Silicate dissolution boosts the CO$_2$ concentrations in subduction fluids

S. Tumiati$^1$, C. Tiraboschi$^2$, D.A. Sverjensky$^3$, T. Pettke$^4$, S. Recchia$^5$, P. Ulmer$^6$, F. Miozzi$^{1,7}$ & S. Poli$^1$

Estimates of dissolved CO$_2$ in subduction-zone fluids are based on thermodynamic models, relying on a very sparse experimental data base. Here, we present experimental data at 1–3 GPa, 800 °C, and ΔFMQ ≈ −0.5 for the volatiles and solute contents of graphite-saturated fluids in the systems COH, SiO$_2$–COH ( + quartz/coesite) and MgO–SiO$_2$–COH (+ forsterite and enstatite). The CO$_2$ content of fluids interacting with silicates exceeds the amounts measured in the pure COH system by up to 30 mol%, as a consequence of a decrease in water activity probably associated with the formation of organic complexes containing Si–O–C and Si–O–Mg bonds. The interaction of deep aqueous fluids with silicates is a novel mechanism for controlling the composition of subduction COH fluids, promoting the deep CO$_2$ transfer from the slab–mantle interface to the overlying mantle wedge, in particular where fluids are stable over melts.
Subduction of the oceanic lithosphere and its sedimentary cover is accompanied by devolatilization processes. CO₂ removal through dissolution of carbonates occurring in altered oceanic lithosphere and its sedimentary cover, along with diapirism of slab rocks and/or melts, provides an efficient way to recycle carbon back to the mantle wedge and, ultimately, to the Earth’s surface. However, other forms of carbon, often closely associated with silicates, have been reported in slab rocks and in particular in subduction mélanges. For instance, graphite has been described in blue schist-facies mafic rocks, metasediments and hybridized peridotites at Santa Catalina, and in ophiolitic serpentinites from the Western Alps, where also diamond has been found in UHP metasediments. In Alpine Corsica and in the Western Italian Alps, reduction of carbonates during subduction results in graphite-rich metasediments and serpentinites, suggesting that graphite may become a major phase in subduction silicate-rich subduction mélanges. Graphite has been considered to represent a refractory sink of carbon in the subducting slab, owing to its lower solubility in aqueous fluids compared to carbonates. On the other hand, graphite dissolution mechanisms and solute transport in complex COH fluids at high pressures have remained experimentally unconstrained. Moreover, recent thermodynamic models highlight the role of graphite in subduction-zone fluids and suggest that the presence of graphite is capable of modifying fluid properties and promoting the formation of C-bearing anions, possibly enhancing the complexation of major and trace elements at elevated P and T conditions.

Here, we provide comprehensive experimental constraints on the composition of high-pressure graphite-saturated COH fluids in terms of dissolved CO₂, SiO₂, and MgO in increasingly complex petrological systems at controlled redox conditions, buffered by using the double-capsule technique and both the nickel-nickel oxide (NNO) and the fayalite-magnetite-quartz (FMQ) buffers, in order to develop a model for the interaction between deep aqueous fluids and silicates in subduction mélanges. A carbonate-free compositional range has been explored at P = 1 GPa, T = 800 °C and P = 3 GPa, T = 800 °C in order to focus on the role of graphite and silicates in the investigated processes. We synthesized COH fluids in equilibrium with graphite and other minerals representative of subduction mélanges, i.e., Mg-silicates (forsterite and enstatite), representative of the mantle component, and quartz, representative of the sedimentary component. Experimental products were analyzed for their volatile COH composition by quadrupole mass spectrometry (QMS) and for their Mg and Si solute load by cryogenic laser-ablation inductively coupled plasma mass spectrometry (ICP-MS). Measured data were compared to thermodynamic modeling results. Further details are provided in Methods section and as Supplementary Information. Our results suggest that the interaction of deep aqueous fluids with silicates in the presence of graphite in a subduction mélangé promotes the dissolution of graphite and enhances the CO₂ contents of the fluids; this provides a new mechanism for controlling the volatile composition of COH fluids already at depths of ~30 km.

Results

CO₂ contents of fluids in equilibrium with silicates. The volatile compositions of COH fluids were measured by piercing the capsules after quench in a gas-tight vessel and then conveying the emanating gases to a quadrupole mass spectrometer (QMS). Measured data were subsequently compared with the compositions predicted by traditional thermodynamic modeling using different equations of state and mixing properties of H₂O and non-polar species (details in Methods section). Carbon-saturated fluids were synthesized first in the pure COH system, where fluids interacted only with graphite (Supplementary Fig. 1a). As predicted by thermodynamic modeling, all analyzed fluids are located on the graphite-saturation surfaces (black lines in Fig. 1). The measured XCO₂ = CO₂/(H₂O + CO₂) mole fraction of the fluids, shown in the zoom boxes, increases in silicate-bearing systems.

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**Fig. 1** Measured volatile composition of graphite-saturated fluids interacting with silicates. C-O-H diagram showing the volatile composition of fluids, measured by quadrupole mass spectrometry, synthesized at P = 1 GPa, T = 800 °C and fH₂ = NNO in equilibrium with graphite only (COH system; green dots), graphite + forsterite + enstatite (MgO-SiO₂-COH system; ochre dots) and graphite + quartz (SiO₂-COH system; pink dots). The graphite-saturation surfaces, i.e., the loci of points representing all possible compositions of graphite-saturated COH fluids (G-COH) at fixed P, T and variable fO₂ conditions, calculated by thermodynamic modeling, are shown for comparison (black curves) along with the volatile fluid composition predicted by the EoS of Zhang and Duan using the H₂ fugacity coefficient of Connolly and Cesare (blue squares; Methods, Supplementary Fig. 2 and Supplementary Table 2 for details). Compared to the pure COH system, the XCO₂ = CO₂/(H₂O + CO₂) of the fluids, shown in the zoom boxes, increases in silicate-bearing systems.
Si and Mg contents of fluids in equilibrium with silicates. The interpretation of the observed differences in volatile content of COH fluids that do and do not interact with silicates is not straightforward. Because, we did not find any evidence of hydration and/or carbonation reactions in the run products, our preferred interpretation is that dissolution reactions of silicates are influencing the XCO₂ of the fluid, provided that graphite is present in excess. We therefore measured additionally the dissolved Si and Mg in the synthetic COH fluids at 1 GPa and 800 °C by using a modified version of the cryogenic LA-ICP-MS technique. This technique was originally developed for the analysis of solutes in pure water, which is frozen in the experimental capsules and analyzed via laser-ablation ICP-MS. In the case of COH fluids, an immiscible mixture of water and non-polar gases is expected at the investigated P, T conditions (inset in Supplementary Fig. 1e). The cryogenic technique, operating at approximately −35 °C, only keeps water in a solid state. Therefore, the other volatiles (including CO₂) are lost when the capsule is opened for analysis. Consequently, the solute contents retrieved by ICP-MS pertain to the aqueous part of the bulk COH fluid only (Supplementary Table 3; other details in Methods section). In Fig. 2, we report the solubility data of quartz (SiO₂–COH system) and forsterite + enstatite (MgO–SiO₂–COH system) at 1 GPa and 800 °C, where SiO₂ molalities have been obtained by correcting the concentration of the internal standard (Cs) on the basis of the measured fluid XCO₂ (Supplementary Fig. 3; Supplementary Table 3). The measured dissolved Si in COH fluids in equilibrium with quartz and graphite at 1 GPa, 800 °C and fH₂NNO conditions (XCO₂ = 0.83; Supplementary Table 1; Supplementary Fig. 1d) is 0.30 ± 0.04 mol kgH₂O⁻¹, which is much lower than the quartz solubility in pure water (1.23 mol kgH₂O⁻¹ ref. 18), but much higher than previously reported quartz solubilities in H₂O–CO₂ fluids characterized by similar XCO₂ but without graphite (0.04 mol kgH₂O⁻¹ ref. 19, for XCO₂ = 0.75; 0.01 mol kgH₂O⁻¹ for XCO₂ = 0.94 ref. 20). The dissolved silica in COH fluids in equilibrium with forsterite, enstatite and graphite (XCO₂ = 0.84; Supplementary Table 1; Supplementary Fig. 1e) is much higher compared to the SiO₂–COH system (1.24 ± 0.19 mol kgH₂O⁻¹), resembling the solubility of quartz in pure water. The solubility of forsterite and enstatite has not previously been measured in mixed H₂O–CO₂ fluids, but it has been investigated in pure water21–24, amounting to 0.21–0.30 mol SiO₂ kgH₂O⁻¹ refs. 24. We additionally performed a dissolution experiment of forsterite and enstatite in pure water (MgO–SiO₂–H₂O system; black dot in Fig. 2), obtaining very similar results (0.22 ± 0.06 mol SiO₂ kgH₂O⁻¹), clearly testifying that the solubility of forsterite and enstatite in pure water is much lower than in COH-bearing fluids.

Constraints on the increased solubility of silicates. Our solubility results indicate that in both the graphite-saturated SiO₂–COH and MgO–SiO₂–COH systems, the carbon dissolved in fluids does not behave merely as an inert diluent, but promotes
the models we developed was able to account for the large increase in the CO₂ solubility in the fluid that was experimentally determined in SiO₂–COH or MgO–SiO₂–COH systems. Several possible explanations for this novel effect can be suggested. For instance, very large amounts of HCO₃⁻ or CO₃²⁻ species that would occur in the SiO₂-bearing fluids could be converted to CO₂ through reactions of the type:

\[
\text{CO}_3^{2-} + 2\text{H}^+ \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O}.
\] (1)

However, theoretical model results indicate that at 1 GPa and 800 °C insignificant amounts of HCO₃⁻ or CO₃²⁻ are present in the fluids. Actually, the association forsterite + enstatite at 0.5 GPa and 600 °C buffers the pH of the coexisting aqueous fluid to between 2.5 and 4 ref. 14. Our model predicts that at 1 GPa and 800 °C the pH of the fluid is 5.57 in the MgO–SiO₂–H₂O system and 3.73 in the MgO–SiO₂–COH system (Supplementary Table 4). These pH values would favor the stability of the species CO₂aq against HCO₃⁻ and CO₃²⁻. Moreover, reaction (Eq. 1) is independent on the presence of silica, thus it cannot explain the influence exerted by silicate dissolution in enhancing the XCO₂ of the fluid.

Alternatively, a change in fCO₂ at fixed fH₂ imposed by the buffers could result from a change in H₂O or fO₂ associated with dissolved silica. In our double-capsule experiments, silicate dissolution reactions in both the MgO–SiO₂–COH and SiO₂–COH systems proceed together with the dissolution of graphite. In the pure COH system, the dissolution of graphite at the investigated relatively oxidizing conditions is controlled by the reaction C + 2H₂ + 2O₂ ⇌ CO₂ + 2H₂O (see Eq. 12 in Methods section; Supplementary Fig. 4) until the fugacity of H₂ in the inner capsule, containing a COH fluid, equals that in the outer capsule, containing C-free water in equilibrium with the NNO or the FMQ buffers. The equilibrium constant of the reaction above is:

\[
K = \frac{f\text{CO}_2 \times (f\text{H}_2\text{O})^2}{(f\text{H}_2)^2 \times (f\text{O}_2)^3}.
\] (2)

Our experimental data (runs COH70 and COH69 in Supplementary Table 1) and the thermodynamic model of Zhang and Duan (ZD09mod in Supplementary Table 2; details in Methods section) allow retrieving K in the pure COH system at 1 GPa and 800 °C resulting both in the NNO- and the FMQ-buffered experiments a value of log K = 37.5, assuming log fH₂NNO = 1.775 and log fH₂FMQ = 1.889, and log fO₂ = −14.28 (inner capsule buffered by NNO) and log fO₂ = −14.31 (inner capsule buffered by FMQ), respectively.

The observed increase in fluid XCO₂ in SiO₂–COH and MgO–SiO₂–COH systems will result in an increase of fCO₂. Therefore, it is convenient to express Eq. 2 as a function of fCO₂:

\[
f\text{CO}_2 = \frac{K \times (f\text{H}_2)^3 \times (f\text{O}_2)^2}{(f\text{H}_2\text{O})^2},
\] (3)

and

\[
\log f\text{CO}_2 = \log K + 2\log f\text{H}_2 + 2\log f\text{O}_2 - 2\log f\text{H}_2\text{O}.
\] (4)

By fixing log fH₂ and log K, fCO₂ is expressed as a function of the two variables fO₂ and fH₂O, which can be represented as two tri-dimensional surfaces, one calculated for log fH₂NNO (Fig. 3a) and one calculated for log fH₂FMQ (Fig. 3b). In order to move from the fCO₂ of the pure COH system (green dots in Fig. 3) to
Table 5). However, in view of the absence of redox sensitive components in the minerals under investigation, even small variations of $fO_2$ are highly unlikely in our experimental system and therefore we suggest that a decrease in $fH_2O$ is the culprit of the observed increase in $fCO_2$ in the MgO–SiO₂–CO₂ systems. By using the H₂O fugacity coefficient from Zhang and Duan [1] and assuming the decrease in water activity ($aH₂O$) being equal to $-2.59 \log$ units in MgO–SiO₂–CO₂ systems, we argue that dissolved silica monomers [Si(OH)₄] and dimers [Si₂O(OH)₆] are much more effective than MgO–SiO₂–CO₂ complexes in decreasing water activity. The activity of total silica can be calculated on the basis of the measured SiO₂ molality in the experiments buffered with NNO and the measured CO₂ of the corresponding COH fluid [20] or $fH₂O$ being equal to $-2.59 \log$ units in MgO–SiO₂–CO₂ and $-2.90 \log$ units in the SiO₂–CO₂ systems. The activity of dissolved silica in the SiO₂–CO₂ and MgO–SiO₂–CO₂ systems is therefore much higher (about 20 times in SiO₂–CO₂ system; 40 times in MgO–SiO₂–CO₂ system) compared to the difference in $fH₂O$ estimated in the SiO₂–CO₂ and MgO–SiO₂–CO₂ systems versus the pure CO₂ system.

In order to match the observed increase in $fCO₂$, we estimated that only 0.31 mol% (SiO₂–CO₂ system; i.e., 0.006 mSiO₂/kgH₂O) and 1.89 mol% (MgO–SiO₂–CO₂ system; i.e., 0.004 mSiO₂/kgH₂O) of the measured dissolved silica are required, assuming that the decrease in water activity is solely related to the formation of hydrated silica monomers [Si(OH)₄] and dimers [Si₂O(OH)₆]. These low solubility data (cf. also Supplementary Table 4) are almost identical to quartz solubility in graphite-free systems bearing very high-XCO₂ H₂O–CO₂ fluid [20], strongly supporting the hypothesis that additional new SiO₂–CO₂ and MgO–SiO₂–CO₂ complexes are required to account for the surprisingly high total dissolved silica measured in our experiments.

**Dissolution of graphite and silicates in subduction mélanges.**

Our results suggest that the silica component derived from the dissolution of either magnesium silicates or quartz/coesite alone, even in absence of carbonates, controls the composition of deep CO₂ fluids in equilibrium with graphite, in particular enhancing their CO₂ content when compared to SiO₂-free systems. This mechanism could be effective especially in cold subduction zones, where suboxidic conditions prevail, and particularly in subduction mélanges, where silicate minerals and graphite [10] are thought to be abundant and flushed by aqueous fluids originating from the dehydration of the subducted lithosphere [32, 33]. Independently from the occurrence of carbonates, the dissolution of silicates can boost the dissolution of graphite in the subduction mélangé in the form of volatile CO₂ dissolved in CO₂ fluids by up to $+30\%$ compared to silicate-free systems. These CO₂-rich fluids will interact with the overlying mantle rocks, influencing metasomatic processes, carbonation/decarbonation reactions, and the melting temperatures of rocks in the mantle wedge [3]. From this perspective, the fact that fluid inclusions in shallow-mantle xenoliths are often dominated by CO₂ over water [34] could be an effect of the inherited CO₂-rich composition of slab-derived fluids, and does not necessarily require extensive diffusional hydrogen loss from the inclusion to the host mineral. Moreover, as this CO₂ boosting effect cannot be predicted by available thermodynamic models that have been used to estimate the amount of CO₂ recycled from subducted carbon-bearing

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**Fig. 3** Model for increased dissolved CO₂ in graphite-saturated fluids interacting with silicates. 3D plot of the equations $\log fCO₂ = \log K + 2 \log fH₂^NNO - 2 \log fH₂O a$ and $\log fCO₂ = \log K + 2 \log fH₂^{FMQ} + 2 \log fO₂ - 2 \log fH₂O b$, assuming $\log K = 37.5$, retrieved from the experimental data and thermodynamic modeling at 1 GPa and 800 °C, using the EoS of Zhang and Duan [10] and the H₂ fugacity coefficient of Connolly and Cesare [5]. The increase in XCO₂ observed experimentally in the systems SiO₂–CO₂ (pink dots) and MgO–SiO₂–CO₂ (ochre dots), compared to the pure CO₂ system (green dots), can be achieved either by decreasing $fH₂O$ (arrays A; preferred interpretation) or by increasing $fO₂$ (arrays B; unlikely because of the lack of Fe and other redox sensitive elements in the considered silicates). The decrease in $fH₂O$ is ascribed to dissolved Si-complexes and almost independent on dissolved Mg-complexes, and therefore attributable to formation of hydrated silica monomers [Si(OH)₄] and dimers [Si₂O(OH)₆].
such fluids, even in the absence of carbonates, as long as graphite is present. Fluids interacting with graphite alone, fluids interacting with graphite and silicates or fluids in equilibrium with graphite in terms of sedimentary organic carbon and graphite (equations that do not consider the complexity related to dissolution processes).

Another fundamental property of H2O-bearing fluids at high-pressure conditions is the capacity to transport dissolved species. The amount of solutes from rock-forming minerals in aqueous fluids increase with increasing pressure until the fluid becomes no longer distinguishable from a silicate melt and a supercritical liquid is formed. The solubility of forsterite and enstatite has been measured in pure water up to 1.5 GPa and at T = 800 °C. Experimental data on mineral dissolution in mixed H2O-CO2 fluid are available only for quartz (9, 53), albite (54), and diopside (28) and suggests that solubility decreases with increasing content of CO2 in the fluid.

The aim of the paper is to provide for the first time experimental constraints on the composition of high-pressure COH fluids in equilibrium with graphite in terms of both volatile content and dissolved solutes in increasingly complex petrological systems at controlled FO2 conditions. Fluids have been investigated in equilibrium with graphite only in the system COH, with graphite + quartz/coesite in the system SiO2-COH, and with graphite + forsterite + enstatite in the system MgO–SiO2–CO2. Two different experimental setups and analytical techniques were employed to determine the volatile composition and the solubility of minerals in COH fluids at pressures up to 3.0 GPa, and T = 800 °C. These conditions were selected for sake of simplicity to avoid the presence of carbonates (magnesite) in the system MgO–SiO2–CO2 and the consequent complexities related to carbonate dissolution. In particular, the link between H2O/CO2 ratio (derived analytically by means of a quadrupole mass spectrometer (QMS) and silicate dissolution (investigated by cryogenic laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is highlighted here and compared with thermodynamic calculations.

**Methods**

**Investigating the fluid composition in COH-bearing systems.** Several experimental studies investigated separately the effect of the volatiles H2O and CO2 on subsolidus and melting relations in peridotitic systems at upper-mantle conditions. Only few studies considered the effect of the simultaneous occurrence of H2O and CO2 or more generally, the influence of CO2 on the peridotitic systems. The H2O/CO2 ratio in COH fluids is crucial because it affects the location of carbonation/decarbonation reactions and the position of the solidus. However, the H2O/CO2 ratio of the fluid in equilibrium with mantle minerals has mainly been estimated through thermodynamic modeling, using equations of state of simple non-polar gas systems (e.g., H2O–CO2–CH4), equations that do not consider the complexity related to dissolution processes.

The addition of a proper amount of Cs-doped water in the capsule allowed to obtain a starting fluid composition with XH2O = 0.5 for the LA-ICP-MS experiments too. Graphite (ceramic-grade powder, checked for purity and crystallinity by X-ray powder diffraction and scanning electron microscopy) was added in all experiments to ensure carbon saturation of the COH fluid (LA-ICP-MS experiments).

**Bulk compositions and starting materials.** COH fluids were generated starting either from oxalic acid dihydrate (OAD; H2C2O4·2H2O) or an equivalent mixture of 1:1 oxalic acid anhydrous (OAA; H2C2O4) + water (Supplementary Fig. 1). OAD was employed in the experimental runs aimed at investigating the COH volatile composition by means of the capsule-piercing QMS technique (QMS experiments; Supplementary Fig. 1a–c). The dissociation of oxalic acid at high temperature is given by the reaction:

$$\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + \text{H}_2$$ (5)

Generating a starting fluid characterized by XH2O = (H2O/CO2 + H2O) = 0.5 and an excess of H2.

Instead of OAD, OAA + Cs-doped (590 µg g−1) water was employed as fluid source in experiments on mineral solubility in COH fluids (LA-ICP-MS experiments; Supplementary Fig. 1d, e), to ensure the presence of a natural standard (Cs) for LA-ICP-MS data quantification. The thermal dissociation of OAA at high-temperature conditions generates a CO2–H2 fluid according to the reaction:

$$\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{H}_2\text{O} + \text{CO}_2 + \text{H}_2$$ (6)

The addition of a proper amount of Cs-doped water in the capsule allowed to obtain a starting fluid composition with XH2O = 0.5 for the LA-ICP-MS experiments.
Experimental conditions and apparatus. Capsules were welded shut in a frozen steel holder to avoid overheating. Capsules were reweighed to ensure no fluid loss during welding occurred. Sintered MgO rods were employed to embed the capsule surrounded by a graphite heater, Pyrex glass and NaCl. A rocking piston-cylinder apparatus was used to reach high-pressure and high-temperature conditions. The rocking piston-cylinder is a regular end-loaded piston-cylinder, which allows forward and backward rotation of 180° during the experimental run, thus inverting its position in the gravity field. Chemical inhomogeneity within the capsule is in fact common in fluid saturated experiments. The rocking piston-cylinder overcomes this problem as the rotation of the sample induces Rayleigh–Taylor instabilities, forcing the fluid to migrate and causing chemical re-homogenization. Pressure calibration of the rocking apparatus is based on the quartz to coesite transitions at P = 3.07 GPa and T = 1000 °C, and P = 2.93 T at T = 800 °C (accuracy ± 0.01 GPa and ± 5 °C). Temperature was measured with a K-type thermocouple located within 0.6 mm from the top of the capsule and is considered accurate to ± 5 °C.

Buffering strategy and thermodynamic modeling. Because the volatile composition of graphite-saturated COH fluids is dependent on the redox state of the system, all PerpleX scripts (http://www.perplex.ethz.ch) using the thermodynamic data set of Holland and Powell revised by the authors in 2004 and the PerpleX-EO n. 16 (H-O HSMRK/ MRK hybrid EoS) (Supplementary Table 2). Subsequently, we calculated the speciation of the graphite-buffered COH fluid in the inner capsule for H2 fixed by both NNO and FMQ by thermodynamic modeling using (i) the software package PerpleX, version X.0 (based on Gibbs free energy minimization) and the EoS of Connolly and Cesare to the hypothetical 1.0 bar ideal gas state. The activity of H2O was approximated in the MgO–SiO2–CO2 system by its mole fraction.

Additional new equilibria for the species Mg(OH)2(aq) and Mg[OSi(OH)4]2– in Supplementary Table 4 were fitted to the experimental solubilities in the systems MgO–SiO2–H2O and MgO–SiO2–CO2, respectively at 800 °C and 1.0 GPa. The calculated solubilities of the most abundant Mg- and Si-bearing species are given in Supplementary Table 4. It can be seen from the model results that both the Mg(OH)2(aq) and Mg[OSi(OH)4]2– species are predicted to contribute significantly to the total solubilities of both Mg and Si in the MgO–SiO2–CO2 system. However, because of the low activity of water in the system the amounts of Mg(OH)2(aq), Si(OH)4(aq), and (OH)2SiOSi(OH)2(aq) are much lower than in the carbon-free system. Under more oxidizing conditions, the Mg[OSi(OH)4]2–(CH3CH2COO)2– species would become unimportant, and the solubilities of Mg and Si in the MgO–SiO2–CO2 system could become extremely low.

Analysis of volatiles. Here, we provide a brief summary of the technique used to measure the volatile composition of the COH fluids in the inner capsule. The full description and the validation of the technique is provided in Tiraboloschi et al. Quenched COH fluids are extracted from the inner capsule and conveyed to a quadrupole mass spectrometer (QMS). The capsule-piercing device consists of an extraction vessel (reactor) that is heated by an electric furnace to T = 80 °C to transform liquid water into water vapor. The reactor, made of Teflon, is composed of a basal part, where the capsule is placed, and a top part, where a steel pointer is mounted. The piercing is executed by screwing the basal part on to the top part until the pointer penetrates the capsule. The capsule, partially embedded in epoxy, is mounted on a steel support, designed to oppose the rotation exerted by the steel pointer during the piercing operation. The furnace design includes a pilot hole in the base part that permits screwing the reactor with a hex key while placed in the furnace. Openings on the top of the reactor allow the carrier gas (ultrapure Ar) to flow inside it and to generate vent or vacuum conditions. The presence of O-rings ensures a tight seal. The reactor is connected to a QMS by a heated line (80 °C) to avoid condensation of water on the metal tubes. The pressure conditions in the line and in the reactor are monitored through high-resolution sensor gauges (± 1 mbar precision). The temperatures of the line, reactor and furnace are monitored with K-type thermocouples. Line and reactor pressures and temperatures are recorded by a Eurotherm Nanodac data recorder with PID control. The internal volume of the extraction vessel (reactor) that is heated by an electric furnace to 80 °C is monitored through high-resolution sensor gauges.

In conclusion, the equilibration of the COH fluid at run conditions implies that CO2 is produced in the inner capsule by oxidation of graphite. As a consequence, the CO2/H2 of the COH fluid in the inner capsule increases until equilibrium in H2 is reached between the inner and outer capsules (Supplementary Fig. 4).

We successfully verified the fluid composition predicted by thermodynamic modeling, by retrieving analytically the XCO2 ratio by means of QMS technique, summarized in the next section. At both P = 1 GPa, T = 800 °C and P = 3 GPa, T = 800 °C measured and calculated ratios are concordant within errors with ZD09mod for both H2O and FMQ-buffered experiments performed in the COH system (Supplementary Tables 1 and 2; Supplementary Fig. 2). Therefore, we conclude that this model can reproduce experimental data in the pure COH system. The SiO2–CO2–MgO–SiO2–CO2 systems, literature data and the new experimental data discussed in this paper demonstrate that dissolved Mg- bearing and Si-bearing species result from dissolution reactions taking place between solid phases and COH fluids occur in addition (Fig. 2; Supplementary Table 3). By retrieving the XCO2 in these systems analytically using the capsule-piercing QMS technique, we have demonstrated that the thermodynamic calculations outlined above, which do not take into account these dissolved species, cannot be applied to predict the fluid composition in complex systems, in particular those bearing silicates.

The aqueous speciation and solubility calculations in the investigated silicate-bearing systems were carried out using mass balance, charge balance, and mass action expressions in the code EQ3. The equilibrium constants involving aqueous ion pairs, and minerals were obtained using the DEW model. Additional new equilibria for the species Mg(OH)2(aq) and Mg[OSi(OH)4]2– (Supplementary Table 4) were fitted to the experimental solubilities in the systems MgO–SiO2–H2O and MgO–SiO2–CO2, respectively at 800 °C and 1.0 GPa. The calculated solubilities of the most abundant Mg- and Si-bearing species are given in Supplementary Table 4. It can be seen from the model results that both the Mg(OH)2(aq) and Mg[OSi(OH)4]2–(CH3CH2COO)2– species are predicted to contribute significantly to the total solubilities of both Mg and Si in the MgO–SiO2–CO2 system. However, because of the low activity of water in the system the amounts of Mg(OH)2(aq), Si(OH)4(aq), and (OH)2SiOSi(OH)2(aq) are much lower than in the carbon-free system. Under more oxidizing conditions, the Mg[OSi(OH)4]2–(CH3CH2COO)2– species would become unimportant, and the solubilities of Mg and Si in the MgO–SiO2–CO2 system could become extremely low.
performing quantitative analyses of H$_2$O, CO$_2$, CH$_4$, CO, H$_2$, and O$_2$. Uncertainties for major species were typically ~1% for H$_2$O and CO$_2$, and ~10% for CO. After piercing has occurred, gases are conveyed to the QMS by opening a valve. For every m/z channel, the QMS counts are measured every 5 s for 310 steps, for a total of 1550 s of measurement time. The moles of gases were obtained by comparing the areas of the m/z peaks to those of the standards, using a least-squares regression method. Monte Carlo simulations provided the propagation of uncertainties for each species, which corresponds to measurement uncertainty of the sample and can be represented as a probability distribution plot in ternary COH diagrams.

**Analysis of solutes.** The solute content in the fluid was measured employing the cryogenic LA-ICP-MS technique also known as the "freezing technique" [28], which is applied for the first time on double capsules bearing COH fluids. The recovered experimental capsule is mounted on a freezing stage, which consists of a stack of two Peltier elements, surrounded by plastic to thermally insulate the elements from the atmosphere [29]. The sample holder is placed on a copper block, in direct contact with the Peltier elements and cooled to T ~ 35 °C. The conventional freezing technique has been updated using a cutter blade mounted on a steel support. This device allows cutting longitudinally double capsules by fastening a screw that pushes the cutter blade via a steel block through the capsule. During this operation, the capsule is enclosed in a copper holder. Once the capsule is cut open, the cutting device is removed from the freezing stage together with the upper part of the capsule holder including the top part of the capsule. The upper half of the capsule is invested using a binocular microscope, while the lower part remains frozen on the stage during the entire laser-ablation analytical session that follows immediately.

Analyses were performed using a 193 nm ArF GeoLas Pro excimer laser system coupled to an ELAN DRCD-e quadrupole mass spectrometer at University of Bern. We analyzed the diamond trap for $^{25}$Mg, $^{25}$Mg, $^{28}$Mg, $^{35}$Si, $^{62}$Ni, $^{133}$Cs, $^{197}$Pd, and $^{197}$Au, using a 60 μm beam diameter, ~13 J/cm laser fluency, and 5 Hz repetition rate. Data were acquired in blocks of up to ~10 individual sample analyses bracketed by three analyses of the standard NIST SRM610, placed in the ablation chamber with the sample. Background was taken for ~50 s and the sample signal, on the diamond trap or on the solid residue, was collected for ~20 s. LA-ICP-MS data reduction employed the SILLIS software [30] and in-house spreadsheets to calculate solute concentrations, employing rigorous limit of detection filtering [31] for each element and each measurement individually.

The cryogenic nature of the aqueous fluids, Cesium, introduced in the starting materials, is employed as an internal standard for data quantification, because it is a highly incompatible element that fractionates completely into the aqueous fluid phase at the given residual mineralogical. In our experiments, we introduced a known amount of water solution doped with 590 μg g$^{-1}$ Cs [as Cs(OH)$_2$]. As the initial Cs/H$_2$O ratio is fixed, once the Cs concentration in the fluid phase coexisting with minerals at run P and T is known, solute concentrations of the fluid can be calculated [32]. However, compared to experiments bearing aqueous fluids, our double-capsule, COH-bearing experiments are more complex, because the initial Cs/H$_2$O is not fixed, as the water content in the inner capsule is variable, depending on P, T and H$_2$-fO$_2$ conditions (Eqs. 11 and 12). In fact, in double-capsule arrangements H$_2$ is a mobile component that can be added or removed from the system through diffusion in and out of the inner capsule. This implies that the initial Cs concentration cannot be used as an internal standard. This value needs to be corrected taking into account the change in total water mass present in the inner capsule relative to initial amount of loaded water, as a consequence of fluid XCO$_2$ re-equilibration at the H$_2$-fO$_2$ conditions imposed by the buffers. If H$_2$O is consumed during fluid re-equilibration at run conditions, Cs concentration in the residual water increases; if H$_2$O is produced, Cs concentration decreases (Supplementary Fig. 3). We estimated the corrected Cs concentration at run P and T using a model, which assumes that fluid equilibration at the hydrogen fugacity conditions imposed by the buffers NNO and FMQ is governed only by H$_2$ mobility and no hydration or assimilation of water. Considering that at fixed pressure and temperature conditions the molar volume of water is constant, we obtain the following dilution equation:

$$C_{\text{Cs}} \times V_{\text{H}_2\text{O}} = C_{\text{Cs}} \times V_{\text{H}_2\text{O}}$$  

where $C_{\text{Cs}}$ is the initial concentration of Cs in the aqueous solution loaded into the capsule (590 μg g$^{-1}$) and $C_{\text{Cs}}$ is the final concentration of Cs after fluid equilibration at H$_2$ conditions. $V_{\text{H}_2\text{O}}$ and $V_{\text{H}_2\text{O}}$ are the initial and final volumes of water.

The volume of water is proportional to the moles according to:

$$V_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}} \times V_{\text{H}_2\text{O}}$$  

where $V$ is the volume of water; $n$ is the number of moles of water; $V$ is the molar volume of water. Considering that at fixed pressure and temperature conditions the molar volume of water is constant, we obtain the following dilution equation:

$$C_{\text{Cs}} \times n_{\text{H}_2\text{O}} = C_{\text{Cs}} \times n_{\text{H}_2\text{O}}$$  

The final Cs concentration in the aqueous fluid fraction will be given by:

$$C_{\text{Cs}} = \frac{C_{\text{Cs}} \times n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}}}$$  

where $n_{\text{H}_2\text{O}}$ is known (the initial amount of water charged into the capsule), this equation can be solved as long as $n_{\text{H}_2\text{O}}$ is constrained, through equation:

$$n_{\text{H}_2\text{O}} = n_{\text{H}_2\text{O}} \times \frac{X_{\text{H}_2\text{O}}}{X_{\text{H}_2\text{O}}}$$  

where X$_{\text{H}_2\text{O}}$ is the final H$_2$O/(CO$_2$ + H$_2$O) ratio measured by QMS analysis, and X$_{\text{H}_2\text{O}}$ is the initial H$_2$O/(CO$_2$ + H$_2$O) ratio retrieved on the basis of the amounts of water and OAA charged into the capsule. Solute concentrations in the aqueous fraction of the COH fluid at run P and T can thus be calculated (Fig. 2; Supplementary Table 3).

**Data availability.** The authors declare that the data supporting the findings of this study are available within the article.

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Additional information

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