Ultra-oxidized rocks in subduction mélanges? Decoupling between oxygen fugacity and oxygen availability in a Mn-rich metasomatic environment

Simone Tumiati[a,*], Gaston Godard[b], Silvana Martin[c], Nadia Malaspina[d] and Stefano Poli[a]

[a] *Dipartimento di Scienze della Terra "Ardito Desio", Università degli Studi di Milano, via Mangiagalli 34, I-20133 Milano, Italy; simone.tumiati@unimi.it*

[b] *Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Université Paris Diderot, UMR 7154 CNRS, 1 rue Jussieu, F-75252 Paris, France*

[c] *Dipartimento di Geoscienze, Università degli Studi di Padova, via Giotto 1, 35137 Padova, Italy*

[d] *Dipartimento di Scienze dell'Ambiente e del Territorio e di Scienze della Terra, Università degli Studi di Milano Bicocca, piazza della Scienza 4, 20126 Milano, Italy*

ABSTRACT

The manganese ore of Praborna (Italian Western Alps) is embedded within a metasedimentary sequence belonging to a subduction mélange equilibrated at high-pressure (HP) conditions (ca. 2 GPa) during the Alpine orogenesis. The pervasive veining of the ore and the growth of "pegmatoid" HP minerals suggest that these Mn-rich rocks strongly interacted with slab-derived fluids during HP metamorphism. These rocks are in textural and chemical equilibrium with the veins and in contact with sulphide- and magnetite-bearing metabasites at the bottom of the sequence. They contain braunite ($Mn^{2+}Mn^{3+}_6SiO_{12}$), quartz, pyroxmangite ($Mn^{2+}SiO_3$), and minor hematite, omphacite, piemontite and spessartine-rich garnet. Sulphides are absent in the Mn-rich rocks, whereas sulphates (barite, celestine) occur together with As- and Sb-oxides and silicates. This rock association provides an excellent natural laboratory to constrain the redox conditions in subducting oceanic slab mélanges at HP and fluid-present conditions. Similarly to Fe-bearing minerals, Mn

oxides and silicates can be regarded as natural redox-sensors. A thermodynamic dataset for these Mn-bearing minerals is built, using literature data as well as new thermal expansion parameters for braunite aud pyrolusite, derived from experiments. Based on this dataset and the observed assemblages at Praborna, thermodynamic calculations show that these mélange rocks are characterized by ultra-oxidized conditions (ΔFMQ up to +12.7) if the chemical potential of oxygen (or the oxygen fugacity fO_2) is accounted for. On the other hand, if the molar quantity of oxygen is used as the independent state variable to quantify the bulk oxidation state, the ore appears only moderately oxidized and comparable to typical subduction-slab mafic eclogites. Such an apparent contradiction may happen in rock systems whenever oxygen is improperly considered as a perfectly mobile component. In the Earth's mantle, redox reactions take place mainly between solid oxides and silicates, because O_2 is a negligible species in the fluid phase. Therefore, the description of the redox conditions of most petrological systems requires the introduction of an extensive variable, namely the oxygen molar quantity (nO_2). As a consequence, the oxygen chemical potential, and thus fO_2, becomes a dependent state variable, not univocally indicative of the redox conditions of the entire rock column of a subduction zone, from the dehydrating oceanic crust to the overlying mantle wedge. On a more general basis, the comparison of fO_2 retrieved from different bulk compositions and different phase assemblages is sometimes challenging and should be undertaken with care. From the study of mélange rocks at Praborna, the distribution of oxygen at subduction zones could be modelled as an oxidation gradient, grading from a maximum in the subducted altered oceanic crust to a minimum in the overlying peridotites of the mantle hanging-wall.

Keywords: manganese, oxidation, oxygen fugacity, subduction, mantle wedge, slab, eclogite

Highlights:

- The manganese-rich rocks of Praborna are high-pressure metacherts belonging to a slab mélange.

- Rocks are veined pervasively suggesting a strong interaction at HP with slab-derived fluids.
- Mn-rich mineral associations suggest ultra-high fO_2 conditions up to ΔFMQ +12.7.
- In terms of quantity of O_2, the same rocks display a moderate oxidation state.
- The decoupling between intensity and extensity of O_2 in metasomatic rocks is highlighted.

1. Introduction

The reduction-oxidation (redox) conditions of rocks are known to affect phase relationships, speciation of volatile elements, trace element partitioning, diffusivity, electrical conductivity and mechanical properties (Arculus, 1985). Redox conditions are traditionally described using the intensive variable oxygen fugacity (fO_2). Variability in fO_2 at subduction zones has been debated since a long time (Gill, 1981; Wood et al., 1990; Foley et al., 2011). Compared to the asthenospheric and lithospheric mantles, relatively high fO_2 has been proposed for subducted slab materials, sub-arc mantle and arc magmas (Hirschmann, 2009; Kelley and Kottrell, 2009; Malaspina et al., 2009, 2010; Groppo and Castelli, 2010; Evans, 2012). However, trace-element and isotope systematics, aimed to constrain the variation of fO_2 in the mantle (Canil, 2002; Lee et al., 2005, 2010), challenge such conclusion, emphasizing a discrepancy between the fO_2 calculated by oxygen thermobarometry and that inferred from V/Sc data on arc lavas.

The redox conditions of rocks could be also expressed in terms of ratios of cations occurring in different oxidation states, such as Fe^{2+} and Fe^{3+}. However, paucity of thermodynamic data on Fe^{3+} end-members of minerals and analytical difficulties in retrieving Fe^{3+}/Fe^{2+} in fine-grained, texturally complex volatile-rich rocks have hindered so far the quantitative assessment of redox conditions in the slab-mantle mixing zone in terms of Fe^{3+}/Fe^{2+} ratio (Bebout, 2007). On the other hand, Mn-rich nodules and crusts, though volumetrically very limited, are nearly ubiquitous on the seafloor (Manheim, 1978) and contain highly oxidized Mn^{4+}-bearing phases, such as amorphous MnO_2, pyrolusite, birnessite, and todorokite (e.g., Ostwald and Frazer, 1973). Upon metamorphism, a variety of Mn^{3+} and Mn^{2+} oxides and silicates may form in subduction mélanges, depending on *P*–

77 *T–X* conditions (e.g., Dasgupta, 1997; Tumiati et al., 2010). The variable oxidation states of
78 manganese make Mn minerals extremely useful sensors to constrain redox conditions of rocks.
79 The present study takes advantage of the manganese ore of Praborna, cropping out in the Italian
80 western Alps, and consisting of Mn-rich metasediments embedded within meta-ophiolites (Tumiati
81 et al., 2010). This ore displays a complex variety of Mn- and Fe-rich mineral assemblages, formed
82 at eclogite-facies conditions in a subduction mélange. Swarms of stockwork high-pressure (HP)
83 veins are cutting the Mn-rich rocks, suggesting an interaction with slab-derived fluids at very high
84 fluid-rock ratio, as expected for such very thin, veined, metasedimentary sequences (Bebout et al.,
85 2013). Praborna represents an excellent natural laboratory for the study of the behaviour of the
86 component oxygen in terms of mobility in oceanic slab mélanges subducted at HP conditions and
87 flushed by fluids. This particular case should be considered as paradigmatic, because it draws the
88 attention to the choice of the independent parameter capable of describing the redox conditions of
89 rocks in a metasomatic environment.
90
91 **2. Concepts and definitions**
92 Oxidation and reduction are defined in general chemistry as loss and gain of electrons, respectively.
93 Since oxygen is the most common electron acceptor in natural systems, because of its high
94 electronegativity, oxidation and reduction generally mean gain and loss of oxygen, by exchange
95 with the external medium. Thus, the redox condition of rocks is described by considering a variable
96 that can potentially rule this exchange. Exception done for a few works (e.g., Chinner, 1960; Evans,
97 2006), the variable traditionally considered in Earth sciences is the oxygen fugacity (fO_2). However,
98 O_2 is not expected to be a major gaseous/fluid species in the Earth's interior, and the chemical
99 potential of oxygen (either μO or μO_2) could appear more appropriate. In this study, we use both
100 variables fO_2 and μO_2 considered as equivalent.
101 The fugacity of a gaseous species is the theoretical partial pressure that this gas would have if it
102 would obey the ideal-gas law ($P \times V = n \times R \times T$). This means that fugacity is equal to partial

pressure only in ideal gases (i.e., for $P \rightarrow 0$ bar). At higher pressures, gases strongly diverge from the ideal gas law, and a fugacity coefficient ($\boldsymbol{\Phi} = f / P$) is introduced accounting for the non-ideal behaviour. The fugacity of a gas is in turn a function of the chemical potential of the relative component. For the component O_2, this relationship is expressed by the following equation:

$$\mu O_2 = G^0_{f,T,O2} + R \times T \times \ln fO_2/f^0O_2$$

where

- μO_2 (J•mol^{-1}) is the chemical potential of the component O_2 at P and T of interest;
- $G^0_{f,T,O2}$ (J•mol^{-1}) is the molar Gibbs energy of formation of pure oxygen (O_2) at P^0 = 1 bar and T;
- R (J•K^{-1}•mol^{-1}) is the gas constant;
- fO_2 (bar) is the fugacity of pure oxygen at P and T of interest;
- f^0O_2 is the fugacity of pure oxygen at the standard-state pressure P^0 (f^0O_2 = 1 bar at all T).

As for any other component of a petrological system, μO_2, and thus fO_2, is ideally homogenous in all phases at equilibrium and independent of the phase abundance; in other terms, it is an intensive variable. The O_2 molar quantity (nO_2) is the conjugate extensive variable of μO_2, since the product ($\mu O_2 \times nO_2$) has the dimension of an energy (J•mol^{-1} × mol = J), similarly to other couples of intensive and extensive variables like ($P \times V$) and ($T \times -S$).

While considering an oxidised system, the set of basis vectors that generate the compositional vector space (i.e. the set of independent components) could be either {Si, Fe, Mn, ..., O} or {SiO_2, FeO, MnO, ..., O_2}. We have chosen here the latter set of independent components, so that μO_2 and nO_2 have to be considered instead of μO and nO. In that case, nO_2 represents the coordinate for the basis vector O_2; it equals zero when all Fe and Mn occur in their divalent oxidation state, i.e. as FeO and MnO (see Fig. 7).

The choice to describe a redox system in terms of intensive variables (fO_2 or μO_2) is entirely valid only if O_2 can be considered a "perfectly mobile" component. As already explained by Korzhinskii (1959, p. 16), the behaviour of a chemical component in a rock system could be "inert" or

129 “perfectly mobile”, depending on its mobility between the system and an external medium. As an
130 example, during a fluid-rock interaction, where the system is the rock and the external medium is a
131 fluid phase flushing the rock, those rock components that are not readily transported by the fluid are
132 considered inert or “immobile”, whereas components that can dissolve into the fluid can be
133 considered “mobile” and rapidly react with the surrounding rock. On this principle, the quantity of
134 inert components has a fundamental role to attain the equilibrium, while it can be neglected for
135 mobile components. Therefore, from a thermodynamic point of view, during the equilibration
136 between a rock and a fluid phase, the molar quantity of material should be considered as an
137 independent state variable for inert components, whereas chemical potential must be used as an
138 independent state variable for perfectly mobile components (Korzhinskii, 1959).
139 A complication arises when we consider the component O_2 in the Earth’s interior, because redox
140 reactions take place mainly between solid oxides and silicates, where oxygen is bonded to relatively
141 inert components such as FeO (forming, for example, Fe_2O_3) and MnO (forming, for example,
142 Mn_2O_3), while it occurs in very limited amounts in fluids. Therefore, O_2 cannot be considered
143 unequivocally a perfectly mobile component. It could well be that, in many cases, O_2 is better
144 regarded as an inert component, so that $n\mathrm{O}_2$, rather than $\mu\mathrm{O}_2$, becomes an independent
145 thermodynamic state variable imposed upon the system.
146 Considering the variable $n\mathrm{O}_2$ instead of $\mu\mathrm{O}_2$ modifies the inspection of phase relationships (e.g.,
147 Hillert, 1985). In particular, when a molar quantity is introduced as an axis instead of its conjugate
148 chemical potential, two one-phase fields will separate from each other, thus leaving room for the
149 two-phase field, and their distance will be equal to the difference in the molar quantity between the
150 two phases (Fig. 1). In addition, when molar quantities other than $n\mathrm{O}_2$ are not constant, $\mu\mathrm{O}_2$ (and
151 $f\mathrm{O}_2$) is not a simple, monotonically increasing function of the quantity of oxygen. Therefore, the
152 reconstruction of the extensive property ($n\mathrm{O}_2$) from the intensive variable ($f\mathrm{O}_2$ or $\mu\mathrm{O}_2$) can be a
153 very inaccurate procedure in natural, multi-component systems (see Malaspina et al., 2009, 2012).
154

3. The Praborna manganese ore

Slices of Mn-rich metasediments are commonly hosted in meta-ophiolites of the Western Alps. Praborna (Saint-Marcel valley, Italy; Fig. 2) is the largest Mn deposit in the Zermatt-Saas unit, which is interpreted as part of the Jurassic oceanic lithosphere of the Tethys, subducted during the Alpine orogeny (e.g., Dal Piaz, 2001). In the Zermatt-Saas unit, Mn-rich rocks from Lago di Cignana (Valtournanche) preserve coesite (Reinecke, 1998) and microdiamonds (Frezzotti et al., 2011), suggesting that the oceanic sediments underwent ultrahigh-*P* (UHP) metamorphism. HP metamorphic peak conditions of 2.1 GPa and 550 °C were recorded also in the meta-ophiolite of the Saint-Marcel valley (Martin et al., 2008), which are the country rocks of the Praborna deposit.

The disused mine of Praborna, known since 1415 CE (Castello, 1982), is world-famous for its peculiar rocks and minerals. In particular, it is the type locality of five mineralogical species, namely piemontite, braunite, romeite, strontiomelane, and manganiandrosite-(Ce) (Ciriotti et al., 2009 and references therein). The Praborna deposit displays a continuous change in mineralogy from the basal contact with metabasites (now glaucophanites) towards the upper contact with Mn-poor metasediments (Figs. 2, 3), and consists of boudinaged Mn-rich metasediments cropping out in a "mélange" composed of serpentinite, ophicarbonate breccias, metagabbro and metabasalt with N-MORB affinity (Fig. 2; Martin and Kienast, 1987; Martin et al., 2008; Tumiati et al., 2010). Swarms of stockwork HP veins cut the Mn-rich rocks especially near the basal contact (Fig. 3), suggesting an interaction with slab-derived fluids. On the basis of the mineralogical composition, several "levels" have been recognized (Martin and Kienast, 1987; Tumiati et al., 2010). Basal levels and veins contain braunite (the ore mineral), piemontite and jadeite-rich Mn-bearing omphacite, whereas upper levels are characterised by the abundance of garnet ± pyroxmangite ± jadeite-poor clinopyroxene. Quartz is generally abundant in all the levels. In Table 1, we report representative mineral compositions of the basal and upper levels, the HP veins and the SiO_2-undersaturated assemblages found at Praborna. Other details concerning mineralogy and petrography of the ore are provided in Section 5, as Supplementary Material (SM), and in Tumiati et al. (2010).

4. Materials and methods

Several thin sections of the basal and upper levels (Table SM-1 in the Supplementary Material) have been analysed at the petrographic and scanning electron microscopes. Chemical analyses reported in Table 1 were performed using the Cameca SX100 (Paris) and JEOL 8200 (Milano) wavelength-dispersive electron microprobes (EMP), at 15-kV accelerating potential, 15-nA sample current and 1-μm beam diameter. Standards used were albite (Na), diopside (Ca, Mg and Si), Fe_2O_3 (Fe), orthoclase (Al and K), $MnTiO_3$ (Mn and Ti), Cr_2O_3 (Cr) and barite (Ba). A counting time of 30 s was applied for all elements.

The Fe^{3+}/Fe_{TOT} and Mn^{3+}/Mn_{TOT} ratios in minerals have been calculated by stoichiometry. Because of the relative electronegativity of Fe and Mn, the pair Fe^{3+}–Mn^{2+} is more stable than the pair Fe^{2+}–Mn^{3+}, which has never been reported in minerals (Sherman, 1990). In fact, values of standard redox potential (or electromotive force) are 0.77 V for the pair Fe^{3+}–Fe^{2+} and 1.51 V for Mn^{3+}–Mn^{2+}. Therefore, the charges were calculated iteratively, by adjusting first Fe^{3+}/Fe_{TOT}, and then, if necessary, Mn^{3+}/Mn_{TOT}. In any case, this study is mainly focused on simple manganese oxides and silicates characterized by fixed Mn^{3+}/Mn_{TOT}, so that uncertainties related to this procedure do not affect the conclusions provided here.

For more complex phases, crystal chemistry has been evaluated mostly using the principal component analysis (PCA). In particular, this method was used to unravel substitution vectors in solid solutions. PCA is a statistical procedure that transforms a number of possibly correlated variables into the same number of uncorrelated variables given by the eigenvectors of the covariance matrix, and called principal components. The first principal component (F1) account for as much of the variability in the data as possible, and thus corresponds to the highest eigenvalue of the covariance matrix; each of the succeeding components (F2, F3…) accounts for as much of the remaining variability as possible. For other details and examples of PCA applied to EMP data, refer to Tumiati et al. (2005 A, 2005 B, 2008, 2013).

207 Raman spectroscopy of selected samples has been carried out using a green (514 nm) laser
208 radiation, at the *Muséum National d'Histoire Naturelle* of Paris. In particular, Raman spectroscopy
209 was required for the identification of the HP $MnSiO_3$ polymorph pyroxmangite.
210
211 **5. Mineralogy and petrography of the Praborna ore**
212 *5.1 Basal levels*
213 The basal levels (Fig. 3; Table 1) are in contact with glaucophanite made up of glaucophane +
214 garnet + chloritoid + chlorite + paragonite and showing pseudomorphs after lawsonite (Martin et
215 al., 2008). These basal levels mainly contain braunite ($Mn^{2+}Mn^{3+}{}_6SiO_{12}$) and piemontite (Fig. 3),
216 minor quartz, omphacite, garnet, phengite and pyroxmangite, the HP polymorph of $Mn^{2+}SiO_3$ (Fig.
217 4A; see Raman spectrum of sample SM93 in Fig. 5). Hematite is the stable iron oxide (Fig. 4a),
218 while magnetite was never observed. Rutile and As-bearing apatite (Fig. 6a) are common
219 accessories. Sulphides were not observed, although they are reported in the host metabasites of the
220 Saint-Marcel valley, where Fe–Cu ores have been exploited in the past centuries (mines of Servette
221 and Chuc; e.g. Martin et al., 2008; Tumiati et al., 2008).
222 Omphacite in these levels is dark purple and known as a semiprecious stone called *violan* (Bondi et
223 al., 1978). It is a solid solution of jadeite (up to Jd_{64}), diopside and aegirine, with minor contents in
224 johansennite ($CaMn^{2+}Si_2O_6$) and namansilite ($NaMn^{3+}Si_2O_6$), often showing a complex zoning.
225 PCA indicates that the main substitution vector in omphacite, represented by the first principal
226 component F1 (79.55 % of the total eigenvalues), concerns augite (elements Ca, Mg, Fe^{2+}, Mn^{2+})
227 vs. jadeite + aegirine + namansilite (elements Na, Al, Fe^{3+}, Mn^{3+}). The second principal component
228 F2 (18.98 % of the eigenvalues) mainly represents the jadeite (Al) and namansilite (Mn^{3+}) vs.
229 aegirine (Fe^{3+}) substitution.
230 Omphacite always coexists with braunite and piemontite, forming cm-sized boudinaged bands
231 hosted by massive quartz. Braunite crystals can contain included and/or exsolved barite and
232 hollandite ($BaMn^{3+}{}_2Mn^{4+}{}_6O_{16}$), suggesting a possible presence of Ba in the initial braunite. Tumiati

et al. (2010) reported up to 194 ppm (µg/g) of Ba in these crystals, in addition to other trace elements (e.g. 2015 ppm Cu, 1101 ppm Zn, 272 ppm Sr, 2543 ppm Co and 404 ppm Ni). Piemontite is typically Sr-bearing and shows oscillatory zoning, following the coupled piemontite-(Sr) vs. Fe-epidote substitution. Tumiati et al. (2010) have shown that the Sr-rich parts of piemontite contain up to 459 ppm As, 361 ppm Zn, 937 ppm P, 508 ppm Ni and 767 ppm Ba. In some samples, epidote-group minerals display Mn-poor cores and Mn-rich piemontite rims. The transition between the two compositions is gradual without an obvious solution gap, and follows the substitution $Mn^{3+}_{+2}Al^{3+}_{-1}Fe^{3+}_{-1}$.

Garnet is a solid solution of spessartine and grossular with minor contents in calderite ($Mn^{2+}_3Fe^{3+}_2Si_3O_{12}$) and pyrope. The garnet crystals are generally only slightly zoned in these levels.

5.2 High-P veins

Veins crosscutting the basal levels are quartz-rich and contain piemontite, omphacite, braunite (Fig. 4b; Table 1), pyroxmangite and hematite. Piemontite is euhedral and commonly displays oscillatory zoning with REE and Sr substituting for Mn following the exchange $2\ Ca^{2+}_A + 1\ Mn^{3+}_M = 2\ Sr^{2+}_A + 1\ REE^{3+}_M$ (first eigenvector of the PCA; 80.4% of the total eigenvalues). The maximum contents in REE and Sr observed are 0.24 atoms per formula unit (a.p.f.u.) (Ce/La = 2.36) and 0.17 a.p.f.u., respectively (for 12.5 equivalent O). These oscillatory zones are sharp and superimposed to a weaker and more regular zoning involving Fe^{3+} *vs*. Mn^{3+}, suggesting an increase of the piemontite endmember from core to rim (second eigenvector of the PCA; 15.0% of the total eigenvalues).

Veins often contain pink Mn-bearing phengite, known as *alurgite*. Occasionally, As and Sb silicates and oxides occur, in particular ardennite (a rare hydrous silico-arseniate of aluminium and manganese; Fig. 6B) and the calcium antimonate romeite (Fig. 6c).

A quartz-rich vein, between the basal braunite/piemontite-rich and the upper garnet-rich levels (Fig. 3), contains emerald-green omphacite (Jd_{70}), minor Cr-rich phengite and (Cr, REE)-rich epidote-group minerals. Accessory minerals are Cr-bearing hematite (up to 3.51 wt% Cr_2O_3) and braunite

(up to 0.52 wt% Cr_2O_3). As-bearing apatite (up to 9.22 wt% As_2O_3), native Au and REE-vanadates (wakefieldite; M. Merlini pers. comm.; details provided elsewhere) have been found as accessory phases.

5.3 Upper levels

Upper levels (Fig. 3; Table 1) are dominated by garnet and quartz associated with hematite, pyroxmangite (Fig. 4c; see Raman spectrum of sample 1601 in Fig. 5) and/or an aegirine-rich Mn-bearing clinopyroxene known as *schefferite*. Garnet is zoned with grossular- and/or calderite-rich core and spessartine-rich rim (cf. also Cenki-Tok and Chopin, 2006). In the Fe^{3+}-rich core, Cr is present up to $Uv_{1.1}$ (0.022 a.p.f.u. per 12 equivalent O; 0.32 wt% Cr_2O_3). The epidote-group mineral manganiandrosite-(Ce) occurs instead of piemontite as an accessory phase (Cenki-Tok et al. 2006). Sb-rich pyrophanite ($MnTiO_3$) was also observed (Fig. 6d).

In one sample, dominated by tephroite, hausmannite and rhodochrosite, we observed a peculiar quartz-free assemblage, where braunite and pyroxmangite show resorption microstructures (Fig. 4d; Table 1).

6. Thermodynamic modelling

At Praborna, the occurrence of omphacite + quartz and of pyroxmangite (e.g. Maresch and Mottana, 1979) confirms that these Mn-rich metasediments equilibrated at HP conditions in the eclogite facies. Jadeite-rich omphacite in equilibrium with quartz occurs also in the pervasive veins that crosscut the basal layers, suggesting that an interaction with vein-forming fluids occurred also at HP. These fluids are likely derived from the dehydration of the slab and flushed the mélange rocks, like the serpentinite and glaucophanite now cropping out at the bottom of the sequence. This is the best of all possible environments to be considered, for verifying the mobility of the component oxygen in the slab. The importance of fO_2 in controlling the phase relationships of Mn-rich systems was first recognised by Muan (1959) and Huebner (1967), who demonstrated that, analogously to

285 the Fe–O system, Mn-oxides can be used as oxygen buffers because Mn shows changes in the
286 oxidation state from +2 to +4. Also, the presence of piemontite requires very high fO_2 to be
287 stabilized over garnet, as experimentally demonstrated by Anastasiou and Langer (1977), and
288 Keskinen and Liou (1979). However, such systems have been rarely adopted as redox sensors in HP
289 rocks, because the available experimental data are currently restricted to the $MnO–SiO_2–O_2$ and
290 $Al_2O_3–MnO–SiO_2–O_2$ systems at 0.4–2.5 GPa (Abs-Wurmbach et al., 1983; Abs-Wurmbach and
291 Peters, 1999).
292 At Praborna, the basal levels are characterised by the assemblage braunite + quartz, the stability of
293 which requires very high fO_2 ($\Delta FMQ = \log (fO_2^{sample} / fO_2^{fayalite+magnetite+quartz}) = +11$ at 0.8 GPa and
294 500 °C, estimated by Brown et al., 1978). These high fO_2 values have been interpreted as indicative
295 of highly oxidized rocks, inheriting the fO_2 of the sedimentary protolith. In this section, we quantify
296 the μO_2, fO_2 and nO_2 variables at Praborna, using a specific thermodynamical dataset customized
297 for Mn-rich systems and presented in Appendix.
298
299 *6.1 Modelling of the $MnO–SiO_2–O_2$ system*
300 The $MnO–SiO_2–O_2$ is the simplest petrological system that describes the phase relations between
301 Mn-silicates and oxides. Pure phases belonging to this system are: quartz, manganosite ($Mn^{2+}O$),
302 tephroite ($Mn^{2+}{}_2SiO_4$), pyroxmangite ($Mn^{2+}SiO_3$), rhodonite ($Mn^{2+}SiO_3$), hausmannite
303 ($Mn^{2+}Mn^{3+}{}_2O_4$), braunite ($Mn^{2+}Mn^{3+}{}_6SiO_{12}$), bixbyite ($Mn^{3+}{}_2O_3$) and pyrolusite ($Mn^{4+}O_2$). Solid
304 solutions are not expected in this system. Using literature (Table A-1 in Appendix) and new
305 experimentally derived thermodynamic data for these phases (Table A-2 and A-3 Appendix), we
306 were able to construct two diagrams (Figs. 7a and 7b), calculated at P = 2.1 GPa and T = 550 °C,
307 i.e. at the metamorphic conditions recorded by the slab lithologies in the Saint-Marcel valley
308 (Martin et al., 2008). Diagrams 7a and 7b consider, respectively, the component O_2 as "perfectly
309 mobile" (i.e., μO_2 and fO_2 are intensive independent state variables) and "inert" (nO_2 is an extensive
310 independent state variable). We recall that in these diagrams and in the following calculations, nO_2

311 is set to zero value for rocks in which all Fe and Mn occur exclusively in their divalent oxidation
312 state. Therefore, nO_2 could be regarded as extra moles of the component O_2 relative to a Fe^{3+}- and
313 Mn^{3+}-free reference composition (see also Section 2).
314 Figure 7a displays log (fO_2/1 bar) – μO_2 vs. X_{SiO2} (=SiO_2/($Mn^{2+}O$+SiO_2)). The bulk Mn^{3+}/Mn_{tot}
315 ratio is also reported (shaded areas in Fig. 7a and black dotted isopleths in Fig. 7b). For comparison,
316 reference redox buffers, such as, hematite + magnetite, pyrite + Fe-sulphate and piemontite + garnet
317 are shown in Figure 7a, where they are expressed as ΔFMQ, i.e. with reference to the fayalite +
318 magnetite + quartz buffer (FMQ).
319 The braunite + quartz + pyroxmangite assemblage of the basal levels at Praborna is stable for
320 almost the entire X_{SiO2} range (except for very low SiO_2 contents, where quartz disappears) at very
321 high fO_2 (ΔFMQ = +12.7), above the hematite–magnetite buffer and slightly above the piemontite–
322 garnet buffer. This is consistent with the occurrence of piemontite and hematite in basal levels
323 (Figs. 4a, b).
324 The upper levels of Praborna are characterised by the equilibrium between pyroxmangite, quartz,
325 garnet and hematite (Figs. 3, 4c), which are stable at ΔFMQ < +12.7 and X_{SiO2} > 0.5 according to
326 Figure 7a. In one quartz-free sample, we observed the assemblage braunite + hausmannite +
327 tephroite (blue fields in Figs. 7a, b; see also Fig. 4d) with relics of pyroxmangite. This latter
328 assemblage can be attained only for X_{SiO2} < 0.33 and log (fO_2/1 bar) between FMQ+4.1 and
329 FMQ+9.7. A further constraint is given by the occurrence of sulphates at Praborna (e.g. barite and
330 celestine), and the absence of sulphides. Chalcophile elements, such as Sb and As, partitionate into
331 silicates, phosphates and oxides (Fig. 6), suggesting that the fO_2 at Praborna is higher than the
332 pyrite–$FeSO_4$ buffer (i.e. ΔFMQ > +5.7), even in the most retrograde assemblages. Values of log
333 (fO_2/1 bar) in the range from FMQ+5.7 to FMQ+12.7 widely exceed those previously evaluated for
334 subduction environments (see Introduction and Section 7.2 below).
335 Figure 7b is the ternary chemography of the system $Mn^{2+}O$–SiO_2–O_2. Compositions are portrayed
336 in barycentric mole fractions. This diagram plots the relative positions of the phase assemblages

337 shown in Figure 7a, therefore unravelling the relationships between μO_2 (or fO_2) and the conjugate
338 variable nO_2 (see also Fig. 1). In terms of nO_2, the most reduced possible assemblages (i.e., the
339 poorest in component O_2) consist of tephroite + manganosite, pyroxmangite + tephroite, and quartz
340 + pyroxmangite, depending on $X SiO_2$ (Fig. 7a). These associations fall on the join SiO_2–$Mn^{2+}O$,
341 where nO_2 is null and $Mn^{3+}/Mn_{tot} = 0$. On the other hand, the most oxidized assemblage (i.e., the
342 richest in component O_2) is braunite + bixbyite, for which nO_2 and Mn^{3+}/Mn_{tot} range from 0.16 to
343 0.20 and from 0.86 to 1.00, respectively, depending on the phase proportions. The assemblage
344 bixbyite + hausmannite and bixbyite + hausmannite + braunite can therefore have the same
345 Mn^{3+}/Mn_{tot} ratio, provided that the abundance of hausmannite is sufficiently low. The Mn^{3+}/Mn_{tot}
346 ratio and nO_2 values are directly proportional only on the $Mn^{2+}O$–O_2 subspace of the chemographic
347 diagram. As a consequence, the equilibrium tie-lines of Figure 7b, which delimit the phase fields
348 with identical chemical potentials, crosscut the nO_2 and Mn^{3+}/Mn_{tot} isopleths at high angle. This
349 translates into a decoupling between μO_2, nO_2 and Mn^{3+}/Mn_{tot}, when comparing Figures 7a and 7b.
350 To better understand this concept, we reported a hypothetical metasomatic path represented by the
351 black arrow of Figure 7b. Evolution of the bulk composition along this path from the starting point
352 to the ending point induces a change of the assemblage hausmannite + braunite + tephroite (blue
353 field: $Mn^{3+}/Mn_{tot} = 0.70$; $\mu O_2 = -267$ kJ•mol^{-1}; $nO_2 = 0.13$) to the assemblage braunite +
354 pyroxmangite + quartz (red field: $Mn^{3+}/Mn_{tot} = 0.30$; $\mu O_2 = -219$ kJ•mol^{-1}; $nO_2 = 0.03$). Counter-
355 intuitively, it is therefore possible to *increase* μO_2 (and fO_2), while nO_2 and Mn^{3+}/Mn_{tot} actually
356 *decrease*. In this case, oxidation in terms of an increase of the intensive variable μO_2 (or fO_2)
357 actually corresponds to a decrease in nO_2 and Mn^{3+}/Mn_{tot}, and thus to a bulk reduction. The
358 Mn^{3+}/Mn_{tot} ratio is also depicted in Figure 7a by greyscale tones grading from black ($Mn^{3+}/Mn_{tot} =$
359 1) to white ($Mn^{3+}/Mn_{tot} = 0$), showing that the same Mn^{3+}/Mn_{tot} ratio can be found at different μO_2
360 conditions. Figures 7a and 7b show that the decrease in fO_2 from the basal (red) to the upper (blue)
361 levels of Praborna does not necessarily correspond to an increase in bulk Mn^{3+}/Mn_{tot} as one would
362 expect. The Mn^{3+}/Mn_{tot} ratio is also a function of phase abundances, which cannot be evaluated

using μO_2 (or fO_2) diagrams. Therefore, the high fO_2 values observed at Praborna cannot be considered a straightforward sign of high degrees of oxidation.

6.2 Comparison with the FeO–SiO₂–O₂ system

The peculiarity of the MnO–SiO₂–O₂ system is mostly related to the occurrence of braunite, a compound that does not have an analogue in the well known FeO–SiO₂–O₂ system. In order to explore differences and similarities between Mn- and Fe-bearing assemblages, we have constructed a four-component, FeO–MnO–SiO₂–O₂, compositional space shown in Figure 8. Analogously to Figure 7b, also in this diagram the quantity of the component oxygen (nO_2) is treated as an independent state variable, and fO_2 (expressed as ΔFMQ in the figure) is dependent. Every Mn-bearing phase has a corresponding Fe-bearing phase, except braunite. While hematite and magnetite can coexist with quartz, hausmannite and bixbyite cannot, because of the stability of braunite. In Figure 8, the high-fO_2 phase assemblage braunite + pyroxmangite + quartz + hematite of the basal levels (red volume) can be accessed from the low-fO_2 braunite + hausmannite + tephroite + hematite assemblage of the upper levels (blue volume) just by adding silica (e.g. via a metasomatic agent), even decreasing nO_2, similarly to what displayed in Figure 7b. The grey plane in Figure 8 represents the surface where nO_2 is constant and is drawn to highlight the decoupling between oxygen intensity (fO_2) and extensity (nO_2). Moving along this plane it is possible to cross ultra-high fO_2 (e.g. red volume, ΔFMQ = +12.7) and ultra-low fO_2 (e.g. light green, ΔFMQ = -18.1) assemblages at constant nO_2, which means without changing the bulk "redox budget" (Evans, 2006) of the rock.

Therefore, although the braunite + pyroxmangite + quartz + hematite assemblage of the basal levels of Praborna shows an ultra-oxidized redox state in terms of intensive redox parameters (ΔFMQ = +12.7), it could have the same quantity of O_2 component as magnetite- and even ultra-reduced wüstite-bearing assemblages.

7. Discussion

In this section, we re-discuss the concept of oxidation degree of slab rocks, emphasizing the choice between intensive (μO_2 or fO_2) and extensive (nO_2) parameters to describe properly redox conditions. In general, we will demonstrate that the oxidation degree of rocks is definitely a relative concept, dependent on the variable used to describe it.

7.1 Oxygen chemical potential versus oxygen molar quantity: is oxygen a "perfectly mobile" or an "inert" component?

The rocks of Praborna clearly suggest that even in the presence of pervasive flux of fluids, the homogenization of μO_2 was not attained. In fact, if oxygen had been perfectly mobile, μO_2 (and fO_2) would have been constant but, on the contrary, while the country-rock pyrite-magnetite-bearing glaucophanite records $\Delta FMQ < +2.6$ (Fig. 7a), the adjacent basal Mn-rich quartzites attain $\Delta FMQ \geq +12.7$. Moreover, we recognised a mineralogical variability between the basal and upper levels, reflecting ΔFMQ down to +5.7. These observations suggest that, in these rocks, oxygen can hardly be considered a "perfectly mobile" component, as defined by Korzhinskii (1959); thus, the description of the redox conditions of such petrological systems should not be described by μO_2 (or fO_2) as an *independent* state variable. The introduction of its conjugate variable nO_2 is instead required, μO_2 becoming *dependent* of nO_2. Figures 7a, 7b and 8 warn against the undiscriminating use of μO_2 (or fO_2) as univocal indicator of the redox state of a rock system. Especially in multi-component and metasomatic systems, the nO_2 and μO_2 (or fO_2) could be well decoupled.

In order to enlighten this concept, we can make a comparison with a more intuitive analogue: P and V is a couple of intensive and extensive variables similar to μO_2 and nO_2, respectively. Pressure P (like μO_2 or fO_2) is generally considered as an independent variable imposed upon the system by its environment, to which the system responds by adapting the conjugate variable V (similarly to nO_2), in order to reach the state of equilibrium. However, in a few particular cases, like fluid inclusions, V

414 is imposed by the surroundings, which may induce local *P* heterogeneities, like overpressures at the
415 inclusion scale; in that case, *V* should be considered as the independent variable and *P* the conjugate
416 dependent variable. This occurs when volumes cannot adjust as easily as pressures. In our case,
417 nO_2, in part inherited from the sedimentary protolith, cannot adjust itself easily – in other terms, O_2
418 not a "perfectly mobile" component. This generates local μO_2 heterogeneities, and nO_2 should be
419 considered as the independent variable that determines the redox state.
420
421 *7.2 Consequences for fO_2 estimates in subduction zones*
422 In a multi-component system, the chemical potential of each component, including oxygen, is
423 ideally homogeneous, i.e. equal in all the phases at equilibrium. As seen in Figures 7a, 7b and 8,
424 different mineralogical associations will be characterised by different chemical potentials, including
425 μO_2, and thus fO_2, even when they display the same nO_2 or the same Fe^{3+} and Mn^{3+} contents. In
426 fact, two variables in a conjugate pair, such as μO_2 (or fO_2) and nO_2, are coupled, i.e. both increase
427 or both decrease, only if all the other molar quantities are kept at constant values. The addition of
428 SiO_2 or FeO components, for example via a metasomatic process, can produce assemblages
429 characterised by different fO_2 without necessarily changing the redox budget. This consideration
430 warns against the indiscriminate comparison of fO_2 data for rocks characterized by different bulk
431 composition or simply by different mineral assemblages, because it may lead to apparent redox
432 heterogeneities, wherever μO_2 cannot be considered as an independent variable (i.e., where O_2 is
433 not "perfectly mobile" and therefore rocks could be not in equilibrium to each other). Therefore,
434 heterogeneities in fO_2 do not necessarily require the mobility of redox species.
435 In subduction zones, fO_2 corresponding to a range of ΔFMQ from 0 to +2 has been estimated on
436 carbonate-bearing mantle-wedge peridotite from the Sulu UHP terrane (China) by Malaspina et al.
437 (2009), whereas eclogites from the same area are characterised by ΔFMQ from +2.5 (Cao et al.,
438 2011; massive lawsonite eclogite) to ca. +4 (Cao et al., 2011; foliated clinozoisite + glaucophane
439 eclogite) and ca. +4.5 (amphibole eclogite; Mattinson et al., 2004). Difference in fO_2 between

peridotite and eclogite are reported also in the Western Gneiss Region of Norway, where Malaspina et al. (2010) estimated ΔFMQ of -2–0 for garnet websterites, while Donohue and Essene (2000) and Boundy et al. (2002) estimated ΔFMQ in the range +2.5– +3.0 for eclogite-facies marbles.

Although it is unclear, at present, whether heterogeneities in fO_2 in the slab (see also Foley, 2011) should be ascribable to differences in chemical–mineralogical composition, to lack of μO_2 equilibration, or to differences in redox budget, the case of Praborna appears paradigmatic and suggests that metasomatic processes could lead to ultra-high fO_2 conditions despite a modest, if any, bulk oxidation in terms of nO_2,

In order to compare the Praborna metasediments with other slab rocks and the corresponding mantle wedge, we need to evaluate the oxidation states of representative rocks in terms of nO_2. Unlike for μO_2 (or fO_2), the quantification of nO_2 depends on the mineral abundances. Typically, nO_2 may vary in an oxygen buffer assemblages (i.e., oxygen can be added or subtracted) without a change of μO_2 (or fO_2). For example, 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).

Estimates of nO_2 provided below take into account the mineral mode in different subduction-related rock types. They should be regarded as an attempt to assess the magnitude of the redox budget of the subducting slab pile and its overlying mantle wedge. Concerning HP rocks, only few analytical data allowing a mass balance of the component oxygen are reported in literature. We profit of the case of HP rocks from Sulu (China), a unique region where the Fe^{3+} contents of garnet and clinopyroxene have been measured both in wedge peridotite (Malaspina et al., 2009; 2012) and in slab eclogite (Proyer et al., 2004).

For peridotite mineral assemblages, the contribution of garnet to nO_2 (cf. Fig. 7b and 8) is the amount of excess oxygen with reference to a Fe^{3+}-free system, provided by the skiagite ($Fe^{3+}_2Fe^{2+}_3Si_3O_{12}$) component. In the following idealized mass balance, oxygen (O_2) is not regarded

as a phase or species but merely as a component and therefore can be made explicit:

$1.00 \times (FeO)_{0.59}\bullet(SiO_2)_{0.35}\bullet(O_2)_{0.06}$ [skiagite] =

$0.71 \times (FeO)_{0.67}\bullet(SiO_2)_{0.33}$ [fayalite] + $0.24 \times (FeO)_{0.50}\bullet(SiO_2)_{0.50}$ [ferrosilite] + 0.06 O_2 (Eq. 1).

This equation, after Luth et al. (1990), has been rewritten here expressing compounds as molar fractions of the independent components SiO_2, FeO, MnO and O_2 (see Section 2; Spear et al., 1982), allowing a direct comparison of the excess O_2 with different barycentric representations (Figs. 7b and 8). In the discussion below, we will use the same convention to express chemical compositions of minerals and rocks.

According to Eq. 1, one mole of pure skiagite would lead to 0.06 mole of excess O_2. Because Malaspina et al. (2009) reported garnet containing up to 6 mol% of skiagite, one mole of garnet from Sulu peridotite contributes for the 6 percent of 0.06 mole of O_2, i.e. for 3.6 millimoles of excess O_2.

In mafic eclogites, a model redox mass balance for skiagite can be written as:

$1.00 \times (FeO)_{0.59}\bullet(SiO_2)_{0.35}\bullet(O_2)_{0.06}$ [skiagite] = $+1.37 \times (FeO)_{0.43}\bullet(Al_2O_3)_{0.14}\bullet(SiO_2)_{0.43}$ [almandine] - $0.39 \times (Al_2O_3)_{0.5}\bullet(SiO_2)_{0.5}$ [kyanite] - 0.04 SiO_2 [quartz/coesite] + 0.06 O_2 (Eq. 2).

The coefficients for O_2 are the same in Equations 1 and 2, suggesting that in both mafic and ultramafic rocks the excess oxygen is 0.06 mole of O_2 per 1 mole of skiagite component.

Profiting of the garnet composition reported by Proyer et al. (2004), containing up to 5 mol% of skiagite, the contribution of one mole of garnet from Sulu eclogite is therefore the 5 percent of 0.06 moles of O_2 (v. Eq. 2), i.e. 3.0 millimoles of excess O_2 per 1 mole of garnet.

As peridotitic and eclogitic garnets display comparable skiagite content (~5% in eclogite and ~6% in peridotite), the nO_2s for one mole of garnet are also comparable (3.6 and 3.0 millimoles in

peridotite and eclogite, respectively).

The contribution of clinopyroxene to the bulk oxidation can be evaluated on the basis of the aegirine ($NaFe^{3+}Si_2O_6$) component, which can be expressed in the following way, for peridotite (Eq. 3) and eclogite (Eq. 4) assemblages respectively.

$$1.00 \times (Na_2O)_{0.13}\bullet(FeO)_{0.27}\bullet(SiO_2)_{0.53}\bullet(O_2)_{0.07}\ [\text{aegirine}] = 0.80 \times (Na_2O)_{0.17}\bullet(Al_2O_3)_{0.17}\bullet(SiO_2)_{0.67}\ [\text{jadeite}] - 0.80 \times (FeO)_{0.50}\bullet(SiO_2)_{0.50}\ [\text{ferrosilite}] + 0.13 \times (FeO)_{1.00}\bullet(SiO_2)_{1.00}\bullet(Al_2O_3)_{-1.00}\ [\text{Fe Tschermak}] + 0.80 \times (FeO)_{0.67}\bullet(SiO_2)_{0.33}\ [\text{fayalite}] + 0.07\ O_2 \qquad \text{(Eq. 3)}.$$

$$1.00 \times (Na_2O)_{0.13}\bullet(FeO)_{0.27}\bullet(SiO_2)_{0.53}\bullet(O_2)_{0.07}\ [\text{aegirine}] = 0.80 \times (Na_2O)_{0.17}\bullet(Al_2O_3)_{0.17}\bullet(SiO_2)_{0.67}\ [\text{jadeite}] + 0.53 \times (FeO)_{0.50}\bullet(SiO_2)_{0.50}\ [\text{ferrosilite}] - 0.13\ SiO_2\ [\text{quartz/coesite}] - 0.27 \times (Al_2O_3)_{0.5}\bullet(SiO_2)_{0.5}\ [\text{kyanite}] + 0.07\ O_2 \qquad \text{(Eq. 4)}.$$

Similarly to equalities involving garnet in Equations 1 and 2, the coefficients of O_2 in Equations 3 and 4 are identical and independent on the system chosen, accounting for 0.07 mole of excess O_2 per 1 mole of pure aegirine. Clinopyroxene from Sulu peridotite contains 5 mol% of aegirine endmember (Malaspina et al., 2012), while clinopyroxene from eclogite contains 6 mol% of aegirine (Proyer et al., 2004). Therefore, one mole of clinopyroxene contributes to 3.5 and to 4.2 millimoles of excess O_2 in peridotites and mafic eclogites, respectively.

On the basis of the above considerations, a bimineralic eclogite composed of 50 mol% of garnet and 50 mol% of clinopyroxene would be characterized by 3.6 millimoles of excess O_2 per mole of a rock, whose composition is expressed as molar fractions of oxides. On the other hand, assuming 5 mol% of garnet and 5 mol% of clinopyroxene, a peridotite would be characterized by 0.36 millimoles of excess O_2 per mole of rock, which means one order of magnitude less.

Metasedimentary rocks at Praborna display nO_2 that can be estimated on the basis of the proportions between pyroxmangite, braunite and quartz (see Fig. 7b). Considering the bulk

chemical and mineralogical compositions reported by Tumiati et al. (2010), we estimated average contents of ca. 95 mol% of quartz and 5 mol% of pyroxmangite + braunite. Although the available data are not sufficient to determine the pyroxmangite/braunite ratio, we can estimate that the braunite abundance equals that of pyroxmangite, being the first mineral more abundant in the basal levels and the second in the upper levels. Braunite and pyroxmangite can be written respectively as $(MnO)_{0.74}•(SiO_2)_{0.11}•(O_2)_{0.16}$ and $(MnO)_{0.50}•(SiO_2)_{0.50}$ (see Fig. 7b). Therefore, only braunite can contribute to the excess O_2 of the Mn-rich metasediments of Praborna, at the rate of 2.5% of 0.16 moles of excess O_2, i.e. 4.0 millimoles of excess O_2 per 1 mole of rock. This value is nearly identical to the excess O_2 of the Sulu eclogite, suggesting that the Mn-rich metasediments of a subduction mélange can display towards the mantle an oxidizing power comparable to that of slab rocks, despite the presence of ultra-high fO_2 mineral assemblages.

As a consequence, a likely scenario for the slab-mantle interface in natural geodynamic environments is illustrated in Figure 9. Mass transport and metasomatism are supported by chemical gradients, notably by gradient in nO_2 across rocks of the subduction channel towards the mantle hanging-wall. Dehydration processes trigger fluid flow, which is localized in shear zones, and open fractures and pervasive microfractures. While ΔFMQ is likely very inhomogeneous, reflecting the different bulk chemical–mineralogical compositions and the limited mobility of oxygen, the oxidation degree of the subduction channel, expressed in terms of nO_2, is expected to be much smoother. In the conceptual model of Figure 9, a sort of metasomatic front develops from the slab to the overlying mantle wedge passing through a transitional layer of mélange rocks. Although fluids cannot transport oxygen as a major volatile species, they are expected to promote mass transfers and to affect the attainment of equilibrium and kinetics of reactions (Lasaga and Rye, 1993; Marschall and Schumacher, 2012). Therefore, oxygen is expected to be transported, especially along fractures and veins (see inset of Fig. 9), possibly through mechanisms of dissolution-reprecipitation of O-enriched oxides and silicates. The front is possibly sustained also by the strong inverse thermal gradient across the slab surface, which is evaluated to be in the order

544 of -20 °C/km (Arcay et al., 2007). Whether a thermophoretic effect at the slab–mantle interface is
545 able to contribute to the O_2 component redistribution or mass-transport is driven mainly by
546 chemical potential gradients and to advective processes (e.g., Gerya and Yuen, 2003; Marschall and
547 Schumacher, 2012) is an open challenge for understanding rock diversity at subduction zones.
548
549 **8. Conclusions**
550 Praborna HP veined Mn-rich rocks record environmental conditions typical for a subducting slab
551 setting. Although veining and growth of "pegmatoid" HP minerals might suggest an open system,
552 characterized by large fluid-rock ratios, the extremely high fO_2 deduced from Mn–Fe-rich mineral
553 assemblages clearly indicates that oxygen can hardly be considered as a perfectly mobile
554 component. As a consequence, μO_2, and therefore fO_2, should not be regarded as long-range
555 properties, indicative of the redox state of the entire rock column of a subduction zone, from the
556 dehydrating oceanic crust to the overlying mantle wedge. On a more general basis, the comparison
557 of fO_2 retrieved from different bulk compositions and phase assemblages may suggest redox
558 heterogeneities in subduction zones, even if the distribution of oxygen is expected to be much more
559 continuous, ranging from a maximum in the mafic eclogites, derived from the altered oceanic
560 basalts and gabbros, and in the sediments of the slab, down to a minimum in the overlying
561 peridotites of the mantle hanging-wall.
562
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Appendix A. Thermodynamic calculations and supplementary data

Phase diagrams of Figures 6 and 7 have been drawn on the basis of thermodynamic calculation performed with the Perple_X computer package (http://www.perplex.ethz.ch; Connolly, 1990) using a specifically compiled thermodynamic dataset of Mn-rich minerals and oxygen buffers (see Table A-1). Thermodynamic parameters are available in the literature apart from the thermal expansion coefficients of braunite and pyrolusite, unknown as far as we are aware, and which we derived experimentally from their cell-volume changes during heating (cf. Tables A-2 and A-3). The dataset used has proven to be robust in reproducing the results of the HP experiments of Abs-Wurmbach et al. (1983).

Thermal expansion of braunite

Braunite at Praborna is invariably polycrystalline. Consequently, powder X-ray diffraction methods rather than single crystal methods were used to measure the thermal expansion of this mineral. Average composition of 11 analyses can be expressed on the basis of 8 cations and 12 O as (standard deviation in parenthesis):

$Mn^{3+}_{5.92(8)}\ Mn^{2+}_{0.82(6)}\ Mg_{0.13(2)}\ Fe^{3+}_{0.06(3)}\ Ca_{0.05(2)}\ Al_{0.03(1)}\ Si_{0.99(5)}\ O_{12}$.

Powder diffraction patterns were recorded on a Philips X'Pert PRO automatic powder diffractometer, using a normal focus Cu X-ray tube operating at 40 kV and 40 mA**.** The vertical goniometer in Bragg-Brentano geometry (with 240 mm radius) was equipped with a first divergence slit, a Soller slit and a 0.2 mm receiving slit upstream of a curved graphite diffracted-beam monochromator PW3123/10. For high temperature data collection, the diffractometer was equipped with a heating camera Anton Paar HTK16.

The powder was spread as a thin film directly on the platinum thermocouple (heating strip) and the beam impingement area was restricted to a narrow central section of the strip, so that thermal gradients through and across the sample were minimized. The expansion of Al_2O_3 NIST standard reference material 676 was used for temperature calibration. We estimate the uncertainty of temperature measurement at the sample to be 10 °C.

A first data collection performed in continuous mode in the 16–120° 2θ range revealed the good crystallinity and the purity of the phase. Successively, data were collected with a step increment of 0.02° and a step counting time of 5 seconds in the 90–120° 2θ range.

The position of each Bragg peak was measured by means of "X'pert high score" program and indexed by comparison with the calculated pattern obtained by GSAS program (Larson and Von Dreele, 1994). Angular values and respective crystallographic planes were used to refine lattice parameters *a* and *c* by means of the XLAT program (Rupp, 1988). Diffractometer alignment was repeatedly checked by carrying out data collection of NBS640B silicon standard and obtaining *a* values of 5.4308(1) and 5.4310(1) Å.

In Table A-2, we reported the molar volume of braunite at *T* ranging from 25 to 600 °C. These data have been fitted with the expression reported in Table A-1, in order to obtain the volumetric expansion parameter *b1*.

Thermal expansion of pyrolusite

Although pyrolusite has proven to be unstable at the investigated conditions, this mineral was included in calculations because it belongs to the investigated petrological system. Thermal expansion data were collected in Bragg-Brentano mode on a Bruker AXS D8 Advance, operating in θ:θ geometry equipped with Nickel filtered Cu-Kα radiation and a position-sensitive Lynxeye detector. Generator settings were 40 kV and 40 mA. Reagent-grade MnO_2 was deposited in the aluminium sample holder of a custom-made heating chamber, operating in air, supplied by *Officine*

619 *Elettrotecniche di Tenno*, Ponte Arche, Italy. A series of scans, lasting ca. 30 min each, were
620 collected in isothermal conditions, in the *T* range 100–600 °C at 50 °C steps.
621 Cell parameters were refined by the whole pattern structureless refinement technique (Le Bail et al.,
622 1988) with the aid of the TOPAS-R program (V. 3.0, Bruker AXS, Karlsruhe, Germany). Estimated
623 standard deviations were computed under the assumption that, in the absence of systematic effects,
624 errors followed a normal distribution. Similarly to braunite, cell volume data (Table A-3) have been
625 fitted with the expression reported in Table A-1, in order to obtain the volumetric expansion
626 parameter *b1*.
627

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823

824 **Tables**

825 Table 1: Representative compositions of major minerals forming the assemblages of Praborna
826 occurring in the basal levels, upper levels, HP veins and the SiO_2-undersaturated sample C4.

827 Table A-1: Thermodynamic database used for calculations.

828 Table A-2: *V*-*T* data of braunite**.**

829 Table A-3: *V*-*T* data of pyrolusite**.**

830

831 **Figure captions**

832 Figure 1: Appearance of two-phase field (A + B) between two one-phase fields (A, B) in a unary
833 system, when the molar quantity nO_2 is introduced instead of its conjugate potential μO_2. Vertical
834 lines in *b* are isothermal tie-lines accounting for the difference in molar quantity nO_2. Redrawn
835 from Hillert (1985).

836

837 Figure 2. Geological sketch map of the Saint-Marcel valley showing the Praborna mine (45.6796°
838 lat. N; 7.4495° long. E) and the principal lithologies occurring in the area.

839

840 Figure 3. Schematic section of the Mn ore. Basal levels are highly fractured and show pervasive
841 veining. The enlargement shows a stockwork of quartz- and feldspar-filled veins cutting the
842 massive ore mainly consisting of braunite (black) and piemontite (purple) (orange crusts are
843 lichens). Note that the growth of "pegmatoid" piemontite crystals is perpendicular to the fracture
844 walls (black arrow). Basal levels and veins contain omphacite in equilibrium with quartz and are in
845 contact with glaucophanites. The upper part of the ore gradates into garnet + quartz ± pyroxmangite
846 assemblages, and is overlaid by Mn-poor micaschists.

847

848 Figure 4. Representative mineral assemblages characterizing the Mn ore of Praborna. (a) Colorized
849 Back Scattered Electron (CBSE) image of braunite (blue), pyroxmangite (green) and hematite
850 (violet) coexisting with quartz in the basal level. (b) Transmitted Light Photomicrograph (TLP) of
851 the vein containing Mn-rich purple omphacite (violan) in equilibrium with quartz, braunite and
852 piemontite. (c) TLP of hematite in equilibrium with garnet, pyroxmangite and quartz in the silica-
853 rich assemblages of the upper level. (d) CBSE image of quartz-free sample from the upper level,
854 showing the replacement of pyroxmangite (yellow) + braunite (blue) by tephroite (blue-green) and
855 hausmannite (violet). Rhodochrosite (red) is a late mineral.
856
857 Figure 5. Raman spectra of $MnSiO_3$ in selected samples (basal levels: SM93; upper levels: 16/01)
858 compared with those of reference pyroxmangite and rhodonite from the mineralogical collection of
859 the *Muséum National d'Histoire Naturelle* in Paris. These spectra show that $MnSiO_3$ at Praborna is
860 the high-pressure pyroxmangite polymorph.
861
862 Figure 6. As- and Sb-bearing minerals characterizing the parageneses at Praborna. (a) basal levels;
863 zoned apatite crystal richer in As at the rim (cathodoluminescence image); (b) basal levels;
864 ardennite-(As) $(Mn,Ca,Mg)_4(Al,Mg,Fe)_6(SiO_4)_2(Si_3O_{10})(AsO_4,VO_4)(OH)_6$ in equilibrium with
865 garnet and rutile showing a Sb-rich rim (BSE image); (c) basal levels; romeite
866 $(Ca,Fe,Mn,Na)_2(Sb,Ti)_2O_6(O,OH,F)$ showing oscillatory zoning (BSE image); (d) upper levels;
867 hematite associated to Sb-rich pyrophanite ($MnTiO_3$) (BSE image).
868
869 Figure 7. Thermodynamic model of the system $MnO–SiO_2–O_2$, calculated for P = 2.1 GPa and T =
870 550 °C. (a) μO_2 (kJ•mol^{-1}) and log (fO_2/1 bar) vs. $SiO_2/(MnO+SiO_2)$ phase diagram. Compositions
871 are represented in barycentric mole fractions. Considered phases are: quartz (qtz); manganosite
872 (mang); pyroxmangite (pxmn); tephroite (teph); hausmannite (hsm); braunite (braun); bixbyite
873 (bxb); pyrolusite (not stable at these conditions). In addition to μO_2 (right vertical axis), the

corresponding log (fO_2/1 bar) and ΔFMQ values (black and grey numbers, respectively, on the left vertical axis) are also reported for comparison. Dashed grey lines are the univariant equilibria piemontite = garnet + H_2O + O_2, CuO = Cu_2O + O_2, Cu_2O = Cu+O_2, $FeSO_4$ = pyrite + hematite + O_2, hematite = magnetite + O_2, and magnetite + quartz = fayalite + O_2. The red and blue horizontal lines indicate the associations quartz–braunite–pyroxmangite (basal levels) and braunite–haussmanite–tephroite (upper levels), respectively. Shaded fields represents in grey scale the ratio Mn^{3+}/Mn_{tot} as suggested by Figure 7b. (b) Ternary chemography of the system MnO–SiO_2–O_2. Compositions are represented in barycentric mole fractions (i.e., sum of coordinates = 1). The diagram is stretched vertically (the upper O_2 vertex is not shown) in order to highlight the assemblages without oxygen as a free phase. nO_2 represents the excess of O_2 component with reference to the Mn^{3+}-free system SiO_2–MnO. μO_2 (kJ•mol^{-1}) is reported for each divariant field. Thick dotted lines are Mn^{3+}/Mn_{tot} isopleths, whereas horizontal dotted lines are nO_2 isopleths. The quartz–O_2, braunite–O_2 and bixbyite–O_2 tie-line (dotted arrows) are virtual, because O_2 is not thought to be a real phase at these conditions. The coloured fields correspond to the typical Praborna assemblages as in Figure 7a. Black arrow is a hypothetical metasomatic path from SiO_2-poor to SiO_2-enriched assemblages, where nO_2 and the ratio Mn^{3+}/Mn_{tot} decrease while μO_2 increases.

Figure 8. Thermodynamic model of the system MnO–FeO–SiO_2–O_2 calculated for P = 2.1 GPa and T = 550 °C. Compositions are represented in barycentric mole fractions. nO_2 represents the excess of component O_2 with reference to the Fe^{3+}- and Mn^{3+}-free system FeO–SiO_2–MnO. ΔFMQ is reported for each 4-phases assemblage (e.g., +12.7 for pyroxmangite–quartz–braunite–hematite). The grey plane represents the locus of points at constant value of nO_2 and intersects all the assemblages, with ΔFMQ ranging from -18.1 (wüstite–fayalite–magnetite–manganosite, light green volume), to +9.7 (tephroite–hausmannite–braunite–hematite, blue volume, upper levels), and to +12.7 (braunite–quartz–pyroxmangite–hematite, red volume, basal levels).

Figure 9. Oxygen in the subduction channel. Cartoon redrawn after Konrad-Schmolke et al. (2011) showing a patchy and heterogeneous distribution of fO_2 (see ΔFMQ; see also Fig. 12 in Foley, 2011), but a more regular gradient of nO_2 (i.e. the quantity of oxygen in excess compared to Fe^{3+}- and Mn^{3+}-free systems). In terms of nO_2, the mélange appears as a metasomatic front from the more oxidized slab to the less oxidized mantle wedge. Oxygen can be transported along fractures and veins through dissolution-reprecipitation of oxides and silicates fluxed by fluids. See text for further details.