Redox processes and the role of carbon-bearing volatiles from the slab-mantle interface to the mantle wedge

Simone Tumiati¹, Nadia Malaspina²

¹ Dipartimento di Scienze della Terra, Università degli Studi di Milano, via Mangiagalli 34, 20133 Milano, Italy
² Dipartimento di Scienze dell’Ambiente e della Terra, Università degli Studi di Milano Bicocca, Piazza della Scienza 4, 20126 Milano, Italy *Correspondence: (nadia.malaspina@unimib.it)

Abstract
The valence of carbon is governed by the oxidation state of the host system. The subducted oceanic lithosphere contains considerable amounts of iron so that Fe³⁺/Fe²⁺ equilibria in mineral assemblages are able to buffer the fO₂ and the valence of carbon. Alternatively, carbon itself can be a carrier of redox budget when transferred from the slab to the mantle, prompting the oxidation of the sub-arc mantle. Also, the oxidation of sedimentary carbonaceous matter to CO₂ in the slab could consume the available redox budget. Therefore, the correct use of intensive and extensive variables to define the slab-to-mantle redox budget by C-bearing fluids is of primary importance when considering different fluid/rock ratios.

Fluid-mediated processes at the slab–mantle interface can be investigated also experimentally. The presence of CO₂ (or CH₄ at highly reduced conditions) in aqueous COH fluids in peridotitic systems affects the positions of carbonation/decarbonation reactions and of the solidus. Some methods to produce and analyse COH fluid-saturated experiments in model systems are introduced, together with the measurement of experimental COH fluids composition in terms of volatiles and dissolved solutes. The role of COH fluids in the stability of hydrous and carbonate minerals is discussed comparing experimental results with thermodynamic models.

Keywords
Carbonates, oxygen fugacity, subduction, COH fluids, peridotite.
The major volatiles in the Earth are nitrogen, carbon and hydrogen. The distribution of these volatiles between the Earth's principal reservoirs (core, mantle, crust and atmosphere) has had and continues to have great influence on both surface and interior dynamics. During the early stages of the Earth's history, the abundances of these volatiles in the different reservoirs were determined by the coupled evolution of the terrestrial magma ocean and the primitive atmosphere (Hier-Majumder & Hirschmann 2017). Since the Archean, the efficient deep subduction of organic carbon produced by photosynthesis could have promoted carbon burial in the mantle and an increase of atmospheric levels of oxygen through time (Duncan & Dasgupta 2017). Carbon at the modern terrestrial surface is largely divided between carbonates and organic deposits, with total budget of $1 \times 10^{23}$ g C, corresponding to about 100 ppm in the primitive mantle (Porcelli & Pepin 2013). Recent estimates from volcanic degassing suggest that the carbon content in the modern deep mantle is even higher (263 ±81 -62 ppm; (Anderson & Poland 2017; Barry 2017). In fact, the fate of carbonates and organic carbon in modern subduction zones is still largely unconstrained, although recent studies suggest that most of the subducted carbon, under the form of carbonates and organic matter, could be recycled back to the surface (Kelemen & Manning 2015). The investigation of redox processes and the role of volatiles especially at the slab-mantle interface is therefore crucial for depicting the framework of Earth carbon cycling.

In this contribution we aim to introduce some basic principles regarding the importance of the use of intensive and extensive variables in order to define the redox budget transferred from the slab to the overlying mantle by C-bearing fluids, both from the natural and experimental point of view.

**Slab-to-mantle carbon transport: the message from the nature**

The slab-mantle interface is a key location where fluid-mediated element transfer and redox processes occur. At pressures up to 3 GPa the slab-mantle interface is composed by the mixing of slab and suprasubduction mantle slices in a metasedimentary or ultramafic matrix, to form mélange zones (Bebout 2007; Konrad-Schmolke et al. 2011; Marschall & Schumacher 2012; Bostock 2013; Guillot et al. 2015 ; Bebout & Penniston-Dorland 2016). The key point of such geodynamic environment is the presence of high fluid fluxes, due to devolatilisation reactions in the slab (Schmidt & Poli 2013), which allows the chemical exchange within the mélange materials forming hydrated and low-viscosity layers atop the subducting plate. A different scenario is proposed at higher pressures, where the formation of silicate supercritical liquids from dehydration and/or melting of the subducted oceanic crust and metasediments induce percolation by porous flow processes. This process leads to the formation of several hydrous phases, such as amphibole and
phlogopite or, occasionally, forms near-monomineralic metasomatic rocks like orthopyroxenite or
phlogopitite layers, acting as a filter for aqueous fluid percolation in the mantle (Manning 2004;
Hermann et al. 2006; Malaspina et al. 2006; Scambelluri et al. 2006; Spandler & Pirard 2013).
Carbon plays a major role in the initiation of metasomatic-related redox processes at the slab-
mantle interface. It is mainly transported to depth by metasediments in the form of carbonates (C\(^{4+}\))
and graphite organic carbon (C\(^{0}\)). Relevant examples of carbonate-bearing metasediments
equilibrated at HP and UHP are given by eclogitic rocks from the Italian Alps. In his study of
impure marbles from the internal Sesia-Lanzo Zone, Castelli (1991) reports a foliation of calcite
and dolomite parallel to the eclogitic foliation developed by phengite, quartz, omphacite, grossular-
rich garnet, zoisite and Al-rich titanite equilibrated at P > 1.5 GPa and T ~ 600 °C. Another
occurrence from the Dora-Maira UHP terrane is represented by impure calcite- and dolomite-
bearing marbles from Costa Monforte (Castelli et al. 2007), which show a foliation dominated by
carbonates. In these rocks Ferrando et al. (2017) reported the evidence of dissolution of dolomite,
indicating that carbon occurs in the oxidised form also as molecular CO\(_2\) dissolved by metamorphic
fluids. The best evidence of the dissolution process promoting the carbon transport at depths is
given by the discovery of fluid inclusions in the metamorphosed seafloor Mn-rich sediments from
Lago di Cignana (Zermatt-Saas, Italy), containing bicarbonate and carbonate ions, together with
crystals of dolomite, magnesite and diamond (Frezzotti et al. 2011). In these occurrences carbon is
present ubiquitously as C\(^{4+}\) and C\(^{0}\).
Relevant quantities of carbon in its oxidised form are also transported during the subduction of
carbonates and elemental carbon in meta-ophiolites equilibrated at HP conditions. One example is
shown by the work of Ague & Nicolescu (2014), who report fluid-mediated decarbonation reactions
of metacarbonate layers in contact with serpentinite mélangé from the Syros and Tinos islands
(Greece). Carbonate-rich fluid inclusions occur in HP minerals such as omphacite and glaucophane
in altered layers surrounding carbonate veins. Graphite associated with calcite has been detected in
the serpentinites of Cogne (Italian Western Alps) (Carbonin et al. 2015). These phases formed by
seafloor metamorphism of mantle peridotites, triggered by carbon-bearing fluids during an
advanced stage of the opening of the Alpine Tethys in the Late Jurassic (Toffolo et al. 2017). Also
the interaction between metacarbonate rocks and serpentinised mantle occurring at HP has strong
implications for the deep transport of oxidised carbon at depths. As shown by Scambelluri et al.
(2016), dolomite marbles and serpentinites may react during deserpentinisation to form
carbonate+olivine hybrid rocks, as those cropping out in the ophicarbonate unit of the Ligurian
Western Alps (Italy). A lower degree of carbonate dissolution in serpentinite-derived fluids at more
reducing conditions may lead to precipitation of graphite. One example is shown in the Malaspina
outcrop (Alpine Corsica) where the sediments in contact with serpentinites develop a reaction zone of graphitic carbonaceous material in the blueschist facies during the Alpine orogeny (Galvez et al. 2013). Similar occurrences are reported in the work of Vitale Brovarone et al. (2017) in samples from the Sesia Lanzo zone in the Western Alps. In this case the reduction of carbonates in ophicarbonates occurring within serpentinitised peridotites induces the precipitation of graphite and the formation of methane- and hydrogen-bearing fluid, preserved as inclusions within the matrix calcite. Finally, nearly pure methane or methane-rich fluid inclusions have been found also in UHP eclogites from Dabie-Shan (Fu et al. 2003) and in jadeite from Myanmar, the Himalayan border of China (Shi et al. 2005).

Direct evidence of the transport of carbon-bearing fluids in the suprasubduction mantle and in the mantle wedge are represented by fluid inclusions in peridotites, which are mostly CO₂ bearing (Andersen & Neumann 2001; Frezzotti & Touret 2014; Seo et al. 2016). Rarely, fluid inclusions contain methane instead of CO₂ (Song et al. 2009), suggesting that strongly reducing conditions are not a common feature in the lithospheric mantle. CO₂ has been often detected up to 3000 ppm in melt inclusions in olivine from subduction-related igneous rock. However, it is widely accepted that the concentration of CO₂ in these inclusions is lower compared to their source magmas because of the partial degassing before melt entrapping (e.g., Metrich & Wallace 2008).

**Oxidation state of a rock system: some principles**

The valence state of carbon and its speciation are governed by the oxidation state of the host system, i.e. by the equilibria among mineral assemblages containing redox-sensitive major elements (e.g. Fe, Mn). Alternatively, the carbon species in subducted rocks and in the deep fluids may control the oxidation state of the host system by redox reactions during metamorphic reactions and fluid/rock interactions. As an example, the so-called DCDD decarbonation-redox reaction occurring in subducted metacarbonates, where dolomite reacts with silica to form diopside, carbon and oxygen has long been considered one of the redox equilibria at the most oxidising conditions at which diamond can form in eclogites (Luth 1993):

\[
[\text{dolomite}] \text{CaMg(CO}_3\text{)}_2 + 2 [\text{coesite}] \text{SiO}_2 = [\text{diopside}] \text{CaMgSi}_2\text{O}_6 + 2 [\text{diamond}] \text{C} + 2 \text{O}_2 \quad (1)
\]

A dilemma arises about whether the rock system buffers the redox state of carbon or the carbonate-involved redox reactions define the redox state of the rock. To solve this dilemma one must consider (i) the definition of “oxidation state (or redox state) of a rock” (host system) and the proper...
use of intensive and extensive variables; (ii) the role of “perfectly mobile and inert components”; (iii) the degree of fluid/rock interaction at the slab-mantle interface controlling the C-bearing mass transfer.

A redox equilibrium is defined as a process characterised by the flow of electrons from the substance being oxidised (“reducing medium”) to the substance being reduced (“oxidising medium”). For instance, ionic iron in aqueous solutions is present in two valence states, related by the redox equilibrium:

$$Fe^{3+} + e^- = Fe^{2+}$$ (2)

From left to the right we have reduction, from right to the left we have oxidation. Since oxygen is the most common electron acceptor in natural systems, in Earth Sciences oxidation and reduction generally mean gain and loss of oxygen, by the exchange with an external medium. To rule this exchange, the variable traditionally considered in Earth sciences is the oxygen fugacity: $f_{O_2}$ [bar].

Because iron is the fourth most abundant element in the Earth’s crust, we use oxygen redox buffers considering reactions involving iron-bearing phases (Frost 1991). In the simple system $Fe-O-SiO_2$, as a first approximation the amount of oxygen is the variable that predicts whether iron can be found as native state, as $Fe^{2+}$ in silicates or as $Fe^{3+}$ in oxides:

- [wustite] $FeO = [iron] Fe^0 + 0.5 O_2$ (IW buffer) (3)
- [fayalite] $Fe_2SiO_4 = [iron] 2 Fe^0 + [quartz] SiO_2 + 2 O_2$ (QIF buffer) (4)
- [magnetite] $2 FeO_4 + [quartz] 3 SiO_2 = [fayalite] 3 Fe_2SiO_4 + O_2$ (FMQ buffer) (5)
- [hematite] $6 Fe_2O_3 = [magnetite] 4 Fe_3O_4 + O_2$ (HM buffer) (6)

Because in nature solid phases do not usually display pure end-member compositions, most of the redox reactions (including the equilibria 3-6) are not univariant curves, becoming multivariant fields. Particularly, the replacement of Mg, Ca by $Fe^{2+}$, and of Al, Cr by $Fe^{3+}$ into iron silicates stabilises them to higher $f_{O_2}$ (see Figure 9 of Malaspina et al. 2009). Similarly, the addition of Fe and the consequent dolomite/diopside activities <1, shift the DCDD buffer (equilibrium 1) to higher $f_{O_2}$ (see Figure 2 of Luth 1993). As already pointed out by Frost (1991), in many rocks it is therefore more appropriate to say that oxygen fugacity is a function of the $Fe/Mg$ ratio (and $Ca/Mg$) of the rock-forming silicates and carbonates.

**Oxidation state of “dirty” rock systems: playing with components**

The oxidising or reducing capacity of a rock is determined by the amount and by the oxidation state of redox-sensitive major elements, and also by the composition of solid solutions of the mineral assemblages of the rock. As a consequence, $f_{O_2}$ is likely very inhomogeneous in a subducting
slab, reflecting the different bulk chemical–mineralogical compositions of the slab lithologies. An attempt to picture this concept has been made by Cannào and Malaspina (2018) who show a very complex and inhomogeneous \( f_O^2 \) pattern in subduction environments, particularly at the interface between the slab and the overlying mantle. While the subducted oceanic crust records \( \Delta F_MQ \) (= log \( f_{O_2}^{\text{sample}} - f_{O_2}^{FMQ} \), see equilibrium 5) comprised between \( \Delta F_MQ \leq 0 \) and \( \Delta F_MQ = +2.5 \pm +4 \), slices from the slab and from the supra-subduction mantle in the subducted mélange look variously oxidised, from FMQ-1 to FMQ+12. In this framework, oxygen fugacity is more likely an intensive variable that is governed by the mineral assemblages in the rock, rather than a variable that is imposed from the environment.

The choice to describe the oxidation state of rock systems in terms of the intensive variables \( f_O^2 \) [bar] and \( \mu_O^2 \) which are linked by the following relation:

\[
\mu_O^2 [J \text{ mol}^{-1}] = G_0^{\text{FMQ}} + R \times T \times \ln f_O^2/f^0O_2
\]

(7)
is entirely valid only if \( O_2 \) can be considered a “perfectly mobile” component (Korzhinskii 1936).

In open systems a component is defined “perfectly mobile” when, during the exchange between the system (e.g. a mineral) and the external medium (e.g. a fluid), the chemical potentials equalize (i.e., they reach the equilibrium) in a short time. A component is “inert” when its exchange between the system and the external medium is difficult and the chemical potentials do not equalize. In the case of perfectly mobile components, the independent parameter must be the chemical potential (e.g. \( \mu_O^2 \)), whereas if a component is inert the mass of that component (e.g. \( n_O^2 \)) must be considered as independent parameter. The \( O_2 \) molar quantity \( n_O^2 \) is the conjugate extensive variable of \( \mu_O^2 \), similarly to other couples of intensive and extensive variables like \( (P \times V) \) and \( (T \times S) \) (see details in Hillert 2008). As shown in a general example by Tumiati et al. (2015), considering the variable \( n_O^2 \) as molar axes, instead of \( \mu_O^2 \), the univariant curve separating a phase A and a phase B leaves room for a di-variant two-phase field (A+B). This difference can be easily seen in Figure 1, where a comparison of the variables \( \mu_O^2 \) and \( n_O^2 \) with \( T \) is reported for the simple system Fe-O2.

Considering the intensive variable \( \mu_O^2 \) as independent (Fig. 1a), the equilibria between magnetite and hematite (blue curve, equilibrium 6) and between iron and magnetite (pink curve) are univariant. If the extensive variable \( n_O^2 \) is considered as independent (Fig. 1b), the univariant curves open to di-variant areas, where the relative proportions between magnetite and hematite and between iron and magnetite (horizontal black lines) are ruled by \( n_O^2 \). As a consequence, oxygen can be added or subtracted in oxygen buffer assemblages without changing \( \mu_O^2 \) (or \( f_O^2 \)). The addition of oxygen to a hematite + magnetite assemblage leads thus to an increase in the abundance of hematite, an increase of Fe3+/Fe2+ and an increase of \( n_O^2 \), without changing \( f_O^2 \), as long as both minerals are present. The system is therefore buffered at constant \( f_O^2 \) and \( \mu_O^2 \).
In geodynamic settings where a high fluid/rock ratio is expected, such as subduction mélanges, oxygen is likely transported along fractures and veins, possibly through mechanisms of dissolution–replication of O-enriched oxides and silicates (Tumiati et al. 2015), or by advective processes (Marschall & Schumacher 2012; Tumiati et al. 2013; Nielsen & Marschall 2017). On the other hand, fluid percolation at low fluid/rock ratios occurs when the metasomatic fluid phases produced at UHP interact with peridotitic rocks at the slab-mantle interface. In such occurrences O cannot be considered a perfectly mobile component, because most of the redox reactions take place between solid oxides and silicates, where O is bonded. On this principle, the amount of inert components (e.g. FeO then forming FeO and vice versa) has a fundamental role and the molar quantity of O must be considered as an independent state variable.

This concept is well shown in Figure 2, where the redox state of the slab-mantle interface at UHP is portrayed in terms of intensive \( f_{O_2} \), normalised to the FMQ buffer (Fig. 2a) and of extensive \( n_{O_2} \) (Fig. 2b). Figure 2a shows a patchy inhomogeneous redox state of the slab-mantle interface. In this schematic representation three different rock systems are considered: (i) slab eclogite, (ii) a Grt+Opx-rich layer forming during the reaction of slab-derived supercritical liquids and (iii) a suprasubduction metasomatised mantle peridotite. In order to quantify the redox budget of these three rock systems in terms of extensive \( n_{O_2} \) (Fig. 2b), we must consider \( Fe^{3+} \)-bearing minerals (i.e. garnet and clinopyroxene) and their contribution in terms of excess O with respect to a reference state where only Fe\(^{2+}\) is present. This approach has been proposed by Tumiati et al. (2015) and applied to natural case studies of HP and UHP slab-mantle interaction by Li et al. (2016) and Malaspina et al. (2017). In the following section we will report step by step how to play with these components.

From \( f_{O_2} \) to \( n_{O_2} \) in \(^*\)dirty\(^*\) rock systems and the role of carbon in the slab-to mantle oxidation front

Consider the above three rock systems as composed by:

(i) eclogite = 50 mol% garnet + 50 mol% clinopyroxene;
(ii) Grt-Opx-rich layer = 10 mol% of garnet (+ 90 mol% of orthopyroxene);
(iii) metasomatised peridotite = 5 mol% garnet + 5 mol% clinopyroxene (+ 90 mol% of olivine and orthopyroxene).

Consider also the \( Fe^{3+} \)-bearing component in garnet as skiagite (\( Fe^{2+}_{2.5}Fe^{3+}_{1.5}Si_3O_{12} \)) and the \( Fe^{3+} \)-bearing component in clinopyroxene as aegirine (\( NaFe^{3+}Si_2O_6 \)). If O\(_2\) is not regarded as a phase or species but merely as a “stoichiometric” component expressing \( Fe^{3+} \), it can be made explicit in the skiagite \( ([FeO]_{0.5}(SiO_2)_{0.5}O_{2})_{0.0} \) and aegirine \( ([Na_2O]_{0.15}(FeO)_{0.25}(SiO_2)_{0.5}O_{2})_{0.0} \) formulae,
rewritten in terms of barycentric molar fractions of oxides and O\(_2\) (Tab. 1). This means that 1 mole of pure skiaigite and of pure aegirine would produce 0.06 and 0.07 moles of excess nO\(_2\) respectively. Taking into account the garnet (up to 5 mol% of skiaigite) and omphacite (up to 6 mol% of aegirine) composition of a mafic eclogite (Proyer et al. 2004), 1 mole of eclogite provides 3.6 mmol of excess O\(_2\), i.e. 1 m\(^3\) of eclogite contributes for 200 moles of excess O\(_2\) (Fig. 2b). Following the same simple calculation, 1 m\(^3\) of Grt-Opx-rich layer likely occurring at the slab-mantle interface with a garnet composition of up to 1.5 mol% of skiaigite (Malaspina et al. 2017) would contribute for 11 molar excess of O\(_2\). As a consequence, as shown in Figure 2, at low fluid-rock ratios mass transfer is supported by a gradient in nO\(_2\) and a metasomatic oxidation front likely develops from the oxidised slab to the overlying mantle. The comparison between Figures 2(a) and (b) clearly indicates that the equilibrium attainment is difficult since the oxygen chemical potentials of these different lithologies do not equalize.

The contribution of excess O\(_2\) due to reduction of carbonates during the slab-to-mantle metasomatism is potentially two orders of magnitude higher than that of the iron-bearing minerals described before. As discussed by both thermodynamic and experimental models (e.g., Gorman et al. 2006; Poli et al. 2009), decarbonation due to metamorphic reactions are not efficient mechanisms to transfer carbon from the slab to the mantle, because carbonates are stable at P-T conditions characterising subduction zones. Assume equilibrium 1 just as an “extreme” example of possible redox-induced decarbonation reaction occurring in the slab during subduction. Carbon and oxygen occur as C\(^2\) and O\(^2\) in the mantle reference state, and as C\(^{4+}\) and O\(^2\) in the crust reference state (see: Evans 2012). We can use the same approach described above to model equilibrium 1, making explicit the oxygen produced by reduction of the carbonate ion CO\(_3\)\(^2\) in dolomite to C\(^{4+}\) (graphite/diamond). 1 mole of pure dolomite, whose formula can be written as

\[
\text{(CaO)}_{0.17} \text{(MgO)}_{0.17} \text{(C)}_{0.33} \text{(O}_2\text{)}_{3.33}
\]

would be characterised by 0.33 moles of excess oxygen.

Applying equilibrium 1 to a siliceous dolomite composed by 40 mol% of dolomite (+60 mol% of quartz) (Bucher and Grapes 2011), 1 m\(^3\) of this rock would contribute for 6.5\(\times\)10\(^4\) moles of excess nO\(_2\).

Effects of COH fluids in the metasomatism and melting of mantle rocks
The interaction of mantle rocks with carbon-bearing fluids is evidenced by metasomatic assemblages containing carbonates and by carbon-bearing fluid inclusions in mantle minerals. Case studies of slices of metasomatised supra-subduction mantle dragged by the continental crust during subduction and/or exhumation are rare. Among them, we can mention garnet peridotites and websterites from Ulten Zone (Italian Alps), Donghai County (Sulu, China) and from Bardane and Ugelvik (Western Gneiss Region, Norway), which experienced metasomatism by ±C-bearing subduction fluid phases up to 200 km depth. Ulten garnet peridotites were metasomatised by slab-derived fluids, which enhanced the crystallisation of pargasitic amphibole and dolomite (Sapienza et al. 2009; Malaspina and Tumiati 2012; Förster et al., 2017). Sulu peridotites record a multistage metasomatism by alkali-rich silicate melt, and a subsequent influx of a slab-derived incompatible element and silicate-rich fluid which crystallised phlogopite and magnesite during the Triassic UHP metamorphism (Zhang et al. 2007; Malaspina et al. 2009). Websterites from Bardane preserve remnants of crust-derived fluids which precipitated graphite/diamond + dolomite/magnesite + Cr-spinel + phlogopite/K-amphibole in multiphase inclusions hosted by majoritic garnet (Van Roermund et al. 2002; Scambelluri et al. 2008; Malaspina et al. 2010). Peridotites from Ugelvik are interlayered with meter-thick lenses of garnet-pyroxenites parallel to the compositional banding. These pyroxenites have been described by Carswell (1968; 1973) and interpreted as crystallised at very high temperatures from mantle-derived melts. They are made of porphyroblastic majoritic garnets in equilibrium with clinopyroxene and K-rich amphibole.

Fe\(^{3+}\) measurements of garnets and the calculated \(f_{\text{O}_2}\) of the above peridotites in relation with the metasomatic phase assemblages formed by C-saturated (Bardane), C-undersaturated (Ulten and Sulu) and C-free (Ugelvik) slab-derived fluid phases are reported in Figure 3. An apparent correlation between the composition of the metasomatic agent (C- and alkali-bearing) and the fluid-induced oxidation of the peridotite mineral assemblage may exist.

The growth of carbonates in mantle rocks can occur only at relatively low temperature and high pressure conditions, above the so-called carbonation surface, represented by the reactions:

\[
\text{[forsterite]} \text{Mg}_2\text{SiO}_4 + \text{CO}_2 = \text{[enstatite]} \text{MgSiO}_3 + \text{[magnesite]} \text{MgCO}_3
\]  
(7)

in Ca-free systems (Koziol & Newton 1998)

and

\[
\text{[forsterite]} 2 \text{Mg}_2\text{SiO}_4 + \text{[diopside]} \text{CaMgSi}_2\text{O}_6 + 2 \text{CO}_2 =
\]

\[
= \text{[enstatite]} 2 \text{Mg}_2\text{Si}_2\text{O}_6 + \text{dolomite} \text{CaMg(CO}_3)_2
\]
(8)

in Ca-bearing systems (Wyllie et al. 1983).

These reactions are sensitive to the XCO\(_2\) (= CO\(_2\)/H\(_2\)O+CO\(_2\)) of the fluid phase, since the lower the XCO\(_2\), the higher the pressures are required to accomplish them. Moreover, the position of these
reactions in the P–T field varies as a function of the chemical complexity of thermodynamic system
e.g., Olafsson & Eggler 1983; Wallace & Green 1988). Tumiati et al. (2013) suggested the
following carbonation reaction in the system NKCFMASH+COH, occurring at T < 950°C and P = 1.5 GPa:
olivine + clinopyroxene + amphibole(I) + COH fluid =
= orthopyroxene + dolomite + amphibole(II) + phlogopite + garnet
implying that dolomite is produced at the expenses of clinopyroxene and olivine in lherzolites
metasomatised by CO₂-bearing fluids. This is consistent for example with the occurrence of
clinopyroxene-free, dolomite + amphibole peridotites in the Ulten Zone peridotites (Sapienza et al. 2009), for which the growth of dolomite in equilibrium with orthopyroxene has been estimated at
about 2 GPa and 850 °C (Malaspina & Tumiati 2012). In fact, the upper stability of dolomite was
defined by Brey et al. (1983) in the simple CaO–MgO–SiO₂ system by the reaction
\[
\text{[enstatite]} \ 2 \text{MgSiO₃} + \text{[dolomite]} \ \text{CaMg(CO₃)}₂ = \\
= \text{[diopside]} \ \text{CaMgSi₂O₆} + \text{[magnesite]} \ 2 \text{MgCO₃} \\
\]
being magnesite the only stable carbonate at high pressure conditions (P > 2.5 GPa at T = 900°C;
Tumiati et al. 2013).
The occurrence of CO₂ in the metasomatizing fluids also affects the melting temperature of mantle
rocks and, even more important, the composition of the melting products. In particular, high
pressure near-solidus melts forming at P > 2 GPa and T = 1050 °C are carbonatitic or carbonate-
silicate melts with Ca/Mg ratio near 1, rich in dolomitic component (Dasgupta & Hirschmann 2006;
Tumiati et al. 2013). However, melting of supra-subduction metasomatised mantle is not thought to
be feasible, due to the relatively lower temperatures with respect to the mantle wedge.

Sources of COH fluids in the mantle

The subduction slab is a major carrier of carbon in the deep Earth. It contains hydrothermally
altered oceanic crust, ophicarbonates and sediments bearing both carbonates and organic carbon.
Although metamorphic decarbonation is not predicted to be an efficient process at pressures and
temperatures typical of subduction zones, as discussed before, aqueous dissolution of carbonates
(Caciagli & Manning 2003; Pan et al. 2013) and carbonatitic melts originating from carbonated
oceanic crust (Poli 2015) are considered the most promising ways to remobilise carbonates in the
slab, along with diapirism of carbonated subduction mélangé (Marschall & Schumacher 2012;
Tumiati et al. 2013; Kelemen & Manning 2015).
The oxidation of organic matter and graphite is another efficient mechanism to produce CO$_2$-rich fluids, especially in the presence of silicates (Tumiati et al. 2017), although the total amount of carbon released by this process is poorly constrained due to the uncertainties associated with the estimated abundance of these phases in subducted rocks (Plank & Langmuir 1998). In addition, reduction of carbonates and/or graphite during serpentinization can lead to the production of C-rich fluids bearing abiotic methane and hydrocarbons (Galvez et al. 2013; Lazar et al. 2014; Vitale Brovarone et al. 2017). Actually, the composition of COH fluids in equilibrium with elemental carbon (i.e., graphite, diamond) is depending on the redox state of the system and on the P–T conditions and can be predicted by conventional thermodynamic models, which relies on equations of state that consider molecular species only (e.g., Connolly & Cesare 1993; Zhang & Duan 2009). On the basis of these models, at fixed P and T aqueous fluids become enriched in CO$_2$ in oxidized systems, and in CH$_4$ in reduced systems, passing through intermediate redox conditions where the abundance of dissolved carbon species is minimized and the activity of water is therefore maximized. The other COH species (CO, hydrocarbons, H$_2$, free O$_2$) have been considered only as minor species at conditions relevant to the upper mantle. However, recent more complex thermodynamic models highlighted the importance of charged carbon species, such as carbonate/bicarbonate ions in relatively oxidized systems and organic dissolved compounds (acetates, formates, propionates) in relatively reduced systems (Sverjensky et al. 2014; Pan & Galli 2016; Tiraboschi et al. 2018). While the occurrence of carbonate and bicarbonate species has been demonstrated experimentally in particular at low T and high P conditions (Facq et al. 2014), organic compounds have not been detected yet in experimental fluids. The presence of small Raman peaks ascribable to aromatic species have been interpreted as quench products (Li 2016). At fixed redox state, assuming for instance the buffering assemblage (equilibrium 6) FMQ (or the equivalent HP assemblage ferrosilite–magnetite–coesite) as a reference redox state, the composition of COH fluids following conventional thermodynamic models is predicted to be a H$_2$O–CH$_4$ mixture at low T and low P (e.g., seafloor metamorphic conditions), nearly pure water at low T and high P (e.g., cold subducting slabs) and a mixture of H$_2$O and CO$_2$ at high T conditions (e.g., mantle wedge) (Schmidt & Poli 2013). By considering simultaneously the variables P, T and fO$_2$, a 3D diagram for graphite/diamond-saturated COH fluids can be constructed (Fig. 4), showing that the FMQ surface (in green) is not parallel to the fluids compositional isopleths. In particular, the FMQ surface intersects the blending red and yellow CCO surface (i.e., the upper fO$_2$ stability of elemental carbon described by the reaction C + O$_2$ = CO$_2$). This means that at low P and high T conditions (e.g., 2 GPa and 900 °C) graphite and diamond are not stable at FMQ conditions, because they are fully oxidized to CO$_2$ at equilibrium conditions. On the other side, at high P and low T conditions (e.g., 5
GP and 600 °C), methane-bearing fluids produced by reduction of graphite/diamond are stable at FMQ conditions.

**Redox buffered fluid-rock interaction: the experimental point of view**

Experiments on mantle rocks interacting with carbon-bearing slab-derived fluids have been conducted since decades to retrieve phase stability and melting relations in metasomatised bulk compositions (e.g., Wallace and Green, Olafsson & Eggler). Other Recent experiments focused on the composition of the equilibrated metasomatising fluid in terms of dissolved volatile and solute species (e.g., Tumiati et al. 2017; Tiraboschi et al. 2018). Challenging issues of these last experiments are related to the difficulty in extracting fluids avoiding back-reactions in the fluid phase during quench. Further complexities are related to the low amount of fluid present in mm-sized experimental capsules, and the tendency of water to condense on the tubing systems, preventing quantitative analyses. In-situ experiments, carried out in hydrothermal anvil cells, could bypass most of these problems, but are to date limited to relatively low temperatures and simple chemical systems (e.g., McCubbin et al. 2014). In ex-situ experiments are more versatile, because a wide range of P–T–X conditions can be explored using, for instance, piston cylinders and multi-anvil apparatuses. Moreover, in these experiments the fugacity of oxygen can be controlled using the double capsule technique (Eugster & Skippen 1967), and the volatiles in fluid phase can be analysed by mass spectrometry, a technique that provided great sensitiveness to volatile COH species. The first analyses of experimental COH fluids were provided by Eggler et al. (1979), who investigated the solubility of CO and CO$_2$ in different silicate melts at 3 GPa and 1700 °C. Recent attempts to measure volatile in experimental capsules are described by Dvir et al. (2013), who used an infrared-gas analyser suitable to oxidised H$_2$O-CO$_2$ fluids, and by Tiraboschi et al. (2016) who used quadrupole mass spectrometry to analyse quantitatively small amount of fluids down to 1 micromole with uncertainties of about 1 mol% for molecular H$_2$O, CO$_2$, CO, CH$_4$, H$_2$ and O$_2$. With this technique, Tumiati et al. (2017) demonstrated that while the composition of COH fluids in equilibrium with graphite at 1–3 GPa and 800 °C is consistent with conventional thermodynamic models (Connolly & Cesare 1993; Zhang & Duan 2009), the addition of either quartz or magnesium silicates (forsterite, enstatite) enhances the CO$_2$ content in high pressure fluids by 10–30 mol%. In relatively complex systems, therefore, C–O–H models are not fully adequate to predict the composition of slab-derived fluids in terms of dissolved volatiles, and more complex models including dissolved charged species are needed (Sverjensky et al. 2014; Galvez et al. 2015; Pan & Galli 2016). However, these thermodynamic models still rely
on a very limited experimental dataset, so more data on the solubility of minerals in COH fluids would be extremely useful. Only few papers have been published on this topic yet. Newton & Manning (2000) employed the weight-and-loss technique (Anderson & Burnham, 1965) to retrieve the quartz solubility in H$_2$O-CO$_2$ fluids, suggesting that it decreases by increasing the CO$_2$ fraction in the fluid (Newton & Manning 2009). Tumiati et al. (2017) and 2018 Tiraboschi et al. (2018) used a modified version of the so-called cryogenic (or freezing) LA-ICP-MS technique (Kessel et al., 2004; 2005) to retrieve the solubility of quartz, forsterite+enstatite and enstatite+magnesite in H$_2$O-CO$_2$ fluids in equilibrium with graphite. In contrast to what observed in graphite-free fluids, the solubility of minerals in the presence of graphite is largely enhanced, presumably because organic Si- and Si–Mg–bearing compounds can form at relatively reduced conditions (Tiraboschi et al. 2018).

Conclusions

The correct use of extensive and intensive parameters in the definition of the redox state of the system depends on whether oxygen can be considered a perfectly mobile component. In natural systems, at low fluid/rock ratios, oxygen is inert and its molar quantity (redox budget) must be considered. Alternatively, at high fluid/rock ratios such as the conditions attained during experiments, the independent parameter is f$O_2$. Such aware distinction helps to solve the dilemma about whether the valence state of carbon and the speciation of its compounds is governed by the equilibria among mineral assemblages containing redox-sensitive major elements (e.g. Fe, Mn), or the carbon species in subducted rocks and deep fluids control the oxidation state of the host system by redox reactions during fluid/rock interactions.

At fixed redox state, the composition of C-bearing fluids following conventional thermodynamic models is predicted to be a H$_2$O+CH$_4$ mixture at low T and low P, nearly pure water at low T and high P and H$_2$O+CO$_2$ at high T conditions. The occurrence of carbon species in different oxidation states may not be directly related to a drastic change in f$O_2$ (i.e. CH$_4$ reduced conditions – CO$_2$ oxidised conditions), but all the variables P, T and f$O_2$ must be considered simultaneously. As shown in Figure 4, graphite/diamond-saturated COH fluids can be methane-bearing at FMQ conditions (“oxidised” condition in the mantle) at UHP and relatively low temperature.

Finally, the dissolution of silicates controls the composition of deep COH fluids in equilibrium with graphite, even in absence of carbonates, boosting the dissolution of graphite in subduction environments at high fluid/rock ratios (mélange) in the form of volatile CO$_2$.

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Figure Captions

**Fig. 1.** Comparison between univariant and bi-variant fields in a $\mu$O$_2$ (a) and $n$O$_2$ (b) plot versus T, calculated at 0.7 GPa for the system Fe$_2$O$_3$. Abbreviations: mt = magnetite, hem = hematite.

**Fig. 2.** Schematic cartoon showing various redox conditions in terms of intensive $\Delta$FMQ (a) and extensive oxygen molar mass ($n$O$_2$) of subducted lithosphere and suprasubduction mantle at UHP. The colour scale bar is arbitrary, from more reduced rocks (blue) to oxidised rocks (red to yellow).

In (a), modified from Cannão and Malaspina (2018), the values of $\Delta$FMQ are from the following literature: eclogite (Li et al., 2016; Cao et al., 2011; Mattinson et al., 2004); antigorite breakdown (Debret et al., 2015); subducted lithospheric mantle (Foley 2010); grt-opx-rich layer/veins (Malaspina et al. 2017); orogenic peridotite** (Malaspina et al. 2009); orogenic peridotite*** (Malaspina et al. 2010; Rielli et al. 2017); orogenic peridotite**** (Rielli et al. 2017). For comparison, the oxygen fugacities of Island Arc Basalts (IAB) sources (Ballhaus, 1993; Parkinson and Arculus, 1999) are also reported. In (b) a gradient in $n$O$_2$ develops a metasomatic oxidation front from the oxidised slab to the overlying mantle. See text for explanation in the calculation of O$_2$ molar quantities.

**Fig. 3.** Ranges of Fe$^{3+}$ contents in garnets from Ulten (Italy), Sulu (China), Bardane and Ugelvik (Norway) peridotites plotted versus Mg (atoms per formula unit) as representative of pyrope
concentration, modified from Cannò and Malaspina (2018). Minerals reported to the right of the square brackets indicate the metasomatic hydrous and/or carbonate phases in equilibrium with the analysed garnets.

Fig. 4. Compositional isopleths COH fluids in the P–T–log fO₂ field in the presence of graphite/diamond. The surface FMQ indicates the univariant equilibrium \( 3 \text{Fe}_2\text{SiO}_3 + \text{O}_2 = 2 \text{Fe}_3\text{O}_4 + 3\text{SiO}_2, \text{XCO}_2 \) and \( \text{XCH}_4 \) indicate the ratios \( \text{CO}_2/\text{H}_2\text{O}+\text{CO}_2 \) and \( \text{CH}_4/\text{H}_2\text{O}+\text{CH}_4 \) in the fluid phase, respectively. At \( \text{XCO}_2 = 1 \), carbon polymorphs are in equilibrium with pure \( \text{CO}_2 \) (CCO). This surface represents the upper \( fO_2 \) stability limit for graphite/diamond in the C–O–H system. At \( \text{XCH}_4 = 1 \), the fluid consists of pure methane. This surface represents the lower \( fO_2 \) stability limit of graphite/diamond in the C–O–H system. Below this surface, only reduced \( \text{C}_4 \) is stable. The locus of points where the activities of both \( \text{CO}_2 \) and \( \text{CH}_4 \) are minimized, and thus the activity of \( \text{H}_2\text{O} \) is maximum, is represented by the grey surface “max aH₂O”. Above this surface, \( \text{CO}_2 \)-bearing aqueous fluids are stable, while below \( \text{CH}_4 \) is the dominant carbon species. All calculations were performed using Perple_X (routine “fluids”; Eq. 11) and the COH fluids EoS of Connolly and Cesare (1993).

Fig. 5. descrivere, se vogliamo metterla, va inserito qualcosa anche nel testo

Table 1. Skaigite and aegirine formulae rewritten using \( \text{O}_2 \) as a component expressing \( \text{Fe}^{3+} \).

|                | Skaigite  | Aegirine   |
|----------------|-----------|------------|
| \( \text{Fe}^{2+} \) | 3         | 2          |
| \( \text{Fe}^{3+} \) | 5         | 1          |
| \( \text{Na}_2\text{O} \) | 0         | 0.5        |
| \( \text{O}_2 \) | 2 x 0.25 = 0.5 | 1 x 0.25 = 0.25 |
| \( \text{Si}_2\text{O}_3 \) | 8.5       | 3.75       |

\( \text{Fe}^{2+} = \text{Fe}^{3+} + \text{e}^- \)
\( 2 \text{O}^{2-} = \text{O}_2 + 4 \text{e}^- \)
\( 0.25 \text{O}^{2-} = 0.25 \text{O}_2 + \text{e}^- \)