of stearic acid added, or ~4wt\% of the total sample mass (i.e. ol+opx, buffer excluded). The graphite-saturated CH\textsubscript{4}-H\textsubscript{2}O bearing fluid produced at the onset of each experiment was reduced to ~IW+0.2 to IW+0.8 (Table S2). The previous study of Matjuschkin et al. \cite{33} demonstrated that these $f$O\textsubscript{2} conditions could be maintained for at least 24 hours and that CH\textsubscript{4} remains in equilibrium with a harzburgite (±cpx, ±grt) and silicate melt (1-3%) during this time. Following the model of Huizenga \cite{39} and elaborated by Matjuschkin et al. \cite{33}, the fluid composition should exhibit only a limited variation over the
temperature range of our experiments (Figure S1). A significant change in CH$_4$ mole fraction only occurs upon cooling below 1000°C and the extent is $fO_2$-dependent.

Figure S1: Fluid composition calculated from the model of Huizenga [39] at 7 GPa, for $\Delta \log fO_2$ between IW and IW+2 for unit activity of carbon ($a_C=1$). Note that decreasing temperature only has a significant effect on fluid composition at $\Delta \log fO_2 >$ IW+1.0 and $T<1100°C$. At IW+0.5 (solid line) the fluid has a methane mole fraction of 0.96, similar to experimental results reported in this study and by Matjuschkin et al. [33].
Figure S2: Diamond-bearing experiments in a P-T-field. The graphite-diamond boundary was calculated after Kennedy&Kennedy [2] and Day [4] and melting point of pure gold after by Akella [58].

Analytical techniques. The recovered capsules were mounted in epoxy and ground down to expose the sample material. They were then polished with paraffin, Al₂O₃ since liquid oils can penetrate deep into graphite pockets and is difficult to remove, even when placed under vacuum. Samples were treated in an ultrasonic bath to remove the grinding material from the surface. No Al₂O₃ was detected during the subsequent microprobe investigation. The samples were investigated promptly after experiments using a Renishaw micro-Raman spectrometer (RM-1000), which is equipped with a Leica DMLM microscope, a 1800 groove per mm grating and a CCD detector. The spectra were obtained using the 532nm emission line of a Nd:YAG laser or the 633nm emission line of a HeNe laser that were calibrated using the 519 cm⁻¹ band of a Si wafer. Spectra were collected over several accumulations operating at 10-50% laser power with 3-6min acquisition time for each scan. Analysis of fluid inclusions was mostly performed in confocal mode, while other measurements were made in non-confocal mode to investigate the olivine host for the inclusions. Large areas of each sample were investigated and in several cases additional measurements were made after repeated regrinding and polishing, allowing the sample to be sequentially investigated in the third dimension.

The run products, including the Ir-Fe redox sensors were chemically analysed using a JEOL JXA-8900 Superprobe at the University Frankfurt am Main. Analyses were performed at 15kV and 20nA for the silicate phases and at 20kV and 20nA for the Ir-Fe alloys employing a 1-3µm diameter beam. Fayalite, forsterite, wollastonite, albite, KTiPO₄ as well as pure Ir, Fe, Au and Ni were used as standards and peak calibration.

The Fe³⁺/ΣFe content of the orthopyroxene starting material was determined by ⁵⁷Fe Mössbauer spectroscopy on optically clean, hand-picked separates following the procedure given by Woodland et al. [59].

Unpolarised FTIR spectra were obtained on selected samples using a Bruker Tensor 27 infrared spectrometer at the Australian National University in Canberra. Samples were prepared as doubly-polished 80-200 µm thick sections of the capsule assemblage to avoid the presence of fluid inclusions. During analysis, the sample chamber was purged with dry air to minimise interferences, while the background information was collected prior to each analysis. The crystal thickness was calculated by integrating the absorbance in the silicate overtone between 1625 and 2150 cm⁻¹ divided by the 0.553 coefficient for unpolarised measurements [60].
Figure S3: Raman spectra documenting the occurrence of diamonds depicted in Figures 1c,f g-h. Note that diamond is not in contact with graphite. Diamonds in figures f-h are exposed to the atmosphere. Therefore, the absence of CH\textsubscript{4} peak and/or additional presence of H\textsubscript{2}O or other higher hydrocarbons can be expected. Unlike fluid inclusion in (c) trapped in olivine, which demonstrates the absence of H\textsubscript{2}O and a sharp peak of CH\textsubscript{4}.

**Other experimental techniques**

A number of previous studies with similar starting materials were apparently unsuccessful in producing diamond, such as we observe in our experiments [25, 61, 62]. Although we have no exact answer for these differences, there are number of possible reasons that can be considered. An overriding aspect is the formation and maintenance of CH\textsubscript{4}-rich fluids over at least 2 hours [25]. The following factors can influence the fluids stability and composition. (i) Catalytic reaction of fluid with metal capsules (e.g. Fe, Ni, Pd, Pt), as observed and described by Sokol et al.[25], Matveev et al.[63] Matjuschkin et al. [33] leading to fluid disequilibrium and methane instability [33]. In addition, the formation of carbides with Fe and Ni capsules can lead to a net loss of carbon from the fluid (sample). (ii) Hydrogen loss from the sample related to the choice of pressure medium material surrounding the capsule [33,64,65,66,67]. Such loss causes fluid oxidation and disequilibrium. (iii) Configuration of the experimental assembly is important for achieving as close to equilibrium conditions as possible and maintaining the system during the experiment. For instance, the position of H\textsubscript{2}-metal buffer is crucial for minimizing the H\textsubscript{2}-loss (see above). The inner buffer capsule should not be in contact with external outer capsule in order to prevent direct H\textsubscript{2}-diffusion out of the sample (rather than into the sample) [33,67]. On the other hand, placing the buffer external to the sample, can lead to hydrogen-loss from the assembly rather than imparting the $f$H\textsubscript{2} on the sample [43,62]. (iv) Instable buffering due to use of talc, to produce higher $f$H\textsubscript{2} [43,61,67]. Dehydration of talc does not guarantee a stable $f$H\textsubscript{2} in experiment, which can affect the fluid composition. (v) Finally, but not least, an
adequate experimental duration is required in order for solid organic materials (e.g. stearic acid) to produce the fluid phase. Run durations of at least 2 hours appear to be necessary [25,62].

All these aspects together may help to explain the differences between our study and previous work. However, there are maybe additional reasons, which we did not consider here. For example, even the production of the identical assembly may lead to differences due to use of materials from different suppliers (e.g. dense polycrystalline CaF$_2$ vs. pressed CaF$_2$ powder [33,67].

**Table S1**: Starting mix composition obtained by mixing of 40% F7-olivine and 60% F7-orthopyroxene from the Finsch mine, South Africa [36]. Rare Earth Elements (REE) Zr, Hf, Sc, V, Ce,Yb were added to the starting mix in 130 ppm concentrations in form of oxides. b.d.l. = below detection limit.

|          | SiO$_2$ | TiO$_2$ | Al$_2$O$_3$ | FeO   | Fe$_2$O$_3$ | MnO  | MgO  | CaO  | Na$_2$O | K$_2$O | P$_2$O$_5$ | NiO  | Cr$_2$O$_3$ | REE  |
|----------|---------|---------|-------------|-------|------------|------|------|------|---------|-------|------------|------|-------------|------|
| Bulk     | 51.31   | 0.01    | 0.35        | 4.95  | 0.23       | 0.10 | 42.29| 0.29 | 0.03    | <0.01 | 0.16       | 0.19 | 0.11        |      |
| Ol       | 41.51   | b.d.l.  | b.d.l.      | 6.71  | -          | 0.09 | 51.25| 0.03 | b.d.l.  | b.d.l. | 0.41       | b.d.l.| -           |      |
| Opx      | 57.84   | 0.02    | 0.59        | 3.78  | 0.39       | 0.11 | 36.32| 0.47 | 0.05    | b.d.l. | b.d.l.     | b.d.l.| 0.32        |      |

**Table S2**: Summary of experimental conditions and run product compositions where diamond crystallized. Values of log$f$O$_2$ were calculated from Ir-Fe redox sensors [34]. Note that additional experiments at 5 GPa that did not produce diamond are reported in Matjuschkin et al. [33]. In all experiments a Mo-MoO$_2$-H$_2$O buffer was employed.

| exp.     | P GPa / T °C | duration, h | Mg# ol/opx | X$_{Fe}$ in Ir-Fe alloy | redox sensor log$f$O$_2$ | redox sensor ΔIW | detected fluid components       |
|----------|--------------|-------------|-------------|-------------------------|-------------------------|-------------------|--------------------------------|
| No diamond in experiment                         |             |             |             |                         |                         |                                 |
| 1583$^a$ | 5/1200       | 20          | 93/94       | 0.35(14)               | -9.5(9)                 | +0.5(9)           | CH$_4$-H$_2$, HC$^b$            |
| 1585     | 5/1250       | 23          | 93/94       | 0.3                  | -8.66                   | +0.78             | CH$_4$-H$_2$, HC$^b$            |
| 1611     | 5/1280       | 12          | 94/94       | 0.33                  | -8.45                   | +0.47             | CH$_4$-H$_2$, HC$^b$            |

Diamond bearing experiments (1332 cm$^{-1}$ Raman peak confirmed)

| exp.     | P GPa / T °C | duration, h | Mg# ol/opx | X$_{Fe}$ in Ir-Fe alloy | redox sensor log$f$O$_2$ | redox sensor ΔIW | detected fluid components       |
|----------|--------------|-------------|-------------|-------------------------|-------------------------|-------------------|--------------------------------|
| 1612     | 5/1250       | 15          | 91/93       | 0.35                    | -8.61                   | +0.5              | CH$_4$-H$_2$, HC$^b$            |
| 1632     | 6/1100       | 13.5        | -           | -                       | -                       | -                 | CH$_4$-H$_2$, HC$^b$            |
| 1837     | 6/1200       | 11          | 93/94       | 0.35                    | -8.95                   | +0.64             | CH$_4$-H$_2$, HC$^b$            |
| 1633     | 6/1300       | 19          | -           | -                       | -                       | -                 | CH$_4$-H$_2$, HC$^b$            |
| 1805     | 7/1200       | 7.5         | -           | -                       | -                       | -                 | CH$_4$-H$_2$, HC$^b$            |
| 1836     | 7/1220       | 7           | 92/95       | 0.42                    | -7.49                   | +0.23             | CH$_4$-H$_2$, HC$^b$            |
| 1838     | 7/1220       | 4           | 94/94       | -                       | -                       | -                 | CH$_4$-H$_2$, HC$^b$            |
| 1839     | 7/1250 to 850| 6h run; 2h cooling | 92/94 | 0.37                  | -                       | +0.52 to +0.69$^c$ | CH$_4$-H$_2$O$_2$, HC$^b$ |
| 1766     | 7/1300       | 15          | 93/94       | 0.35                    | -7.42                   | +0.63             | CH$_4$-H$_2$, HC$^b$            |
| Year | Date    | Run | FeO | FeO2 | FO2  | Uncertainty | Product                      |
|------|---------|-----|-----|------|------|-------------|------------------------------|
| 2008 | 7/1300  | 13  | 94/94 | 0.32 | -7.78 | +0.40       | CH₄-H₂, HC₅                  |
| 2007 | 7/1300  | 10  | 93/94 | 0.32 | -7.66 | +0.52       | CH₄-H₂, HC₅                  |

Conservative uncertainty of $fO_2$ measurements is ±0.05 log units, as determined by the standard deviation calculated from 5 to 20 analyses in each sample.

a Fe-FeO buffered experiment [33]
b Unspecified higher hydrocarbons, including C₂H₆
c Estimated for the temperature range 1250 – 850°C
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