Immiscible C-H-O fluids formed at subduction zone conditions

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Abstract

Earth's long-term carbon cycle, which is regulated by subduction and volcanism, is critical for understanding Earth's structure, dynamics, and climate change. However, the mechanisms for carbon mobility in subduction zones remain largely unresolved. Aqueous fluids produced by slab devolatilisation may dissolve a considerable amount of carbon, but it is usually assumed that aqueous C-H-O fluids in subduction zones are fully miscible. In order to constrain the nature of aqueous C-H-O fluids in subduction zones, experiments were performed at 0.2 to 2.5 GPa and 600 to 700 °C to study the phase relations of C-H-O fluids in the presence of 3 wt. % NaCl, using the synthetic fluid inclusion technique. The results show that at 0.2 GPa and 700 °C, one single C-H-O fluid phase was present; however, at 1.5 to 2.5 GPa and 600 to 700 °C, H_2O and gases of CH_4+H_2, CH_4+CO_2, or CO_2 coexisted as immiscible fluid phases. These results demonstrate that pressure can significantly expand the miscibility gap of C-H-O fluids and immiscible C-H-O fluids may occur in subduction zones. The likely occurrence of immiscible C-H-O fluids in subduction zones may cause extensive decarbonation and the formation of immiscible CO_2-rich fluids, providing an important mechanism for the transfer of slab carbon to the mantle wedge.

Introduction

Thermodynamic simulations and experimental studies demonstrate that carbonate minerals are stable along most subduction *P-T* paths and up to 90 % of the carbon in subduction zones should be subducted into the deep mantle (Kerrick and Connolly, 2001; Dasgupta and Hirschmann, 2010). However, there is compelling evidence suggesting that about 20−80 % of carbon is removed from the downgoing slab and returned to Earth's surface by arc volcanism (Dasgupta and Hirschmann, 2010; Johnston *et al.,* 2011; Kelemen and Manning, 2015). Several models have been proposed to account for the mechanisms of transferring

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slab carbon to the mantle wedge. Among these are metamorphic decarbonation (Poli *et al.,* 2009), carbonate dissolution in the dehydrating fluids as gas molecules and/or ionic carbon species (Caciagli and Manning, 2003; Frezzotti *et al.,* 2011; Sverjensky *et al.,* 2014), infiltrating fluids induced decarbonation (Kerrick and Connolly, 2001; Gorman *et al.,* 2006; Bebout and Penniston-Dorland, 2016), and decarbonation accompanied by silicate precipitation via fluid-carbonate reaction (Ague and Nicolescu, 2014). Nevertheless, the respective contribution of these models in transferring slab carbon to the mantle wedge is unclear. For example, Galvez *et al.* (2013) proposed that the reaction between serpentinite-derived fluids and carbonates may cause the formation of graphite and provide an important mechanism for the deep subduction of carbon; whereas Ague and Nicolescu (2014) showed that fluid-carbonate reaction may cause significant decarbonation and efficient transfer of slab carbon to the mantle wedge.

Subduction zones are undoubtedly the locations where the Earth's mantle is most enriched in C-H-O fluids. However, despite significant progress in experiments and thermodynamic modelling on C-H-O fluids (*e.g.,* Churakov and Gottschalk, 2003; Heinrich, 2007; Zhang and Duan, 2009; Manning *et al.,* 2013), our understanding of the nature of mantle C-H-O fluids is heavily hampered by the lack of experiments at relevant conditions. Previous studies assumed that H_2O and gases of CH_4, CO_2, or H_2 are fully miscible at conditions of most of the crust and the entire mantle (*e.g.,* Heinrich, 2007; Manning *et al.,* 2013). The addition of salt, such as NaCl or $CaCl_2$, may yield an extensive region of immiscibility in the H_2O-CH_4/CO_2-salt system at crustal conditions (Bowers and Helgeson, 1983; Heinrich, 2007; Manning *et al.,* 2013). However, at deep crustal conditions the salt concentration may need to be more than 20 wt. % to yield fluid immiscibility if CO_2 or CH_4 mole fraction in the system is less than 0.5 (Johnson, 1991; Shmulovich *et al.,* 2004). Two previous studies showed that pressure can also expand the miscibility gap of the H_2O-H_2 and H_2O-CH_4 systems (Churakov and Gottschalk, 2003; Bali *et al.,* 2013), but presently no experiments have been performed on the C-H-O-salt system at mantle conditions. Here I show experimentally that in the presence of 3 wt. % NaCl, H_2O and gases of CH_4+H_2, CH_4+CO_2, or CO_2 can coexist as two separate, immiscible fluids at subduction zone conditions, and I suggest that this immiscibility may play an important role in the deep carbon cycle.

Results

High-pressure experiments were designed to entrap C-H-O fluids as fluid inclusions in quartz crystals at 0.2 to 2.5 GPa, 600 to 700 °C, and oxygen fugacity (fO_2 hereafter) buffered by the Fe-FeO, Co-CoO, FMQ, Ni-NiO, or Re-ReO_2 buffer (see Supplementary Information). The starting C-H-O solution was prepared by mixing 78.5 wt. % distilled water, 3 wt. % NaCl, and 18.5 wt. % formic acid (HCO_2H), but the C-H-O fluid speciation present during the run primarily depends on the fO_2 imposed. The results show that at 0.2 GPa, 700 °C, and fO_2

buffered by FMQ and Ni-NiO (Table 1), only one type of fluid inclusion exists in the quartz crystal (Fig. 1a), and CO_2 is the only detectable carbon species (Fig. 2a). At 1.5 to 2.5 GPa and 600 to 700 °C (Table 1), three types of fluid inclusions were found in each run. Type-1 are light-coloured fluid inclusions with weak optical contrast to the surrounding quartz (Fig. 1b,c,d). In Type-1 fluid inclusions, if a vapour bubble occurs in the fluid inclusions, the vapour/liquid ratio is nearly constant (Fig. 1b). Type-2 are dark-coloured fluid inclusions with strong optical contrast to the surrounding quartz (Fig. 1b,c,d,e). Raman measurements show that Type-1 fluid inclusions are H_2O-rich with small but detectable amounts of gases of $CH_4+C_2H_6$, CH_4+CO_2, or CO_2 (Fig. 2a). The gas species vary from $CH_4+C_2H_6$ to CO_2 at $f O_2$ varying from the Fe-FeO to the Re-ReO_2 buffer. The corresponding Type-2 fluid inclusions are pure gases of $H_2+CH_4+C_2H_6$, CH_4+CO_2, or CO_2 without detectable water at room temperatures (Fig. 2b), although a thin film of water may exist on the inner surface of the fluid inclusions (Berkesi *et al.,* 2009; Frezzotti *et al.,* 2012). The coexistence of Type-1 and Type-2 fluid inclusions demonstrates that two separate, immiscible fluid phases must have occurred during the run. The third type of fluid inclusion contains a vapour bubble but shows different vapour/liquid ratios (Fig. 1c). Type-3 fluid inclusions are interpreted to be the entrapment of mixed Type-1 and

Table 1 Summary of experimental conditions and results.

Run No	P GPa	T °C	Duration days	Oxygen buffer	Immiscible fluids	Graphite saturation	ᵃFluid composition	
LY13	0.2	700	3	FMQ	No	No	H_2O-CO_2	
LY14	0.2	700	3	Ni-NiO	No	No	H_2O-CO_2	
							Type-1	**Type-2**
LY01	1.5	600	3	Fe-FeO	Yes	No	H_2O-CH_4-C_2H_6	CH_4-H_2-C_2H_6
LY02	2.5	600	3	Fe-FeO	Yes	No	H_2O-CH_4-C_2H_6	CH_4-H_2-C_2H_6
LY05	2.5	600	2	Ni-NiO	Yes	Yes	H_2O-CH_4-CO_2	CH_4-CO_2
LY08	2.5	600	6	Ni-NiO	Yes	Yes	H_2O-CH_4-CO_2	CH_4-CO_2
LY04	2.5	700	2	Ni-NiO	Yes	Yes	H_2O-CH_4-CO_2	CH_4-CO_2
LY21	2.5	700	2,5	Co-CoO	Yes	Yes	H_2O-CH_4-CO_2	CH_4-CO_2
LY19	2.5	700	2	Re-ReO_2	Yes	Yes	H_2O-CO_2	CO_2

ᵃ The fluid composition was determined by Raman spectroscopy. In each run, 3 wt. % NaCl was added to the starting solution.
Note that the oxygen fugacity in run LY19 may be close to the C-CO_2 buffer. See text for more details.
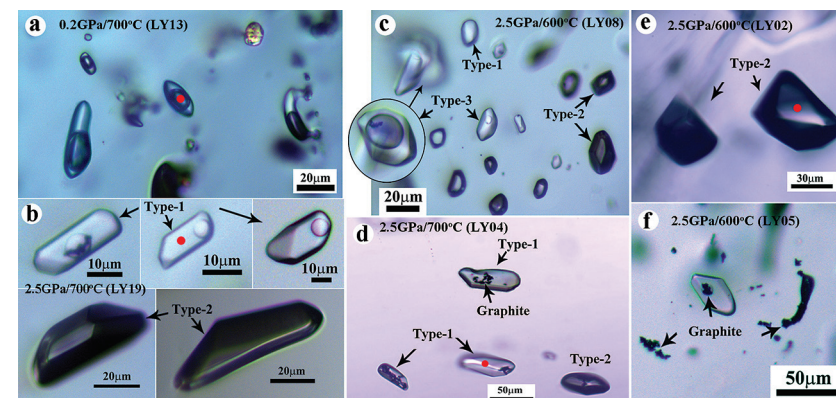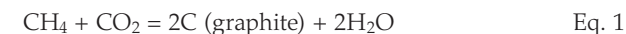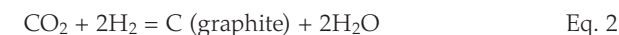
Figure 1 Representative synthetic fluid inclusions in quartz formed at 0.2 to 2.5 GPa, 600 to 700 °C, and $f O_2$ buffered by the Fe-FeO to the Re-ReO_2 buffer. **(a)** At 0.2 GPa, only one type of fluid inclusion was observed and these fluid inclusions show a constant vapour/liquid ratio. At 1.5 and 2.5 GPa, three different types of fluid inclusions were observed: **(b, c, d)** Type-1 fluid inclusions are water-rich and show weak optical contrast to quartz; **(b, c, d, e)** Type-2 fluid inclusions are nearly pure gases and show strong optical contrast to quartz; and **(c)** Type-3 fluid inclusions are mixtures of Type-1 and Type-2 fluids and show variable vapour/liquid ratios. **(d, f)** Graphite occurs in fluid inclusions and also as solid inclusions in quartz. The coexistence of Type-1 and Type-2, together with Type-3, fluid inclusions at 1.5 and 2.5 GPa demonstrates that immiscible fluid phases must have occurred during the run. The red spots refer to the laser spots of Raman measurements, and representative Raman spectra are shown in Figure 2.

Type-2 fluids. In addition, graphite always occurs in fluid inclusions and also as solid inclusions in quartz crystals from the runs buffered by Co-CoO, Ni-NiO, and Re-ReO_2 (Figs. 1b,d,f; 2a). The occurrence of graphite inclusions in quartz crystals indicates that this graphite must be produced during the run probably by the reaction

$$CH_4 + CO_2 = 2C \text{ (graphite)} + 2H_2O \qquad \text{Eq. 1}$$

or

$$CO_2 + 2H_2 = C \text{ (graphite)} + 2H_2O \qquad \text{Eq. 2}$$

The $f O_2$ prevailing in run LY19 buffered by Re-ReO_2 (Table 1) may be close to the C-CO_2 buffer due to the exhaustion of ReO_2 during the run (see Supplementary Information).
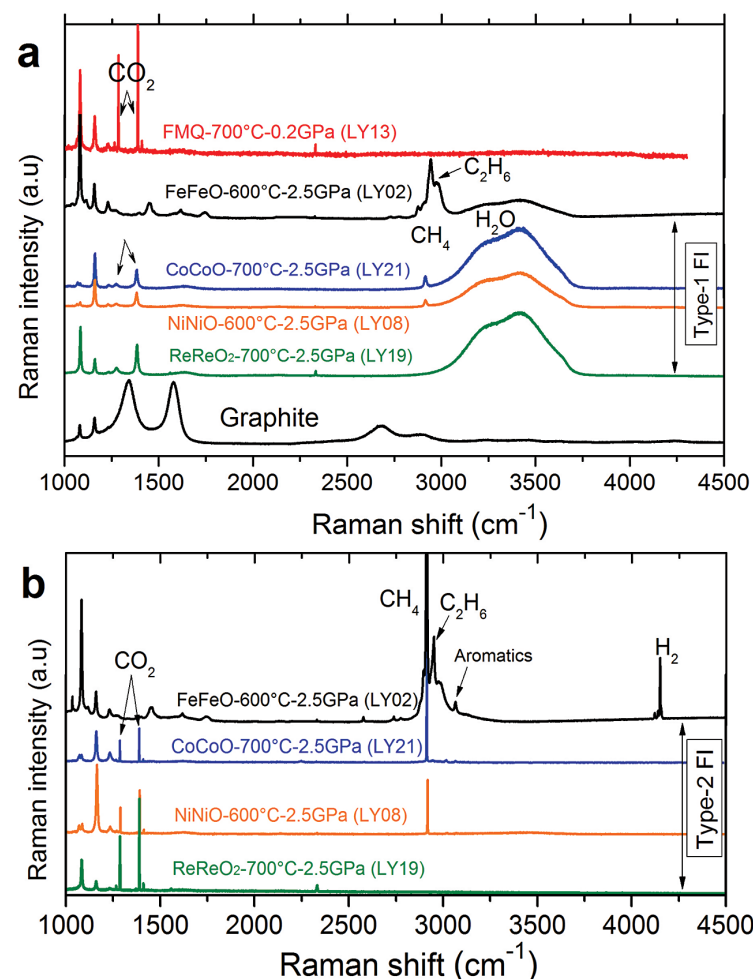
Figure 2 Representative Raman spectra of synthetic fluid inclusions in quartz formed at 0.2 to 2.5 GPa, 600 to 700 °C, and fO_2 buffered by the Fe-FeO to the Re-ReO$_2$ buffer. At 0.2 GPa, 700 °C, and fO_2 at the FMQ buffer, CO_2 was the only detectable carbon species in fluids. At 2.5 GPa, **(a)** Type-1 fluid inclusions are rich in H_2O but with detectable $CH_4+C_2H_6$, CH_4+CO_2, and CO_2; **(b)** the corresponding Type-2 fluid inclusions are nearly pure $CH_4+H_2+C_2H_6$, CH_4+CO_2, and CO_2. Note that the gas species vary as a function of fO_2. Also note that the fO_2 in run LY19 (ReReO$_2$ - 700 °C - 2.5 GPa) buffered by Re-ReO$_2$ may be close to the C-CO$_2$ buffer (see Supplementary Information). The Raman spectra of one graphite inclusion in quartz is also shown in panel (a). The peak positions are about 1285 cm^{-1} and 1388 cm^{-1} for CO_2, 2917 cm^{-1} for CH_4, 4150 cm^{-1} for H_2, 2956 cm^{-1} for C_2H_6, and 3072 cm^{-1} for aromatics. The small peaks at about 2331 cm^{-1} and 1555 cm^{-1} could be N_2 and O_2 from the air, respectively. Aromatics might be produced during quench.

Discussion

The presence of C-H-O fluid immiscibility at 1.5 and 2.5 GPa, and the absence of C-H-O fluid immiscibility at 0.2 GPa demonstrates that pressure significantly expands the C-H-O fluid miscibility gap. This is in good agreement with one recent experimental study (Bali *et al.*, 2013), which shows that the critical temperature of the H_2O-H_2 system increases from below 400 °C at 0.25 GPa to 1050 °C at 2.6 GPa. Theoretical calculations also indicate the expansion of the fluid miscibility gap with pressure; Churakov and Gottschalk (2003) show that pressures higher than 2 GPa would cause immiscibility in the salt-free H_2O-CH_4 system at 450 °C. In addition to pressure, the addition of salt such as NaCl, KCl, MgCl$_2$, and/or CaCl$_2$ can also effectively expand the C-H-O fluid miscibility gap (Bowers and Helgeson, 1983; Johnson, 1991; Shmulovich *et al.*, 2004; Heinrich, 2007). Subduction zone fluids may contain 3 to 50 wt. % NaCl equivalent based on analyses of aqueous fluid inclusions in high-pressure metamorphic rocks from subduction zones (Scambelluri and Philippot, 2001; Frezzotti and Ferrando, 2015), or even more than 50 wt. % based on analyses of fluid inclusions in diamonds (Weiss *et al.*, 2015). In this study, only 3 wt. % NaCl was added to the starting solution, which is at the lower end of subduction zone fluid salinity. Therefore, in conjunction with the combined effects of pressure and salt on expanding the C-H-O fluid miscibility gap, the C-H-O fluid immiscibility observed here suggests that C-H-O fluid immiscibility may also occur in subduction zones. This may particularly hold true when the slab C-H-O fluids are saturated with graphite. This is because the experiments here at 1.5 to 2.5 GPa, 600 to 700 °C, and the Co-CoO to the Re-ReO$_2$ buffer are all saturated with graphite (Table 1), and the bulk composition and species of C-H-O fluids are fixed at graphite saturation at the given *P-T-f*O$_2$ conditions (*e.g.*, Zhang and Duan, 2009). In the subducting slab, graphite could be formed by graphitisation of organic matter or by reduction of carbonates (Galvez *et al.*, 2013; Stagno *et al.*, 2015).

The occurrence of C-H-O fluid immiscibility in subduction zones is supported by the studies of fluids and fluid inclusions in high-pressure metamorphic rocks from subduction zones (Heinrich, 2007; Frezzotti and Ferrando, 2015). For example, Andersen *et al.* (1993) reported coexistence of CO$_2$-N$_2$ fluid inclusions and H$_2$O-rich fluid inclusions with about 30 wt. % NaCl equivalent in eclogites of the Norwegian Caledonides, which represent immiscible fluids at peak metamorphic conditions. Fu *et al.* (2003a,b) found N$_2$-, CO$_2$-, and CH$_4$-rich fluid inclusions coexisting with H$_2$O-rich fluid inclusions with 0-30 wt. % NaCl equivalent in a variety of eclogites from the Dabie-Sulu terranes of China. Based on the fluid activity calculated via mineral equilibrium between millimetre- to centimetre-scale layers in banded mafic elcogites from the Tauern Window of Austria, Selverstone *et al.* (1992) proposed that the combined effects of pressure and salt on expanding the fluid miscibility gap make it likely that blueschist and eclogite facies metamorphism in subduction zones occurs predominantly at H$_2$O-CO$_2$ immiscibility.

It may be worth noting that N_2 is a common component in the C-H-O fluids of high-pressure metamorphism, and the addition of non-polar N_2 usually enlarges the C-H-O fluid immiscibility field (Heinrich, 2007). Recent theoretical calculations also show that depending on the P-T-fO_2 and pH buffered by minerals, carbon could be dissolved in the C-H-O fluids as organic and/or inorganic ionic species (Sverjensky *et al.,* 2014; Galvez *et al.,* 2015). In addition, solutes such as Al_2O_3 and MgO which are commonly dissolved in high-pressure metamorphic fluids are lacking in the present C-H-O fluids. How these ionic carbon species and/or solutes would affect the phase relations of C-H-O fluids at subduction zone conditions remains to be investigated in the future. Nevertheless, combined with the studies on fluids and fluid inclusions in natural high-pressure metamorphic rocks, the experimental work here demonstrates that C-H-O fluid immiscibility may indeed occur in subduction zones.

Implications

The occurrence of immiscible C-H-O fluids may provide new insights into our understanding of decarbonation and carbon mobility in subduction zones. Firstly, C-H-O fluid immiscibility may cause extensive decarbonation in subduction zones. Previous studies show that some low-grade metamorphic reactions may cause extensive decarbonation if these reactions take place at H_2O-CO_2 immiscibility (Yardley and Bottrell, 1988; Heinrich, 2007). Similarly, for a given decarbonation reaction in subduction zones, if it takes places at H_2O-CO_2 immiscibility, significant amounts of carbonates may also be consumed. Taking the decarbonation reaction of carbonate (calcite) dissolution in H_2O-rich fluids (Caciagli and Manning, 2003) as an example

$$CaCO_3 \text{ (calcite)} + H_2O = Ca^{2+} + 2OH^- + CO_2 \qquad \text{Eq. 3}$$
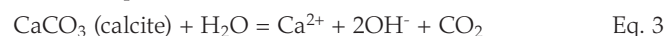
and assuming that this reaction takes place at H_2O-CO_2 immiscibility in subduction zones, extensive slab decarbonation must occur if the H_2O-rich fluids can be segregated from the CO_2-rich fluids and react further with carbonates. Available studies show that at high pressures, the CO_2-rich fluids have higher dihedral angles and density than the H_2O-rich fluids, indicating that the H_2O-rich fluids can be effectively segregated from the CO_2-rich fluids (see Supplementary Information). Furthermore, the ascending H_2O-rich fluids in the subducting slab would experience decompression and heating, and the CO_2 activity in the H_2O-rich fluids usually decreases with increasing temperature or decreasing pressure (Kerrick and Jacobs, 1981; Aranovich and Newton, 1999). Therefore, the segregating H_2O-rich fluids could further react with carbonates during ascent, causing more decarbonation and the formation of immiscible CO_2-rich fluids.

Secondly, immiscible CO_2-rich fluids may be an important agent for the transfer of slab carbon to the mantle wedge. The formation of immiscible CO_2-rich fluids due to slab decarbonation and C-H-O fluid immiscibility indicates that a significant amount of slab carbon may be transferred to the mantle

wedge in the form of CO_2-rich fluids. In subduction zones, the CO_2-rich fluids could be mobilised to the mantle wedge along cracks, veins, shear zones, or fold hinges (see Supplementary Information). As a result, the actual mass of slab carbon transferred to the mantle wedge should be considerably larger than the mass of carbon apparently dissolved in the H_2O-rich fluids. Therefore, C-H-O fluid immiscibility in subduction zones may provide an important but hitherto unappreciated mechanism for the transfer of slab carbon to the mantle wedge.

Additional Information

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Supplementary Information

The Supplementary Information includes:

➤ Methods

➤ Equilibrium and Sample fO_2

➤ Separation of CO_2-rich and H_2O-rich Fluids in Subduction Zones

➤ Figure S-1

➤ Supplementary Information References

Methods

The starting solution includes 78.5 wt. % H_2O, 18.5 wt. % formic acid (HCO$_2$H), and 3 wt. % NaCl. The aim is to obtain H_2O-rich C-H-O fluids with a low salt concentration. As observed in some high-pressure metamorphic rocks from subduction zones, the salt concentration in subduction zone fluids could be between 3 and 50 wt. % (Scambelluri and Philippot, 2001; Frezzotti and Ferrando, 2015). At high *P-T* conditions, formic acid first decomposes into H_2O, CO, CO_2, and H_2 (Fujii *et al.,* 2012), but the final C-H-O fluid speciation present during the run primarily depends on the fO_2 imposed. The experiments at 0.2 GPa and 700 °C were carried out in rapid quench cold-seal pressure vessels housed at Bayerisches Geoinstitut, University Bayreuth, Germany, with water as the pressure media. Overall temperature and pressure uncertainties in the recorded pressure and temperature are less than 50 bar and 15 °C. The starting solution was loaded together with a piece of quartz crystal into an Au or Pt capsule (Fig. S-1a,b). The pressure vessels allow for *in situ* cracking on the quartz crystal, so that the timing of fluid inclusion formation can be controlled, as well as to ensure that the entrapped fluids are in equilibrium with the oxygen buffer (Li

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and Audétat, 2009; Li *et al.,* 2009; Li and Keppler, 2014). Oxygen fugacity (fO_2) at the fayalite-magnetite-quartz (FMQ) buffer was controlled by loading a mixture of synthetic fayalite, magnetite, and SiO_2 powder into the sample Au capsule (Fig. S-1a), and fO_2 at the Ni-NiO buffer was controlled by placing an unsealed Au capsule filled with mixed Ni and NiO powder below the sample Pt capsule (Fig. S-1b). The presence of all the buffer materials after quench was confirmed using X-Ray diffraction.

The experiments at 1.5 to 2.5 GPa and 600 to 700 °C were carried out in an end-loaded piston cylinder apparatus housed at Bayerisches Geoinstitut, University Bayreuth, Germany, with an NaCl-MgO assembly and graphite heater. Overall temperature and pressure uncertainties in the recorded pressures and temperatures are about 0.1 GPa and 10 °C. A modified double capsule technique (Li and Keppler, 2014) was used to encapsulate the starting solution and quartz crystal and to buffer the sample at different fO_2 (Fig. S-1c). The quartz crystal was HF-etched in order to effectively entrap fluids as fluid inclusions (Li and Audétat, 2009). The inner sample capsule was made of Pt$_{95}$Rh$_{05}$ and sealed by arc welding using a method developed by Audétat and Bali (2010). The outer capsule was made of Fe, Co, or Ni metal, which can be mechanically sealed under high pressures. The space between the two capsules was filled with corresponding oxides (FeO, CoO, or NiO) and water. To achieve a relatively high fO_2, the conventional double capsule technique (Chou, 1987) was used. In this technique, the inner Pt$_{95}$Rh$_{05}$ capsule was directly sealed in an outer Pt$_{95}$Rh$_{05}$ capsule and the space between was filled with Re-ReO$_2$ powder and water (Fig. S-1d).
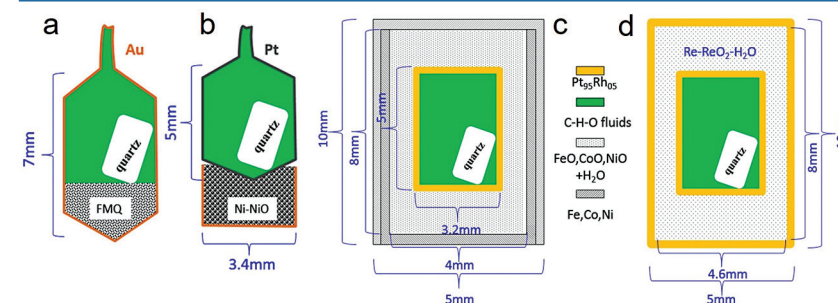

Figure S-1 Sketch of the four experimental capsule setups used in this study. **(a, b)** Panels are for the experiments performed at 0.2 GPa. **(c, d)** Panels are for the experiments performed at 1.5 to 2.5 GPa. The wall thickness of Au or Pt capsule in panels (a, b) and the wall thickness of the inner Pt$_{95}$Rh$_{05}$ capsule in panels (c, d) are about 0.15 mm and 0.2 mm, respectively. FMQ = fayalite + magnetite + quartz. See text for more details.

The use of piston cylinder apparatus at pressures of 1.5 to 2.5 GPa, rather than the cold-seal pressure vessels used at 0.2 GPa, is due to the limited pressures (≤0.25 GPa) that can be achieved by cold-seal pressure vessels. Numerous studies have demonstrated that the presence or absence of immiscible C-H-N-O-salt fluids at high pressures cannot be due to the different pressure vessels used, but

mainly due to the variation of pressure, temperature, and/or salt concentration (*e.g.,* Lamb *et al.,* 2002; Shmulovich *et al.,* 2004; Li *et al.,* 2009; Bali *et al.,* 2013; Li and Keppler, 2014).

Laser Raman was used to determine the C-H-O species in the fluid inclusions. Micro-Raman spectra of fluid inclusions were recorded in back-scattering geometry using a Horiba LabRAM HR UV spectrometer with CCD detector, 1800 mm^{-1} grating, 50× objective, and confocal mode, housed at Bayerisches Geoinstitut, University Bayreuth, Germany. Excitation was performed using the 514.5 nm line of an Ar$^+$ ion laser with an output power of 0.1 W. Most spectra were collected from 200 to 4500 cm^{-1} with acquisition time 2 × 60 s for each range. A confocal pinhole of 100 µm was used, which limits spectral resolution to 3.5 cm^{-1}. The use of a laser output power of 0.015 W and acquisition time 2 × 10 s yielded the same results of C-H-O species, indicating the preservation of C-H-O species during Raman analyses with a laser output power of 0.1 W.

Equilibrium and Sample fO$_2$

Several lines of evidence suggest that equilibrium should be approached in the piston cylinder experiments. First, the experiments started with a single, homogeneous fluid, but ended with two immiscible fluids. Second, the fluid species vary as a function of fO_2 imposed. From low fO_2 buffered by Fe-FeO to high fO_2 buffered by Re-ReO$_2$, the C-H-O species change from H$_2$+C$_2$H$_6$+CH$_4$+H$_2$O to CO$_2$+H$_2$O, which indicates that the C-H-O fluids were entrapped in the quartz crystal after the equilibrium between C-H-O fluids in the inner capsule and oxygen buffer in the outer capsule was approached. Third, analysing the earliest formed fluid inclusions in the quartz crystal from run LY05 (2.5 GPa, 600 °C, Ni-NiO, and run duration of 2 days) and the latest formed fluid inclusions in the quartz crystal from run LY08 (2.5 GPa, 600 °C, Ni-NiO, and run duration of 6 days) yielded the same results (Table 1).

Since the H$_2$O mole fraction in the starting solution is more than 0.9, the fO_2 in the inner sample capsule of the experiments should approximately equal the external oxygen buffer. However, X-Ray diffraction measurements of the buffering materials show that ReO$_2$ in run LY19 (see Table 1) was exhausted during the run. Therefore, the fO_2 in this run should be below the Re-ReO$_2$ buffer. The coexistence of graphite and CO$_2$-rich fluid (see Table 1 and the main text) indicates that the actual fO_2 in this run may be close to the C-CO$_2$ buffer. In the runs buffered by Fe-FeO (Table 1), the fO_2 in the inner capsule should be lower than the Fe-FeO buffer due to the presence of a considerable amount of H$_2$, CH$_4$, and C$_2$H$_6$ in the H$_2$O-rich fluids (Fig. 2). In the *P-T* range of 1.5 to 2.5 GPa and 600 to 700 °C, the order of oxygen buffers in terms of buffering capacity is Re-ReO$_2$ > C-CO$_2$ > Ni-NiO > Co-CoO > Fe-FeO.

Separation of CO$_2$-rich and H$_2$O-rich Fluids in Subduction Zones

Available studies show that CO$_2$-rich and the H$_2$O-rich fluids have very different wetting properties in calcite, quartz, and olivine dominated rocks (Watson and Brenan, 1987; Holness and Graham, 1991). The dihedral angle of the CO$_2$-rich fluids is significantly higher than that of the H$_2$O-rich fluids, but the dihedral angles of both fluids are greater than 60°. However, high contents of dissolved salt and/or silicates have been demonstrated to be capable of decreasing the dihedral angle of the H$_2$O-rich fluids to less than 60° (Watson and Brenan, 1987; Holness and Graham, 1991; Wanamaker and Kohlstedt, 1991); the H$_2$O-rich fluids in deep subduction zones may dissolve up to a few tens of wt. % of silicates and NaCl (Frezzoti and Ferrando, 2015; Weiss *et al.,* 2015). The dihedral angle of the H$_2$O-rich fluids may also decrease to less than 60° with increasing pressure in subduction zones (Mibe *et al.,* 1999). Therefore, it is highly likely that in the subducting slab, the H$_2$O-rich fluids can be effectively segregated from the CO$_2$-rich fluids. However, a large number of recent studies (Zack and John, 2007; Ague, 2014; Manea *et al.,* 2014; Bebout and Penniston-Dorland, 2016) demonstrate that fluids in the subducting slab may be mainly mobilised as channelised fluid flow along cracks, veins, shear zones, or fold hinges. In this case, the segregation of the H$_2$O-rich fluids from the CO$_2$-rich fluids could take place due to the density contrast of the fluids. The density of CO$_2$ at subduction zone conditions, calculated using the equation of state of Sterner and Pitzer (1994), is higher than that of H$_2$O-rich subduction zone fluids at the same *P-T* conditions (Hack and Thompson, 2011). For example, at 620 °C and 3 GPa, the calculated density of CO$_2$ is about 1.7 g cm^{-3}, while the density of H$_2$O-rich subduction zone fluids is about 1.3 g cm^{-3} (Hack and Thompson, 2011). The entrapment of the H$_2$O-rich and the CO$_2$-rich fluids in the same quartz crystal in a ~5 mm length capsule as shown in this study essentially indicates the effective segregation of these two different fluids, which suggests that these fluids are also likely to segregate in channelised fluid flow.

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