

## ■ 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<sub>2</sub>O and gases of CH<sub>4</sub>+H<sub>2</sub>, CH<sub>4</sub>+CO<sub>2</sub>, or CO<sub>2</sub> 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<sub>2</sub>-rich fluids, providing an important mechanism for the transfer of slab carbon to the mantle wedge.

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### 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

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<sub>2</sub>O and gases of CH<sub>4</sub>, CO<sub>2</sub>, or H<sub>2</sub> 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<sub>2</sub>, may yield an extensive region of immiscibility in the H<sub>2</sub>O-CH<sub>4</sub>/CO<sub>2</sub>-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<sub>2</sub> or CH<sub>4</sub> 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<sub>2</sub>O-H<sub>2</sub> and H<sub>2</sub>O-CH<sub>4</sub> 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<sub>2</sub>O and gases of CH<sub>4</sub>+H<sub>2</sub>, CH<sub>4</sub>+CO<sub>2</sub>, or CO<sub>2</sub> 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 (*f*O<sub>2</sub> hereafter) buffered by the Fe-FeO, Co-CoO, FMQ, Ni-NiO, or Re-ReO<sub>2</sub> 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<sub>2</sub>H), but the C-H-O fluid speciation present during the run primarily depends on the *f*O<sub>2</sub> imposed. The results show that at 0.2 GPa, 700 °C, and *f*O<sub>2</sub>

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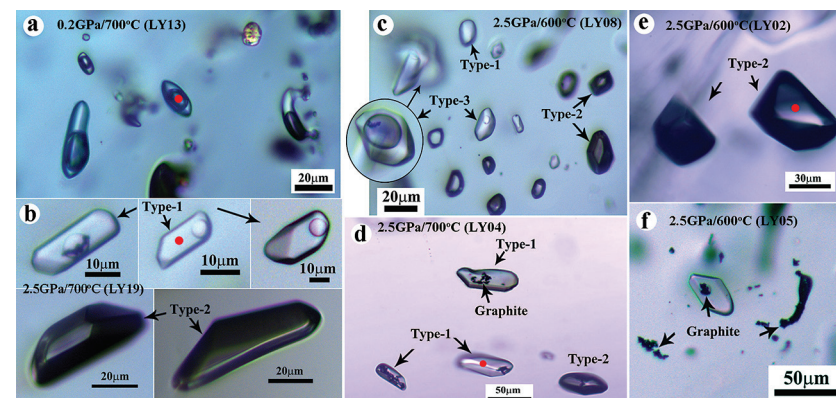
buffered by FMQ and Ni-NiO (Table 1), only one type of fluid inclusion exists in the quartz crystal (Fig. 1a), and CO<sub>2</sub> is the only detectable carbon species (Fig. 2a). At 1.5 to 2.5 GPa and 600 to 700 °C (Table 1), three types of fluid inclusions were found in each run. Type-1 are light-coloured 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<sub>2</sub>O-rich with small but detectable amounts of gases of CH<sub>4</sub>+C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>+CO<sub>2</sub>, or CO<sub>2</sub> (Fig. 2a). The gas species vary from CH<sub>4</sub>+C<sub>2</sub>H<sub>6</sub> to CO<sub>2</sub> at *f*O<sub>2</sub> varying from the Fe-FeO to the Re-ReO<sub>2</sub> buffer. The corresponding Type-2 fluid inclusions are pure gases of H<sub>2</sub>+CH<sub>4</sub>+C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>+CO<sub>2</sub>, or CO<sub>2</sub> 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	<sup>a</sup> Fluid composition	
LY13	0.2	700	3	FMQ	No	No	H <sub>2</sub> O-CO <sub>2</sub>	
LY14	0.2	700	3	Ni-NiO	No	No	H <sub>2</sub> O-CO <sub>2</sub>	
							Type-1	Type-2
LY01	1.5	600	3	Fe-FeO	Yes	No	H <sub>2</sub> O-CH <sub>4</sub> -C <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub> -H <sub>2</sub> -C <sub>2</sub> H <sub>6</sub>
LY02	2.5	600	3	Fe-FeO	Yes	No	H <sub>2</sub> O-CH <sub>4</sub> -C <sub>2</sub> H <sub>6</sub>	CH <sub>4</sub> -H <sub>2</sub> -C <sub>2</sub> H <sub>6</sub>
LY05	2.5	600	2	Ni-NiO	Yes	Yes	H <sub>2</sub> O-CH <sub>4</sub> -CO <sub>2</sub>	CH <sub>4</sub> -CO <sub>2</sub>
LY08	2.5	600	6	Ni-NiO	Yes	Yes	H <sub>2</sub> O-CH <sub>4</sub> -CO <sub>2</sub>	CH <sub>4</sub> -CO <sub>2</sub>
LY04	2.5	700	2	Ni-NiO	Yes	Yes	H <sub>2</sub> O-CH <sub>4</sub> -CO <sub>2</sub>	CH <sub>4</sub> -CO <sub>2</sub>
LY21	2.5	700	2.5	Co-CoO	Yes	Yes	H <sub>2</sub> O-CH <sub>4</sub> -CO <sub>2</sub>	CH <sub>4</sub> -CO <sub>2</sub>
LY19	2.5	700	2	Re-ReO <sub>2</sub>	Yes	Yes	H <sub>2</sub> O-CO <sub>2</sub>	CO <sub>2</sub>

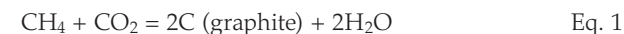
<sup>a</sup> The fluid composition was determined by Raman spectroscopy. In each run, 3 wt. % NaCl was added to the starting solution.

Note that the oxygen fugacity in run LY19 may be close to the C-CO<sub>2</sub> buffer. See text for more details.

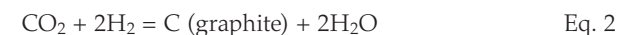


**Figure 1** Representative synthetic fluid inclusions in quartz formed at 0.2 to 2.5 GPa, 600 to 700 °C, and *f*O<sub>2</sub> buffered by the Fe-FeO to the Re-ReO<sub>2</sub> buffer. (a) At 0.2 GPa, only one type of fluid inclusion was observed and these fluid inclusions show a constant vapour/liquid 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<sub>2</sub> (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

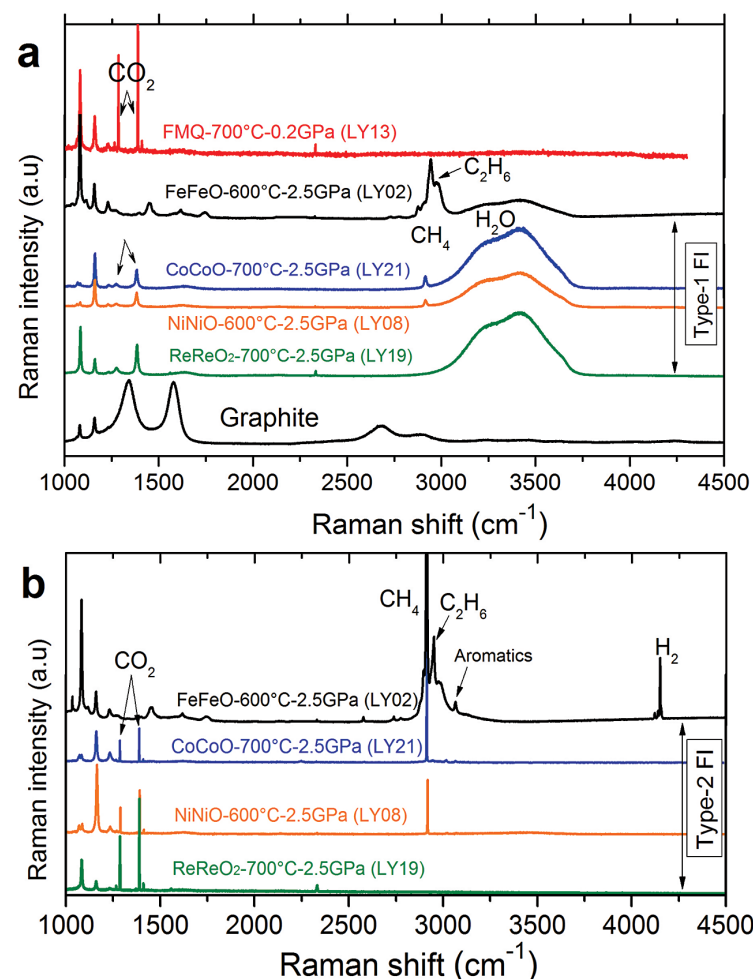


or



The *f*O<sub>2</sub> prevailing in run LY19 buffered by Re-ReO<sub>2</sub> (Table 1) may be close to the C-CO<sub>2</sub> buffer due to the exhaustion of ReO<sub>2</sub> 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  $f_{O_2}$  buffered by the Fe-FeO to the Re-ReO<sub>2</sub> buffer. At 0.2 GPa, 700 °C, and  $f_{O_2}$  at the FMQ buffer, CO<sub>2</sub> was the only detectable carbon species in fluids. At 2.5 GPa, (a) Type-1 fluid inclusions are rich in H<sub>2</sub>O but with detectable CH<sub>4</sub>+C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>+CO<sub>2</sub>, and CO<sub>2</sub>; (b) the corresponding Type-2 fluid inclusions are nearly pure CH<sub>4</sub>+H<sub>2</sub>+C<sub>2</sub>H<sub>6</sub>, CH<sub>4</sub>+CO<sub>2</sub>, and CO<sub>2</sub>. Note that the gas species vary as a function of  $f_{O_2}$ . Also note that the  $f_{O_2}$  in run LY19 (ReReO<sub>2</sub> - 700 °C - 2.5 GPa) buffered by Re-ReO<sub>2</sub> may be close to the C-CO<sub>2</sub> 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<sup>-1</sup> and 1388 cm<sup>-1</sup> for CO<sub>2</sub>, 2917 cm<sup>-1</sup> for CH<sub>4</sub>, 4150 cm<sup>-1</sup> for H<sub>2</sub>, 2956 cm<sup>-1</sup> for C<sub>2</sub>H<sub>6</sub>, and 3072 cm<sup>-1</sup> for aromatics. The small peaks at about 2331 cm<sup>-1</sup> and 1555 cm<sup>-1</sup> could be N<sub>2</sub> and O<sub>2</sub> 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<sub>2</sub>O-H<sub>2</sub> 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<sub>2</sub>O-CH<sub>4</sub> system at 450 °C. In addition to pressure, the addition of salt such as NaCl, KCl, MgCl<sub>2</sub>, and/or CaCl<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>-N<sub>2</sub> fluid inclusions and H<sub>2</sub>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<sub>2</sub>-, CO<sub>2</sub>-, and CH<sub>4</sub>-rich fluid inclusions coexisting with H<sub>2</sub>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 eclogites 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<sub>2</sub>O-CO<sub>2</sub> immiscibility.

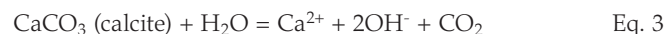




It may be worth noting that N<sub>2</sub> is a common component in the C-H-O fluids of high-pressure metamorphism, and the addition of non-polar N<sub>2</sub> usually enlarges the C-H-O fluid immiscibility field (Heinrich, 2007). Recent theoretical calculations also show that depending on the *P-T-fO<sub>2</sub>* 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O-CO<sub>2</sub> immiscibility (Yardley and Bottrell, 1988; Heinrich, 2007). Similarly, for a given decarbonation reaction in subduction zones, if it takes places at H<sub>2</sub>O-CO<sub>2</sub> immiscibility, significant amounts of carbonates may also be consumed. Taking the decarbonation reaction of carbonate (calcite) dissolution in H<sub>2</sub>O-rich fluids (Caciagli and Manning, 2003) as an example



and assuming that this reaction takes place at H<sub>2</sub>O-CO<sub>2</sub> immiscibility in subduction zones, extensive slab decarbonation must occur if the H<sub>2</sub>O-rich fluids can be segregated from the CO<sub>2</sub>-rich fluids and react further with carbonates. Available studies show that at high pressures, the CO<sub>2</sub>-rich fluids have higher dihedral angles and density than the H<sub>2</sub>O-rich fluids, indicating that the H<sub>2</sub>O-rich fluids can be effectively segregated from the CO<sub>2</sub>-rich fluids (see Supplementary Information). Furthermore, the ascending H<sub>2</sub>O-rich fluids in the subducting slab would experience decompression and heating, and the CO<sub>2</sub> activity in the H<sub>2</sub>O-rich fluids usually decreases with increasing temperature or decreasing pressure (Kerrick and Jacobs, 1981; Aranovich and Newton, 1999). Therefore, the segregating H<sub>2</sub>O-rich fluids could further react with carbonates during ascent, causing more decarbonation and the formation of immiscible CO<sub>2</sub>-rich fluids.

Secondly, immiscible CO<sub>2</sub>-rich fluids may be an important agent for the transfer of slab carbon to the mantle wedge. The formation of immiscible CO<sub>2</sub>-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<sub>2</sub>-rich fluids. In subduction zones, the CO<sub>2</sub>-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<sub>2</sub>O-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.

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## Additional Information

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## References

- AGUE, J., NICOLESCU, S. (2014) Carbon dioxide released from subduction zones by fluid-mediated reactions. *Nature Geoscience* 7, 355-360.
- ANDERSEN, T., AUSTRHEIM, H., BURKE, E.A.J., ELVEVOLD, S. (1993) Fluid-rock Interaction in the Deeper Continental Lithosphere N<sub>2</sub> and CO<sub>2</sub> in deep crustal fluids: evidence from the Caledonides of Norway. *Chemical Geology* 108, 113-132.
- ARANOVICH, L.Y., NEWTON, R.C. (1999) Experimental determination of CO<sub>2</sub>-H<sub>2</sub>O activity-composition relations at 600-1000 °C and 6-14 kbar by reversed decarbonation and dehydration reactions. *American Mineralogist* 84, 1319-1332.
- BALI, E., AUDÉTAT, A., KEPPLER, H. (2013) Water and hydrogen are immiscible in Earth's mantle. *Nature* 495, 220-222.



- BEBOUT, G.E., PENNISTON-DORLAND, S.C. (2016) Fluid and mass transfer at subduction interfaces—The field metamorphic record. *Lithos* 240, 228-258.
- BERKESI, M., HIDAS, K., GUZMICS, T., DUBESSY, J., BODNAR, R., SZABO, C., VAJNA, B., TSUNOGAE, T. (2009) Detection of small amounts of H<sub>2</sub>O in CO<sub>2</sub>-rich fluid inclusions using Raman spectroscopy. *Journal of Raman Spectroscopy* 40, 1461-1463.
- BOWERS, T.S., HELGESON, H.C. (1983) Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H<sub>2</sub>O-CO<sub>2</sub>-NaCl on phase-relations in geologic systems - Metamorphic equilibria at high-pressures and temperatures. *American Mineralogist* 68, 1059-1075.
- CACIAGLI, N.C., MANNING, C.E. (2003) The solubility of calcite in water at 6–16 kbar and 500–800 °C. *Contributions to Mineralogy and Petrology* 146, 275-285.
- CHURAKOV, S., GOTTSCHALK, M. (2003) Perturbation theory based equation of state for polar molecular fluids: II. Fluid mixtures. *Geochimica et Cosmochimica Acta* 67, 2415-2425.
- DASGUPTA, R., HIRSCHMANN, M.M. (2010) The deep carbon cycle and melting in Earth's interior. *Earth and Planetary Science Letters* 298, 1-13.
- FREZZOTTI, M.L., FERRANDO, S. (2015) The chemical behavior of fluids released during deep subduction based on fluid inclusions. *American Mineralogist* 100, 352-377.
- FREZZOTTI, M., SELVERSTONE, J., SHARP, Z., COMPAGNONI, R. (2011) Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps. *Nature Geoscience* 4, 703-706.
- FREZZOTTI, M.L., FERRANDO, S., TECCE, F., CASTELLI, D. (2012) Water content and nature of solutes in shallow-mantle fluids from fluid inclusions. *Earth and Planetary Science Letters* 351-352, 70-83.
- FU, B., TOURET, J.L.R., ZHENG, Y.F. (2003a) Remnants of premetamorphic fluid and oxygen isotopic signatures in eclogites and garnet clinopyroxenite from the Dabie-Sulu terranes, eastern China. *Journal of Metamorphic Geology* 21, 561-578.
- FU, B., TOURET, J.L.R., ZHENG, Y.F., JAHN, B.M. (2003b) Fluid inclusions in granulites, granulitized eclogites and garnet clinopyroxenites from the Dabie-Sulu terranes, Eastern China. *Lithos* 70, 293-319.
- GALVEZ, M.E., BEYSSAC, O., MARTINEZ, I., BENZERARA, K., CHADUTEAU, C., MALVOISIN, B., MALAVIEILLE, J. (2013) Graphite formation by carbonate reduction during subduction. *Nature Geoscience* 6, 473-477.
- GALVEZ, M.E., MANNING, C.E., CONNOLLY, J.A.D., RUMBLE, D. (2015) The solubility of rocks in metamorphic fluids: A model for rock-dominated conditions to upper mantle pressure and temperature. *Earth and Planetary Science Letters* 430, 486-498.
- GORMAN, P.J., KERRICK, D.M., CONNOLLY, J.A.D. (2006) Modeling open system metamorphic decarbonation of subducting slabs. *Geochemistry, Geophysics, Geosystems* 7, doi: 10.1029/2005gc001125.
- HEINRICH, W. (2007) Fluid immiscibility in metamorphic rocks. *Reviews in Mineralogy and Geochemistry* 65, 389-430.
- JOHNSON, E.L. (1991) Experimentally determined limits for H<sub>2</sub>O-CO<sub>2</sub>-NaCl immiscibility in granulites. *Geology* 19, 925-928.
- JOHNSTON, F.K., TURCHYN, A.V., EDMONDS, M. (2011) Decarbonation efficiency in subduction zones: Implications for warm Cretaceous climates. *Earth and Planetary Science Letters* 303, 143-152.
- KELEMEN, P.B., MANNING, C.E. (2015) Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. *Proceedings of the National Academy of Science USA* 112, E3997-E4006.
- KERRICK, D.M., JACOBS, G.K. (1981) A modified Redlich-Kwong equation for H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>O-CO<sub>2</sub> mixtures at elevated pressures and temperatures. *American Journal of Science* 281, 735-767.
- KERRICK, D., CONNOLLY, J. (2001) Metamorphic devolatilization of subducted marine sediments and the transport of volatiles into the Earth's mantle. *Nature* 411, 293-296.

- MANNING, C.E., SHOCK, E.L., SVERJENSKY, D.A. (2013) The Chemistry of Carbon in Aqueous Fluids at Crustal and Upper-Mantle Conditions: Experimental and Theoretical Constraints. *Reviews in Mineralogy and Geochemistry* 75, 109-148.
- POLI, S., FRANZOLIN, E., FUMAGALLI, P., CROTTINI, A. (2009) The transport of carbon and hydrogen in subducted oceanic crust: An experimental study to 5 GPa. *Earth and Planetary Science Letters* 278, 350-360.
- SCAMBELLURI, M., PHILIPPOT, P. (2001) Deep fluids in subduction zones. *Lithos* 55, 213-227.
- SELVERSTONE, J., FRANZ, G., THOMAS, S., GETTY, S. (1992) Fluid variability in 2 GPa eclogites as an indicator of fluid behavior during subduction. *Contributions to Mineralogy and Petrology* 112, 341-357.
- SHMULOVICH, K.I., GRAHAM, C.M. (2004) An experimental study of phase equilibria in the systems H<sub>2</sub>O-CO<sub>2</sub>-CaCl<sub>2</sub> and H<sub>2</sub>O-CO<sub>2</sub>-NaCl at high pressures and temperatures (500-800 °C, 0.5-0.9 GPa): geological and geophysical applications. *Contributions to Mineralogy and Petrology* 146, 450-462.
- STAGNO, V., FROST, D.J., MCCAMMON, C.A., MOHSENI, H., FEI, Y. (2015) The oxygen fugacity at which graphite or diamond forms from carbonate-bearing melts in eclogitic rocks. *Contributions to Mineralogy and Petrology* 169, 1-18.
- SVERJENSKY, D.A., STAGNO, V., HUANG, F. (2014) Important role for organic carbon in subduction-zone fluids in the deep carbon cycle. *Nature Geoscience* 7, 909-913.
- WEISS, Y., MCNEILL, J., PEARSON, D.G., NOWELL, G.M., OTTLEY, C.J. (2015) Highly saline fluids from a subducting slab as the source for fluid-rich diamonds. *Nature* 524, 339-342.
- YARDLEY B.W.D., BOTTRELL, S.H. (1988) Immiscible fluids in metamorphism: implications of two-phase fluid flow for reaction history. *Geology* 16, 199-202.
- ZHANG, C., DUAN, Z. (2009) A model for C-O-H fluid in the Earth's mantle. *Geochimica et Cosmochimica Acta* 73, 2089-2102.

