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

Simone Tumiati[1], Nadia Malaspina[2*]

[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)

Formattato: Italiano (Italia)

Abbreviated Title

Redox processes and carbon-bearing volatiles

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 Fe^{3+}/Fe^{2+} equilibria in mineral assemblages are able to buffer the fO_2 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 CO_2 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 CO_2 (or CH_4 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 x 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 mélange 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 serpentinised 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 jadeitite 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 CO_2 bearing (Andersen & Neumann 2001; Frezzotti & Touret 2014; Seo *et al.* 2016). Rarely, fluid inclusions contain methane instead of CO_2 (Song *et al.* 2009), suggesting that strongly reducing conditions are not a common feature in the lithospheric mantle. CO_2 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 CO_2 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 equilibra at the most oxidising conditions at which diamond can form in eclogites (Luth 1993):

$$[\text{dolomite}]\ CaMg(CO_3)_2 + 2\ [\text{coesite}]\ SiO_2 = [\text{diopside}]\ CaMgSi_2O_6 + 2\ [\text{diamond}]\ C + 2\ O_2 \quad (1)$$

Formattato: Italiano (Italia)

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: fO_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^{2+} or 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] $2\ Fe_3O_4$ + [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 fO_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 fO_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, the fO_2 is likely very inhomogeneous in a subducting

Formattato: Italiano (Italia)

slab, reflecting the different bulk chemical–mineralogical compositions of the slab lithologies. An attempt to picture this concept has been made by Cannaò and Malaspina (2018) who show a very complex and inhomogeneous fO_2 pattern in subduction environments, particularly at the interface between the slab and the overlying mantle. While the subducted oceanic crust records ΔFMQ (= log fO_2^{sample} – log fO_2^{FMQ}, see equilibrium 5) comprised between ΔFMQ ≤ 0 and ΔFMQ = +2.5 ÷ +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 fO_2 [bar] and μO_2, which are linked by the following relation:

$$\mu O_2\,[\text{J mol}^{-1}] = G^0_{f,T,O2} + R \times T \times \ln fO_2/f^0O_2 \quad (7)$$

Formattato: Italiano (Italia)

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. μO_2), whereas if a component is inert the mass of that component (e.g. nO_2) must be considered as independent parameter. The O_2 molar quantity nO_2 is the conjugate extensive variable of μO_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 nO_2 as molar axes, instead of μO_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 μO_2 and nO_2 with T is reported for the simple system Fe–O_2. Considering the intensive variable μO_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 nO_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 nO_2. As a consequence, oxygen can be added or subtracted in oxygen buffer assemblages without changing μO_2 (or fO_2). The addition of oxygen to a hematite + magnetite assemblage leads thus to an increase in the abundance of hematite, an increase of Fe^{3+}/Fe_{tot} and an increase of nO_2, without changing fO_2, as long as both minerals are present. The system is therefore buffered at constant fO_2 and μO_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–reprecipitation 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_2 cannot be considered a perfectly mobile component, because most of the redox reactions take place between solid oxides and silicates, where O_2 is bonded. On this principle, the amount of inert components (e.g. FeO then forming Fe_2O_3 and vice versa) has a fundamental role and the molar quantity of O_2 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 fO_2, normalised to the FMQ buffer (Fig. 2a) and of extensive nO_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 nO_2 (Fig. 2b), we must consider Fe^{3+}-bearing minerals (i.e. garnet and clinopyroxene) and their contribution in terms of excess O_2 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.

Formattato: Inglese (Stati Uniti)

Formattato: Inglese (Stati Uniti)

From fO_2 to nO_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 ($Fe^{2+}{}_3Fe^{3+}{}_2Si_3O_{12}$) 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 $[(FeO)_{0.59}(SiO_2)_{0.35}(O_2)_{0.06}]$ and aegirine $[(Na_2O)_{0.13}(FeO)_{0.27}(SiO_2)_{0.53}(O_2)_{0.07}]$ formulae,

rewritten in terms of barycentric molar fractions of oxides and O_2 (Tab. 1). This means that 1 mole of pure skiagite 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 skiagite) 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 skiagite (Malaspina *et al.* 2017) would contribute for 11 moles of excess O_2. 1 m^3 of suprasubduction metasomatised mantle peridotite such as that from the Chinese Sulu UHP belt, which contains garnet with up to 6 mol% of skiagite and clinopyroxene with up to 5 mol% of aegirine (Malaspina *et al.* 2009, 2012), would contributes for 13 moles of excess 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^0 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 (graphite/diamond). 1 mole of pure dolomite, whose formula can be written as $(CaO)_{0.17}(MgO_2)_{0.17}(C)_{0.33}(O_2)_{0.33}$, 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 6.5×10^4 moles of excess nO_2.

Formattato: Inglese (Stati Uniti)

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 fO_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:

[forsterite] $Mg_2SiO_4 + CO_2 =$ [enstatite] $MgSiO_3 +$ [magnesite] $MgCO_3$ (7)

in Ca-free systems (Koziol & Newton 1998)

and

[forsterite] $2\ Mg_2SiO_4 +$ [diopside] $CaMgSi_2O_6 + 2\ CO_2 =$

$= $ [enstatite] $2\ Mg_2Si_2O_6 +$ dolomite $CaMg(CO_3)_2$ (8)

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

These reactions are sensitive to the XCO_2 ($= CO_2/H_2O+CO_2$) 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 (9)

implying that dolomite is produced at the expenses of clinopyroxene and olivine in lherzolites metasomatised by CO_2-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 othropyroxene 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–SiO_2 system by the reaction

[enstatite] 2 $MgSiO_3$ + [dolomite] $CaMg(CO_3)_2$ =

= [diopside] $CaMgSi_2O_6$ + [magnesite] 2 $MgCO_3$ (10)

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 CO_2 in the metasomatising 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 mélange (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_2O–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_2O 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

GPa 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., ~~refs~~ Wallace and Green, Olafsson e Eggler). ~~Other~~ Recent experiments focused on the composition of the equilibrated metasomatising fluid in terms of dissolved volatile and solute species (~~refs~~ 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). aggiungere Facq et al 2014 già nella lista di refs 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_2O-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_2O, 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

406 on a very limited experimental dataset, so more data on the solubility of minerals in COH fluids
407 would be extremely useful. Only few papers have been published on this topic yet. Newton &
408 Manning (2000) employed the weight-and-loss technique (Anderson & Burnham, 1965) to retrieve
409 the quartz solubility in H_2O-CO_2 fluids, suggesting that it decreases by increasing the CO_2 fraction
410 in the fluid (Newton & Manning 2009). Tumiati *et al.* (2017) and 2018 Tiraboschi *et al.* (2018)
411 used a modified version of the so-called cryogenic (or freezing) LA-ICP-MS technique (Kessel *et*
412 *al.*, 2004; 2005) to retrieve the solubility of quartz, forsterite+enstatite and enstatite+magnesite in
413 H_2O-CO_2 fluids in equilibrium with graphite. In contrast to what observed in graphite-free fluids,
414 the solubility of minerals in the presence of graphite is largely enhanced, presumably because
415 organic Si- and Si–Mg–bearing compounds can form at relatively reduced conditions (Tiraboschi *et*
416 *al.* 2018).
417
418 **Conclusions**
419 The correct use of extensive and intensive parameters in the definition of the redox state of the
420 system depends on whether oxygen can be considered a perfectly mobile component. In natural
421 systems, at low fluid/rock ratios, oxygen is inert and its molar quantity (redox budget) must be
422 considered. Alternatively, at high fluid/rock ratios such as the conditions attained during
423 experiments, the independent parameter is fO_2. Such aware distinction helps to solve the dilemma
424 about whether the valence state of carbon and the speciation of its compounds is governed by the
425 equilibria among mineral assemblages containing redox-sensitive major elements (e.g. Fe, Mn), or
426 the carbon species in subducted rocks and deep fluids control the oxidation state of the host system
427 by redox reactions during fluid/rock interactions.
428 At fixed redox state, the composition of C-bearing fluids following conventional thermodynamic
429 models is predicted to be a H_2O+CH_4 mixture at low T and low P, nearly pure water at low T and
430 high P and H_2O+CO_2 at high T conditions. The occurrence of carbon species in different oxidation
431 states may not be directly related to a drastic change in fO_2 (i.e. CH_4 reduced conditions – CO_2
432 oxidised conditions), but all the variables P, T and fO_2 must be considered simultaneously. As
433 shown in Figure 4, graphite/diamond-saturated COH fluids can be methane-bearing at FMQ
434 conditions ("oxidised" condition in the mantle) at UHP and relatively low temperature.
435 Finally, the dissolution of silicates controls the composition of deep COH fluids in equilibrium with
436 graphite, even in absence of carbonates, boosting the dissolution of graphite in subduction
437 environments at high fluid/rock ratios (mélange) in the form of volatile CO_2.
438
439 **References**

Ague, J.J. & Nicolescu, S. 2014. Carbon dioxide released from subduction zones by fluid-mediated reactions. *Nature Geoscience*, **7**, 355–360, https://doi.org/10.1038/ngeo2143.

Andersen, T. & Neumann, E.-R. 2001. Fluid inclusions in mantle xenoliths. *Lithos*, **55**, 301–320, https://doi.org/10.1016/S0024-4937(00)00049-9.

Anderson, K.R. & Poland, M.P. 2017. Abundant carbon in the mantle beneath Hawaii. **10**, https://doi.org/10.1038/NGEO3007.

Anderson, G.M. & Burnham C.W. 1965. The solubility of quartz in supercritical water. *American Journal of Science*, **263**, 494-511.

Ballhaus, C. 1993. Redox states of lithospheric and asthenospheric upper mantle. *Contributions to Mineralogy and Petrology*, **114**, 331-348.

Barry, P.H. 2017. Deep mantle: Enriched carbon source detected. *Nature Geoscience*, **10**, 625–627, https://doi.org/10.1038/ngeo3001.

Bebout, G.E. 2007. Metamorphic chemical geodynamics of subduction zones. *Earth and Planetary Science Letters*, **260**, 373–393, https://doi.org/10.1016/j.epsl.2007.05.050.

Bebout, G.E. & Penniston-Dorland, S.C. 2016. Fluid and mass transfer at subduction interfaces-The field metamorphic record. *Lithos*, **240**–**243**, 228–258, https://doi.org/10.1016/j.lithos.2015.10.007.

Bostock, M.G. 2013. The Moho in subduction zones. *Tectonophysics*, **609**, 547–557, https://doi.org/10.1016/j.tecto.2012.07.007.

Bucher, K. & Grapes, R. 2011. Petrogenesis of metamorphic rocks. *Springer Heidelberg Dordrecht London New York*. DOI 10.1007/978-3-540-74169-5.

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, https://doi.org/10.1007/s00410-003-0501-y.

Cannaò, E. & Malaspina, N. 2018. From oceanic to continental subduction: implications for the geochemical and redox evolution of the supra-subduction mantle. Geosphere, **14**, accepted.

Cao, Y., Song, S. G., Niu, Y. L., Jung, H. & Jin, Z. M. 2011. Variation of mineral composition, fabric and oxygen fugacity from massive to foliated eclogites during exhumation of subducted ocean crust in the North Qilian suture zone, NW China. *Journal of Metamorphic Geology*, **29**, 699-720.

Carbonin, S., Martin, S., Tumiati, S. & Rossetti, P. 2015. Magnetite from the Cogne serpentinites (Piemonte ophiolite nappe, Italy). Insights into seafloor fluid–rock interaction. *European Journal of Mineralogy*, **27**, 31–50, https://doi.org/10.1127/ejm/2014/0026-2410.

Carswell, D. A., 1968, Possible primary upper mantle peridotite in Norwegian basal gneiss. *Lithos*,

1, 322-355.

Carswell, D.A., 1973, Garnet pyroxenite lens within Ugelvik layered garnet peridotite. *Earth and Planetary Science Letters*, **20**, 347-352.

Castelli, D. 1991. Eclogitic metamorphism in carbonate rocks: the example of impure marbles from the Sesia-Lanzo Zone, Italian Western Alps. *Journal of Metamorphic Geology*, **9**, 61–77, https://doi.org/10.1111/j.1525-1314.1991.tb00504.x.

Castelli, D., Rolfo, F., Groppo, C. & Compagnoni, R. 2007. Impure marbles from the UHP Brossasco-Isasca Unit (Dora-Maira Massif, western Alps): Evidence for Alpine equilibration in the diamond stability field and evaluation of the X(CO2) fluid evolution. *Journal of Metamorphic Geology*, **25**, 587–603, https://doi.org/10.1111/j.1525-1314.2007.00716.x.

Connolly, J.A.D. & Cesare, B. 1993. C-O-H-S Fluid Composition and Oxygen Fugacity in Graphitic Metapelites. *Journal of Metamorphic Geology*, **11**, 379–388, https://doi.org/10.1111/j.1525-1314.1993.tb00155.x.

Dasgupta, R. & Hirschmann, M.M. 2006. Melting in the Earth's deep upper mantle caused by carbon dioxide. *Nature*, **440**, 659–662, https://doi.org/10.1038/nature04612.

Debret, B., Bolfan-Casanova, N., Padrón-Navarta, J. A., Martin-Hernandez, F., Andreani, M., Garrido, C. J., Sanchez-Vizcaìno, V. L., Gòmez-Pugnante. M. T., Munoz, M. & Trcera, N. 2015. Redox state of iron during high-pressure serpentinite dehydration. *Contributions to Mineralogy and Petrology*, **169**, 1-18.

Duncan, M.S. & Dasgupta, R. 2017. Rise of Earth's atmospheric oxygen controlled by efficient subduction of organic carbon. *Nature Geoscience*, **10**, 387–392, https://doi.org/10.1038/ngeo2939.

Dvir, O., Angert, A. & Kessel, R. 2013. Determining the composition of C-H-O liquids following high-pressure and high-temperature diamond-trap experiments. *Contributions to Mineralogy and Petrology*, **165**, 593–599, https://doi.org/10.1007/s00410-012-0825-6.

Eggler, D., Mysen, B. & Hoering, T. 1979. Gas species in sealed capsules in solid-media, high-pressure apparatus. *Carnegie Inst. Wash. Yearb.*, **73**, pp. 228-232.

Eugster, H.P. & Skippen, G.B. (1967). Igneous and metamorphic re- actions involving gas equilibria. *In: Abelson, P. H. (ed.) Researches in Geochemistry*. New York: John Wiley, pp. 450-492.

Evans, K.A. 2012. The redox budget of subduction zones. *Earth-Science Reviews*, **113**, 11–32, https://doi.org/10.1016/j.earscirev.2012.03.003.

Facq, S., Daniel, I., Montagnac, G., Cardon, H. & Sverjensky, D.A. 2014. In situ Raman study and thermodynamic model of aqueous carbonate speciation in equilibrium with aragonite under

subduction zone conditions. *Geochimica et Cosmochimica Acta*, **132**, 375–390, https://doi.org/10.1016/j.gca.2014.01.030.

Ferrando, S., Groppo, C., Frezzotti, M.L., Castelli, D. & Proyer, A. 2017. Dissolving dolomite in a stable UHP mineral assemblage: Evidence from Cal-Dol marbles of the Dora-Maira Massif (Italian Western Alps). *American Mineralogist*, **102**, 42–60, https://doi.org/10.2138/am-2017-5761.

Foley, S.F. 2010. A Reappraisal of Redox Melting in the Earth's Mantle as a Function of Tectonic Setting and Time. *Journal of Petrology*, **52**, 1363–1391, https://doi.org/10.1093/petrology/egq061.

Förster, B., Braga, R., Aulbach, S., Lo Pò, D., Bargossi, G. M. & Mair, V. 2017. A petrographic study of carbonate phases in the Ulten Zone ultramafic rocks: insights into carbonation in the mantle wedge and exhumation-related decarbonation. *Ofioliti* 42, 105– 127.

Frezzotti, M. & Touret, J.L.R. 2014. CO2, carbonate-rich melts, and brines in the mantle. *Geoscience Frontiers*, **5**, 697–710, https://doi.org/10.1016/j.gsf.2014.03.014.

Frezzotti, M.L., Selverstone, J., Sharp, Z.D. & Compagnoni, R. 2011. Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps. *Nature Geoscience*, **4**, 703–706, https://doi.org/10.1038/ngeo1246.

Frost, B.R. 1991. Introduction to oxygen fugacity and its petrologic importance. In: Lindsley, D. H. (ed.) Oxide Minerals: Petrologic and Magnetic Significance. *Mineralogical Society of America, Reviews in Mineralogy* 25, 1-9.

Fu, B., Touret, J.L.R. & Zheng, Y.F. 2003. 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, https://doi.org/10.1046/j.1525-1314.2003.00464.x.

Galvez, M., Alexander, J. & Connolly, 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*, https://doi.org/10.1016/j.epsl.2015.06.019.

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, https://doi.org/10.1038/ngeo1827.

Gorman, P.J., Kerrick, D.M. & Connolly, J. a D. 2006. Modeling open system metamorphic decarbonation of subducting slabs. *Geochemistry, Geophysics, Geosystems*, **7**, https://doi.org/10.1029/2005GC001125.

Guillot, S., Schwartz, S., Reynard, B., Agard, P. & Prigent, C. 2015. Tectonic significance of

542 serpentinites. *Tectonophysics*, **646**, 1–19, https://doi.org/10.1016/j.tecto.2015.01.020.
543 Hermann, J., Spandler, C., Hack, A. & Korsakov, A. 2006. Aqueous fluids and hydrous melts in
544 high-pressure and ultra-high pressure rocks: Implications for element transfer in subduction
545 zones. *Lithos*, **92**, 399–417, https://doi.org/10.1016/j.lithos.2006.03.055.
546 Hier-Majumder, S. & Hirschmann, M.M. 2017. The origin of volatiles in the Earth's mantle.
547 *Geochemistry, Geophysics, Geosystems*, **18**, 3078–3092,
548 https://doi.org/10.1002/2017GC006937.
549 Hillert, M. 2008. Phase Equilibria, Phase Diagrams and Phase Transformations. *Cambridge*
550 *University Press*, New York.
551 Kelemen, P.B. & Manning, C.E. 2015. Reevaluating carbon fluxes in subduction zones, what goes
552 down, mostly comes up. *Proceedings of the National Academy of Sciences*, **112**, E3997–
553 E4006, https://doi.org/10.1073/pnas.1507889112.
554 Kessel, R., Ulmer, P., Pettke, T., Schmidt, M.W. & Thompson, A.B. 2004. A novel approach to
555 determine high-pressure high-temperature fluid and melt compositions using diamond-trap
556 experiments. *American Mineralogist*, **89**, 1078–1086.
557 Kessel, R., Schmidt, M.W., Ulmer, P. & Pettke, T. 2005. Trace element signature of subduction-
558 zone fluids, melts and supercritical liquids at 120-180 km depth. *Nature*, **437**, 724–727,
559 https://doi.org/10.1038/nature03971.
560 Konrad-Schmolke, M., O'Brien, P.J. & Zack, T. 2011. Fluid migration above a subducted slab-
561 constraints on amount, pathways and major element mobility from partially overprinted
562 eclogite-facies rocks (Sesia Zone, Western Alps). *Journal of Petrology*, **52**, 457–486,
563 https://doi.org/10.1093/petrology/egq087.
564 Korzhinskii, D.S. 1936. Mobility and inertness of components in metasomatosis. *Xcarf. Nauk. SSSR*
565 *Bull. Ser. Geol.*, No. I., 35-60.
566 Koziol, A.M. & Newton, R.C. 1998. Experimental determination of the reaction: Magnesite +
567 enstatite = forsterite + CO2 in the ranges 6-25 kbar and 700-1100 °C. *American Mineralogist*,
568 **83**, 213–219.
569 Lazar, C., Zhang, C., Manning, C.E. & Mysen, B.O. 2014. Redox effects on calcite-portlandite-
570 fluid equilibria at forearc conditions: Carbon mobility, methanogenesis, and reduction melting
571 of calcite. *American Mineralogist*, **99**, 1604–1615.
572 Li, Y. 2016. Immiscible C-H-O fluids formed at subduction zone conditions. *Geochemical*
573 *Perspectives Letters*, 12–21, https://doi.org/10.7185/geochemlet.1702.
574 Li, J.L., Gao, J., Klemd, R., John, T. & Wang, X.S. 2016. Redox processes in subducting oceanic
575 crust recorded by sulfide-bearing high-pressure rocks and veins (SW Tianshan, China):

576 *Contributions to Mineralogy and Petrology*, **171**: 72. doi:10.1007/s00410-016-1284-2.
577 Luth, R.W. 1993. Diamonds, Eclogites, and the Oxidation State of the Earth's Mantle. *Science*, **261**,
578 66–68.
579 Malaspina, N., Hermann, J., Scambelluri, M. & Compagnoni, R. 2006. Polyphase inclusions in
580 garnet–orthopyroxenite (Dabie Shan, China) as monitors for metasomatism and fluid-related
581 trace element transfer in subduction zone peridotite. *Earth and Planetary Science Letters*, **249**,
582 173–187, https://doi.org/10.1016/j.epsl.2006.07.017.
583 Malaspina, N., Poli, S. & Fumagalli, P. 2009. The oxidation state of metasomatized mantle wedge:
584 Insights from C-O-H-bearing garnet peridotite. *Journal of Petrology*, **50**, 1533–1552,
585 https://doi.org/10.1093/petrology/egp040.
586 Malaspina, N., Scambelluri, M., Poli, S., Van Roermund, H.L.M. & Langenhorst, F. 2010. The
587 oxidation state of mantle wedge majoritic garnet websterites metasomatised by C-bearing
588 subduction fluids. *Earth and Planetary Science Letters*, **298**, 417–426,
589 https://doi.org/10.1016/j.epsl.2010.08.022.
590 Malaspina, N., Langenhorst, F., Fumagalli, P., Tumiati, S. & Poli, S. 2012. Fe3+ distribution
591 between garnet and pyroxenes in mantle wedge carbonate-bearing garnet peridotites (Sulu,
592 China) and implications for their oxidation state. *Lithos*, **146–147**, 11–17,
593 https://doi.org/10.1016/j.lithos.2012.04.023.
594 Malaspina, N., Langenhorst, F., Tumiati, S., Campione, M., Frezzotti, M.L. & Poli, S. 2017. The
595 redox budget of crust-derived fluid phases at the slab-mantle interface. *Geochimica et*
596 *Cosmochimica Acta*, **209**, https://doi.org/10.1016/j.gca.2017.04.004.
597 Malaspina N & Tumiati S. 2012. The role of C-O-H and oxygen fugacity in subduction-zone garnet
598 peridotites. *European Journal of Mineralogy*, **24**, 607–618, https://doi.org/10.1127/0935-
599 1221/2012/0024-2213.
600 Manning, C. 2004. The chemistry of subduction-zone fluids. *Earth and Planetary Science Letters*,
601 **223**, 1–16, https://doi.org/10.1016/j.epsl.2004.04.030.
602 Marschall, H.R. & Schumacher, J.C. 2012. Arc magmas sourced from mélange diapirs in
603 subduction zones. *Nature Geoscience*, **5**, 862–867, https://doi.org/10.1038/ngeo1634.
604 Mattinson, C. G., Zhang, R. Y., Tsujimori, T. & Liou, J. G. 2004. Epidote-rich talc- kyanite-
605 phengite eclogites, Sulu terrane, eastern China: PT-fO2 estimates and the significance of the
606 epidote-talc assemblage in eclogite. *American Mineralogist*, **89**, 1772-1783.
607 McCubbin, F.M., Sverjensky, D.A., Steele, A. & Mysen, B.O. 2014. In-situ characterization of
608 oxalic acid breakdown at elevated P and T: Implications for organic C-O-H fluid sources in
609 petrologic experiments. *American Mineralogist*, **99**, 2258–2271, https://doi.org/10.2138/am-

610 2014-4947.
611 Metrich, N. & Wallace, P.J. 2008. Volatile Abundances in Basaltic Magmas and Their Degassing
612 Paths Tracked by Melt Inclusions. *Reviews in Mineralogy and Geochemistry*, **69**, 363–402,
613 https://doi.org/10.2138/rmg.2008.69.10.
614 Newton, R.C. & Manning, C.E. 2000. Quartz solubility in H2O-NaCl and H2O-CO2 solutions at
615 deep crust-upper mantle pressures and temperatures: 2-15 kbar and 500-900 °C. *Geochimica et*
616 *Cosmochimica Acta*, **64**, 2993–3005, https://doi.org/10.1016/S0016-7037(00)00402-6.
617 Newton, R.C. & Manning, C.E. 2002. Solubility of enstatite + forsterite in H2O at deep crust /
618 upper mantle conditions: 4 to 15 kbar and 700 to 900 °C. *Geochimica et Cosmochimica Acta*,
619 **66**, 4165–4176.
620 Newton, R.C. & Manning, C.E. 2009. Hydration state and activity of aqueous silica in H2O-CO2
621 fluids at high pressure and temperature. *American Mineralogist*, **94**, 1287–1290,
622 https://doi.org/10.2138/am.2009.3287.
623 Nielsen, S.G. & Marschall, H.R. 2017. Geochemical evidence for mélange melting in global arcs.
624 *Science Advances*, **3**, e1602402, https://doi.org/10.1126/sciadv.1602402.
625 Olafsson, M. & Eggler, D.H. 1983. Phase relations of amphibole, amphibole-carbonate, and
626 phlogopite^carbonate peridotite: petro- logic constraints on the asthenosphere. *Earth and*
627 *Planetary Science Letters*, **64**, 305-315.
628 Pan, D. & Galli, G. 2016. The fate of carbon dioxide in water-rich fluids under extreme conditions.
629 *Science Advances*, **2**, e1601278–e1601278, https://doi.org/10.1126/sciadv.1601278.
630 Pan, D., Spanu, L., Harrison, B., Sverjensky, D. a & Galli, G. 2013. Dielectric properties of water
631 under extreme conditions and transport of carbonates in the deep Earth. *Proceedings of the*
632 *National Academy of Sciences of the United States of America*, **110**, 6646–6650,
633 https://doi.org/10.1073/pnas.1221581110.
634 Parkinson, I.J. & Arculus, R.J. (1999) The redox state of subduction zone: insights from arc
635 peridotites. *Chemical Geology*, **160**, 409–423.
636 Plank, T. & Langmuir, C.H. 1998. The chemical composition of subducting sediment and its
637 consequences for the crust and mantle. *Chemical Geology*, **145**, 325–394,
638 https://doi.org/10.1016/S0009-2541(97)00150-2.
639 Poli, S. 2015. Carbon mobilized at shallow depths in subduction zones by carbonatitic liquids.
640 *Nature Geoscience*, https://doi.org/10.1038/ngeo2464.
641 Poli, S., Franzolin, E., Fumagalli, P. & Crottini, A. 2009. The transport of carbon and hydrogen in
642 subducted oceanic crust: An experimental study to 5 GPa. *Earth and Planetary Science*
643 *Letters*, **278**, 350–360, https://doi.org/10.1016/j.epsl.2008.12.022.

644 Porcelli, D. & Pepin, R.O. 2013. The Origin of Noble Gases and Major Volatiles in the Terrestrial
645 Planets. *In*: *Treatise on Geochemistry: Second Edition*. 383–406.,
646 https://doi.org/10.1016/B978-0-08-095975-7.00412-5.
647 Proyer, A., McCammon, C. & Dachs, E. 2004. Pitfalls in geothermobarometry of eclogites: Fe 3+
648 and changes in the mineral chemistry of omphacite at ultrahigh pressures. *Contributions to*
649 *Mineralogy and Petrology*, **147**, 305–318, https://doi.org/10.1007/s00410-004-0554-6.
650 Rielli, A., Tomkins, A.G., Nebel, O., Brugger, J., Etschmann, B., Zhong, R., Yaxley, G.M. &
651 Paterson, D. 2017. Evidence of sub-arc mantle oxidation by sulphur and carbon. *Geochemical*
652 *Perspectives Letters*, 124–132, https://doi.org/10.7185/geochemlet.1713.
653 Sapienza, G.T., Scambelluri, M. & Braga, R. 2009. Dolomite-bearing orogenic garnet peridotites
654 witness fluid-mediated carbon recycling in a mantle wedge (Ulten Zone, Eastern Alps, Italy).
655 *Contributions to Mineralogy and Petrology*, **158**, 401–420, https://doi.org/10.1007/s00410-
656 009-0389-2.
657 Scambelluri, M., Hermann, J., Morten, L. & Rampone, E. 2006. Melt- versus fluid-induced
658 metasomatism in spinel to garnet wedge peridotites (Ulten Zone, Eastern Italian Alps): clues
659 from trace element and Li abundances. *Contributions to Mineralogy and Petrology*, **151**, 372–
660 394, https://doi.org/10.1007/s00410-006-0064-9.
661 Scambelluri, M., Pettke, T. & van Roermund, H.L.M. 2008. Majoritic garnets monitor deep
662 subduction fluid flow and mantle dynamics. *Geology*, **36**, 59,
663 https://doi.org/10.1130/G24056A.1.
664 Scambelluri, M., Bebout, G.E., Belmonte, D., Gilio, M., Campomenosi, N., Collins, N. & Crispini,
665 L. 2016. Carbonation of subduction-zone serpentinite (high-pressure ophicarbonate; Ligurian
666 Western Alps) and implications for the deep carbon cycling. *Earth and Planetary Science*
667 *Letters*, **441**, 155–166, https://doi.org/10.1016/j.epsl.2016.02.034.
668 Schmidt, M.W. & Poli, S. 2013. *Devolatilization During Subduction*, In: Treatise on Geochemistry
669 2nd ed. Elsevier Ltd., https://doi.org/10.1016/B978-0-08-095975-7.00321-1.
670 Seo, M., Woo, Y., Park, G., Kim, E., Lim, H.S. & Yang, K. 2016. Mantle-derived CO2-fluid
671 Inclusions in Peridotite Xenoliths from the Alkali Basalt, Jeju Island, South Korea. *The*
672 *Journal of the Petrological Society of Korea*, **25**, 39–50,
673 https://doi.org/10.7854/JPSK.2016.25.1.39.
674 Shi, G.U., Tropper, P., Cui, W., Tan, J. & Wang, C. 2005. Methane (CH4) -bearing fluid inclusions
675 in the Myanmar jadeitite. *Geochemical Journal*, **39**, 503–516,
676 https://doi.org/10.2343/geochemj.39.503.
677 Song, S., Su, L., Niu, Y., Lai, Y. & Zhang, L. 2009. CH4 inclusions in orogenic harzburgite:

678 Evidence for reduced slab fluids and implication for redox melting in mantle wedge.
679 *Geochimica et Cosmochimica Acta*, **73**, 1737–1754, https://doi.org/10.1016/j.gca.2008.12.008.
680 Spandler, C. & Pirard, C. 2013. Element recycling from subducting slabs to arc crust: A review.
681 *Lithos*, **170–171**, 208–223, https://doi.org/10.1016/j.lithos.2013.02.016.
682 Sverjensky, D.A., Harrison, B. & Azzolini, D. 2014. Water in the deep Earth: The dielectric
683 constant and the solubilities of quartz and corundum to 60kb and 1200°C. *Geochimica et*
684 *Cosmochimica Acta*, **129**, 125–145, https://doi.org/10.1016/j.gca.2013.12.019.
685 Sverjensky, D. a., Stagno, V. & Huang, F. 2014. Important role for organic carbon in subduction-
686 zone fluids in the deep carbon cycle. *Nature Geoscience*, **7**, 909–913,
687 https://doi.org/10.1038/ngeo2291.
688 Tiraboschi, C., Tumiati, S., Recchia, S., Miozzi, F. & Poli, S. 2016. Quantitative analysis of COH
689 fluids synthesized at HP–HT conditions: an optimized methodology to measure volatiles in
690 experimental capsules. *Geofluids*, **16**, 841–855, https://doi.org/10.1111/gfl.12191.
691 Tiraboschi, C., Tumiati, S., Sverjensky, D., Pettke, T., Ulmer, P. & Poli, S. 2018. Experimental
692 determination of magnesia and silica solubilities in graphite-saturated and redox-buffered
693 high-pressure COH fluids in equilibrium with forsterite + enstatite and magnesite + enstatite.
694 *Contributions to Mineralogy and Petrology*, **173**, https://doi.org/10.1007/s00410-017-1427-0.
695 Toffolo, L., Nimis, P., Martin, S., Tumiati, S. & Bach, W. 2017. The Cogne magnetite deposit (
696 Western Alps , Italy): A Late Jurassic seafloor ultramafic-hosted hydrothermal system ? *Ore*
697 *Geology Reviews*, **83**, 103–126, https://doi.org/10.1016/j.oregeorev.2016.11.030.
698 Tumiati, S., Fumagalli, P., Tiraboschi, C. & Poli, S. 2013. An Experimental Study on COH-bearing
699 Peridotite up to 3.2 GPa and Implications for Crust-Mantle Recycling. *Journal of Petrology*,
700 **54**, 453–479, https://doi.org/10.1093/petrology/egs074.
701 Tumiati, S., Godard, G., Martin, S., Malaspina, N. & Poli, S. 2015. Ultra-oxidized rocks in
702 subduction mélanges? Decoupling between oxygen fugacity and oxygen availability in a Mn-
703 rich metasomatic environment. *Lithos*, **226**, 116–130,
704 https://doi.org/10.1016/j.lithos.2014.12.008.
705 Tumiati, S., Tiraboschi, C., Sverjensky, D.A., Pettke, T., Recchia, S., Ulmer, P., Miozzi, F. & Poli,
706 S. 2017. Silicate dissolution boosts the CO2 concentrations in subduction fluids. *Nature*
707 *Communications*, **8**, https://doi.org/10.1038/s41467-017-00562-z.
708 Van Roermund, H. van, Carswell, D., Drury, M.R. & Heijboer, T.C. 2002. Microdiamonds in a
709 megacrystic garnet websterite pod from Bardane on the island of Fjørtoft, western Norway:
710 evidence for diamond formation in mantle rocks during. *Geology*, **30**, 959.
711 Vitale Brovarone, A., Martinez, I., Elmaleh, A., Compagnoni, R., Chaduteau, C., Ferraris, C. &

712 Esteve, I. 2017. Massive production of abiotic methane during subduction evidenced in
713 metamorphosed ophicarbonates from the Italian Alps. *Nature Communications*, **8**, 14134,
714 https://doi.org/10.1038/ncomms14134.
715 Wallace, M.E. & Green, D.H. 1988. An experimental determin- ation of primary carbonatite
716 magma composition. *Nature*, **335**, 343-345.
717 Wyllie, P.J., Huang, W.-L., Otto, J. & Byrnes, a. P. 1983. Carbonation of peridotites and
718 decarbonation of siliceous dolomites represented in the system CaO-MgO-SiO2-CO2 to 30
719 kbar. *Tectonophysics*, **100**, 359–388, https://doi.org/10.1016/0040-1951(83)90194-4.
720 Zhang, C. & Duan, Z. 2009. A model for C-O-H fluid in the Earth's mantle. *Geochimica et*
721 *Cosmochimica Acta*, **73**, 2089–2102, https://doi.org/10.1016/j.gca.2009.01.021.
722 Zhang, R.Y., Li, T., et al. 2007. Multiple metasomatism in Sulu ultrahigh-P garnet peridotite
723 constrained by petrological and geochemical investigations. *Journal of Metamorphic Geology*,
724 **25**, 149–164, https://doi.org/10.1111/j.1525-1314.2006.00683.x.
725
726 **Figure Captions**
727
728 **Fig. 1.** Comparison between univariant and bi-variant fields in a μO_2 (a) and nO_2 (b) plot versus T,
729 calculated at 0.7 GPa for the system Fe-O_2. Abbreviations: mt = magnetite, hem = hematite.
730
731 **Fig. 2.** Schematic cartoon showing various redox conditions in terms of intensive ΔFMQ (a) and
732 extensive oxygen molar mass (nO_2) of subducted lithosphere and suprasubduction mantle at UHP.
733 The colour scale bar is arbitrary, from more reduced rocks (blue) to oxidised rocks (red to yellow).
734 In (a), modified from Cannaò and Malaspina (2018), the values of ΔFMQ are from the following
735 literature: eclogite (Li et al., 2016; Cao et al., 2011; Mattinson et al., 2004); antigorite breakdown
736 (Debret et al., 2015); subducted lithospheric mantle (Foley 2010); grt-opx-rich layer/veins
737 (Malaspina *et al.* 2017); orogenic peridotite** (Malaspina *et al.* 2009); orogenic peridotite***
738 (Malaspina *et al.* 2010; Rielli *et al.* 2017); orogenic peridotite**** (Rielli *et al.* 2017). For
739 comparison, the oxygen fugacities of Island Arc Basalts (IAB) sources (Ballhaus, 1993; Parkinson
740 and Arculus, 1999) are also reported. In (b) a gradient in nO_2 develops a metasomatic oxidation
741 front from the oxidised slab to the overlying mantle. See text for explanation in the calculation of
742 O_2 molar quantities.
743
744 **Fig. 3.** Ranges of Fe^{3+} contents in garnets from Ulten (Italy), Sulu (China), Bardane and Ugelvik
745 (Norway) peridotites plotted versus Mg (atoms per formula unit) as representative of pyrope

concentrarion, modified from Cannaò 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 fO_2 field in the presence of graphite/diamond. The surface FMQ indicates the univariant equilibrium $3Fe_2SiO_4 + O_2 = 2Fe_3O_4 + 3SiO_2$. XCO_2 and XCH_4 indicate the ratios CO_2/H_2O+CO_2 and CH_4/H_2O+CH_4 in the fluid phase, respectively. At $XCO_2 = 1$, carbon polymorphs are in equilibrium with pure CO_2 (CCO). This surface represents the upper fO_2 stability limit for graphite/diamond in the C-O-H system. At $XCH_4 = 1$, 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 C^{4-} is stable. The locus of points where the activities of both CO_2 and CH_4 are minimized, and thus the activity of H_2O is maximum, is represented by the grey surface "max aH_2O". Above this surface, CO_2-bearing aqueous fluids are stable, while below 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). ~~descrivere~~

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

Table 1. *Skiagite and aegirine formulae rewritten using O_2 as a component expressing Fe^{3+}.*

	Skiagite ($Fe^{2+}_3Fe^{3+}_2Si_3O_{12}$)		**Aegirine ($NaFe^{3+}Si_2O_6$)**	
moles				
SiO_2	3	0.35	2	0.53
FeO	5	0.59	1	0.27
Na_2O	0	0	0.5	0.13
O_2	2 x 0.25 = 0.5	0.06	1 x 0.25 = 0.25	0.07
	8.5	1	3.75	1

$Fe^{2+} = Fe^{3+} + e^-$
$2\ O^{2-} = O_2 + 4\ e^-$
$0.25\ O^{2-} = 0.25\ O_2 + e^-$

Formattato: Non Evidenziato
Formattato: Non Evidenziato
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Tipo di carattere: Corsivo
Formattato: Pedice
Formattato: Tipo di carattere: Corsivo
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Tipo di carattere: Corsivo
Formattato: Pedice
Formattato: Pedice
Formattato: Tipo di carattere: Corsivo
Formattato: Pedice
Formattato: Tipo di carattere: Corsivo
Formattato: Pedice
Formattato: Apice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Pedice
Formattato: Non Evidenziato