

## Article

# Fluid Redox Fingerprint of the $\text{CaCO}_3$ +Antigorite Dehydration Reaction in Subducted Metacarbonate Sediments

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**Abstract:** Antigorite dehydration is a process able to release, in comparison with other minerals, the highest amount of  $\text{H}_2\text{O}$  from a subducting slab. The released fluid delivers critical elements (e.g., S, Cu, and REE) to the overlying subarc mantle, modifying the mantle source of arc magmas and related ore deposits. Whether antigorite breakdown produces oxidising or reducing fluids is debated. Whereas previous studies have investigated antigorite dehydration in serpentinites (i.e., in a (C)AMFS- $\text{H}_2\text{O}$  system), this contribution is devoted to the CMFS-COHS carbonate system, which is representative of the metacarbonate sediments (or carbonate-dominated ophiocarbonate rocks) that sit atop the slab. Thermodynamic modelling is used to investigate the redox effect of the carbonate-buffered antigorite dehydration reactions (i.e., brucite breakdown and antigorite breakdown) on electrolytic fluid geochemistry as a function of  $P$ - $T$ - $f\text{O}_2$ . The influence of  $P$ - $T$ - $f\text{O}_2$  conditions on the solubility of C and S, solute-bound  $\text{H}_2$  and  $\text{O}_2$ , fluid pH, the average valence states of dissolved C and S, and the fluid redox budget indicates that, in metacarbonate sediments, the  $\text{CaCO}_3$ +antigorite reaction tends to produce reducing fluids. However, the redox state of such fluids is buffered not only by the redox state of the system but also, most importantly, by concomitantly dissolving redox-sensitive minerals (i.e., carbonates, graphite, pyrite, and anhydrite). A qualitative correlation between the redox state of the system and the possible depth of fluid release into the mantle wedge is also derived.

**Keywords:** antigorite dehydration; redox; thermodynamic modelling; electrolytic fluid; redox budget; subduction; metacarbonate sediments; subduction zone fluids; carbon; sulfur



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## 1. Introduction

The subarc mantle is more oxidised than the surrounding subcontinental or suboceanic mantle (e.g., [1,2]). This trait dictates mantle melting behaviour and, consequently, the physicochemical properties of the resulting liquids and the related extraction of the critical elements (Cu, Mo, Au, and REE; [3,4]) necessary for ore-forming processes within the arc crust. The mantle wedge's metasomatism and oxidation are thought to be caused by slab-derived fluids that deliver oxidising redox-sensitive elements, such as O, H, S, C, Fe, and N.

Antigorite breakdown is the most significant dehydration event that occurs in the subducting slab at forearc-to-subarc depths. Antigorite is the dominant constituent of subducted serpentinites and ophiocarbonates, and it is also common in the impure marbles derived from metamorphism and the hydration of dolostones (e.g., [5]; Figure 1a). Antigorite dehydration is under scrutiny from the petrologic community due to its ambiguous role in influencing the geochemistry and, most importantly, the redox of fluids that interact with the mantle wedge [6–17]. More specifically, different views are reported in the

literature, stemming from the different strategies adopted for investigating this petrologic process, i.e., direct observations from the study of natural samples or indirect observations from experiments or thermodynamic modelling. Ultimately, three different views can be recognised:

- I. Antigorite breakdown produces oxidising fluids [7,8,11,13,15–17], thus straightforwardly explaining mantle wedge oxidation;
- II. Antigorite breakdown releases reducing fluids [6,9,10], implying that mantle wedge oxidation is either apparent or requires other processes to be explained;
- III. Antigorite breakdown produces either reducing or oxidising fluid (since it spans roughly 8–9 log  $fO_2$  [12,16], from a reduced  $-5$  to an oxidised  $+4$   $\Delta \log fO_2$  units with respect to the Fayalite–Magnetite–Quartz oxygen buffer, FMQ), depending on the  $P$ - $T$  path experienced by the subducted rocks [12] or on the pre-subduction redox state of the system [14].

All these studies investigate antigorite dehydration in serpentinites, i.e., in a (C)AMFS- $H_2O$  system. Interestingly, a recent experimental investigation [15] of carbonate-rich (up to 20 wt%) serpentinites highlights how graphite and, more markedly,  $CaCO_3$  decrease the  $P$ - $T$  conditions of antigorite destabilisation. Thus, this paper reveals that C is important for the metamorphic and redox evolution of antigorite-bearing rocks during subduction. Notably, such a role of C in modulating serpentinite redox evolution has been contemporaneously confirmed by field observations in the Monviso meta-ophiolite [16]. Moreover, most of the above studies investigated antigorite dehydration as a process producing OH or COH fluids, and only a few studies explored the release of SOH fluids [9,10,13,14], while none took into account the production of solute-bearing COHS fluids.

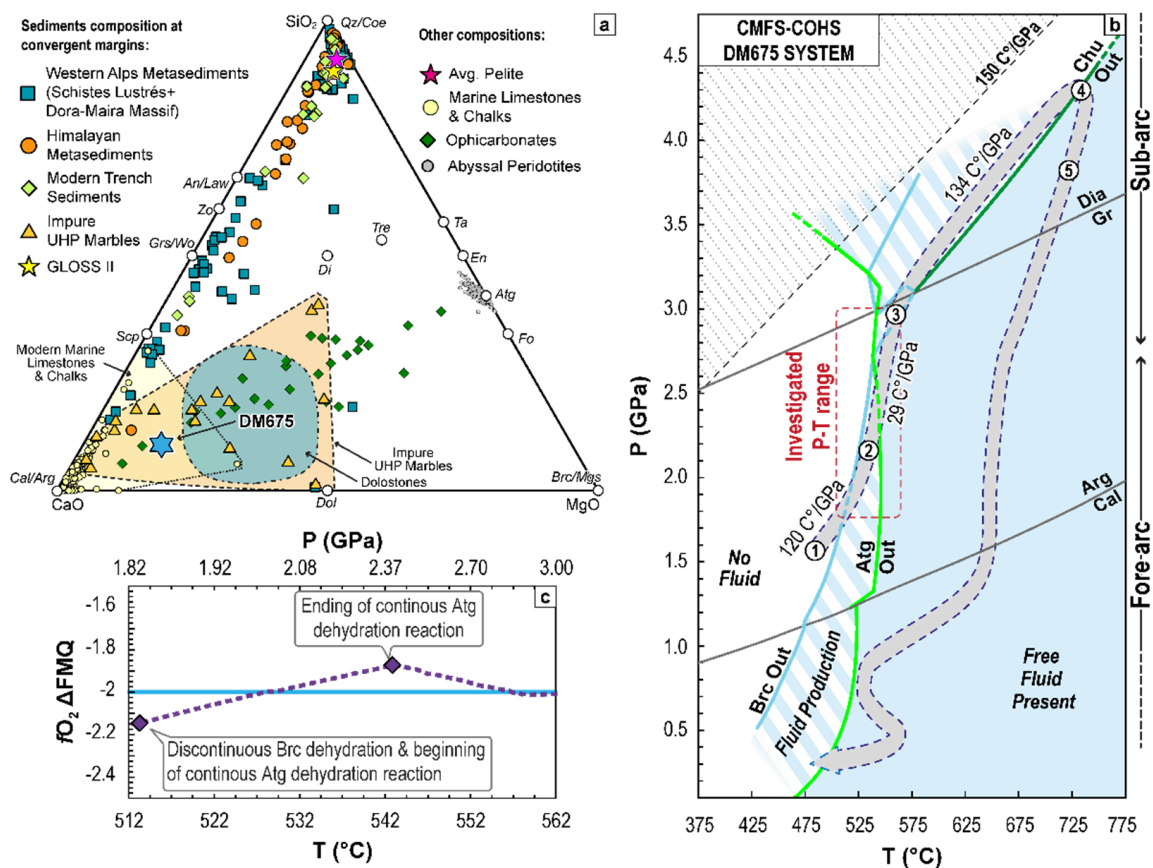
In this work, we model the  $P$ - $T$ - $fO_2$  evolution of an impure carbonatic system (i.e., the CM(F)S-COHS system) by using the electrolytic fluid thermodynamic approach. This work aims to investigate the redox state not only of the dehydration reactions involving antigorite (i.e., brucite and antigorite breakdown) but also of the produced COHS fluid under carbonate-buffered conditions.

Thermodynamic modelling was applied to an ultra-high pressure (UHP) impure marble from the Brossasco-Isasca Unit (BIU) of the Dora-Maira Massif (Italian Western Alps). Because of the mineralogy of such marble (i.e., calcite, dolomite, diopside, forsterite with minor tremolite, antigorite, talc, and brucite), its phase relations during metamorphism are similar to those of the classic ultramafic system represented by serpentinites; however, the presence of carbonates also makes the studied system interesting for application to ophicarbonate rocks (e.g., [5]). The refractory nature of Fe when being mobilised by aqueous fluids under metamorphic conditions diminishes the impact of its low amounts in the studied system on the resulting fluid chemistry (e.g., [18,19]). In addition to this, the lack of Fe allows for the decoupling of its potential influence in buffering the  $fO_2$  evolution of the antigorite dehydration reaction in carbonate-buffered systems.

The investigated  $P$ - $T$  conditions are those of the prograde path of the BIU (see the recent compilation of [20,21]) because (i) we can compare the results from the thermodynamic modelling with the mineral and fluid data available from the natural sample DM675 (see below), and (ii) this  $P$ - $T$  path can be considered representative of the  $P$ - $T$  evolution of the slab in cold subductions (e.g., [22]).

## 2. Geological and Petrological Setting

The investigated metasedimentary rock has been sampled from the Costa Monforte marble lens of the UHP Brossasco-Isasca Unit of the Dora-Maira Massif (e.g., [23–25]). The Alpine polyphasic  $P$ - $T$ - $t$  evolution of this unit has been determined through 40 years of multiple petrologic studies on several lithologies (see [20,21] for a review).



**Figure 1.** (a) Comparison between DM675 bulk composition ([26]; Table 1) and other subducted carbonate and carbonate-bearing metasediments from the Western Alps [27–30], Himalaya [31], modern trench sediments and GLOSS II [32], and other UHP localities (i.e., Sulu, Thiashan, Kokchetav; [33–35]). In addition, modern marine limestones and chalk are shown (see compilation in [36,37]). The average pelite composition is from [38]. Ophicarbonates are compiled from [39,40], and the abyssal peridotites are from [41]. All compositions are calculated as volatile-free and as mol%. (b) BIU  $P$ - $T$  path from [20,21]; the red box highlights the investigated  $P$ - $T$  range. The portrayed phase relationships are from the DM675 isochemical phase diagram in [26]. (c)  $T(P)$   $-fO_2$  evolution of sample DM675 in the investigated  $P$ - $T$  range using the oxygen chemical potentials, calculated along the prograde BIU  $P$ - $T$  path, from the  $P$ - $T$  DM675 isochemical phase diagram in [26].

The prominent petrologic and tectonic processes that occurred in the Brossasco-Isasca Unit during the investigated prograde to early-retrograde evolution are (numbers refer to those reported in Figure 1b) as follows: (1) a prograde stage at 450–570 °C and 1.0–1.8 GPa; (2) prograde dehydration reactions and intense Mg-metasomatism along shear zones at 520–540 °C and 1.6–2.3 GPa; (3) the development of a prograde foliation coupled with dehydration reactions, with multiple carbonate dissolution–precipitation events in marbles and local Mg-metasomatism in metagranitoids, at 540–560 °C and ca. 2.5–3.0 GPa (i.e., at the quartz–coesite transition); (4) UHP peak and low dehydration at ca. 730 °C and 4.3 GPa and dated at ca. 35 Ma; and (5) the development of the UHP main regional foliation during early, nearly isothermal, decompression at ca. 720–740 °C and 3.7–4.0 GPa [20,21,42–48].

The sample DM675 is a UHP impure calcitic–dolomitic marble composed of calcite (after former aragonite), dolomite, forsterite, and diopside. Its bulk composition (Table 1) is located along a chemical trend that joins the (hydrated) abyssal peridotites (i.e., the (C)MFS– $H_2O$  sub-system) to the marine limestones and chalks (i.e., the CM(F)(S)-COHS sub-system), and it is compatible with some carbonate-rich ophicarbonates (Figure 1a). The investigated sample records multiple carbonate dissolution–precipitation events during its HP–UHP prograde dehydration (Ferrando et al. [20]; Maffei et al. [26]). The composition

of the released fluid was a solute-bearing aqueous fluid, i.e., a fluid poor in Cl and in non-polar molecular species (such as CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>) but containing a dissolved load, ranging from a few percent up to 11 wt%, of other charged ions or neutral species (i.e., Si, Ca, Mg, Fe, C, S, O, and H; [26]).

**Table 1.** Bulk-rock composition of marble DM675 used in the calculations, as obtained by Maffei et al. [26]. The “oxidised” version of the DM675 bulk composition is obtained from the “starting” one by increasing only the O<sub>2</sub> in order to stabilise anhydrite. The “oxidised” version of the DM675 is only used for *P-T* phase diagram calculation in the Discussion Section (Section 5.4).

	Used (reduced) DM675 El mol	Oxidised DM675 El mol
Si	3.0186	3.0186
Fe <sup>2+</sup>	0.1171	0.1171
Mg	4.5242	4.5242
Ca	23.5540	23.5540
H <sub>2</sub>	2.7526	2.7526
C	23.5337	23.5337
S <sub>2</sub>	0.0604	0.0604
O <sub>2</sub>	41.7392	42.1649

### 3. Methods

Phase diagram sections ( $T(P) - fO_2$ ; Figure 2) were calculated using Perple\_X software (version 6.9.1; [49,50]) for the Ca–Mg–Fe–Si–C–O<sub>2</sub>–S<sub>2</sub>–H<sub>2</sub> (CM(F)S-COHS) chemical system, modelling part of the prograde BIU *P-T* path, between 512 and 562 °C and between 1.82 and 3.00 GPa (Figure 1b; Supplementary Table S1). Compositional phase diagrams were calculated with the “Lagged Speciation” algorithm [50], with condensed phase and molecular volatile species data from Holland and Powell ([51] revised 2018, version DS6.22) and solute species data from the DEW/HKF model of Sverjensky et al. ([52], revised 2017). For these calculations, the solvent consisted of a mixture of H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S, and C<sub>2</sub>H<sub>6</sub>. In particular, C<sub>2</sub>H<sub>6</sub> was added to the solvent to be used as a control for the molecular fluid model to check the reliability of hydrocarbons (heavier than methane) calculated via electrolytic fluid models in the fluid phase. CO and SO<sub>2</sub> were treated as solute species due to their low molar abundance in exploratory calculations. The Pitzer and Sterner [53] EoS was used to describe pure H<sub>2</sub>O and CO<sub>2</sub>; all other pure fluid properties were computed from the Redlich–Kwong EoS, and the Modified Redlich–Kwong (MRK) EoS of de Santis et al. [54] was used to compute the activities of all solvent species. To model the fluid solute composition and speciation, all fluid species were considered, except for those that replicate solvent species. The selected mineral pure phases were quartz, coesite, chondrodite, pyrite, graphite, and diamond. The used solution models were Holland and Powell [55] for olivine and clinopyroxene; Padrón-Navarta et al. [56] for antigorite; Evans et al. [57] for pyrrhotite; Anovitz and Essene [58] for calcite (and aragonite) and dolomite; the ideal solution model for talc, tremolite, Phase-A, and clinohumite; and the simplicial solution model for periclase.

As explained in a previous paper (i.e., [26]), the used DM675 bulk-rock composition (Table 1) was adjusted for O<sub>2</sub> content until it reproduced the observed microstructures, the presence of graphite as solid inclusions, and the composition of the fluid trapped within prograde-to-peak clinopyroxene as fluid inclusions [20,26].

The obtained bulk composition and *P-T* isochemical phase diagram were used to estimate the DM675  $fO_2$  as a function of *P* and *T* along the prograde *P-T* path of the BIU. The DM675's  $fO_2^{T,P}$  was calculated using the DM675  $\mu O_2$  sampled along the prograde BIU

$P$ - $T$  path ( $\mu_{2ROCK}^{T,P}$ ) in the  $P$ - $T$  isochemical phase diagram—calculated using electrolytic fluid models (Supplementary Figure S4 of [24])—and used in the following equation:

$$fO_2^{T,P} = \exp \frac{\mu_{2ROCK}^{T,P} - \mu_{2PURE}^{T,1bar}}{RT}$$

where  $\mu_{2PURE}^{T,1bar}$  is the chemical potential of pure oxygen calculated between 487 °C and 730 °C at 1 bar with Perple\_X (FRIENDLY subprogram) using the condensed phase and molecular volatile species data from Holland and Powell ([51] revised 2018, version DS6.22) and solute species data from the DEW/HKF model of (Sverjensky et al. [52], revised 2017).  $R$  is the gas constant (8.31446261815324 J/K mol). The position of the Fayalite–Quartz–Magnetite (FMQ) oxygen buffer ([59]; yellow line in Figure 2) was calculated as a univariant equilibrium, i.e., as  $T(P)$ - $fO_2$  Schreinemaker projections along the same  $P$ - $T$  path used for the  $T(P)$ - $fO_2$  isochemical phase diagrams. Perple\_X software (version 6.9.1; [49,50]) was used with the condensed phase and molecular volatile species data from Holland and Powell ([51] revised 2018, version DS6.22).

To evaluate the redox capacity of the fluid produced by the investigated system, a specific redox variable related to the sample's electron availability has to be used [60]. The redox budget (RB) is the product of the amount of redox-sensitive elements  $E$  ( $n_E$ ) and the number of electrons necessary to either oxidise or reduce a given element (at a starting valence state  $v_{sample}$ ) to another (reference) valence state ( $v_{reference}$ ; [60]):

$$RB = \sum n_E v_i = \sum n_E (v_{sample} - v_{reference})$$

The RB, which is expressed as moles, can also be used in terms of the unit of mass, and it is called the “specific redox budget” [61]; it is better suited to evaluate the fluxes of redox capacity carried by a fluid. In this study, the RB of the fluid is expressed as the “specific redox budget” (i.e., as the mol of the RB per kg of fluid:  $\text{mol } e^- / \text{kg}_{fluid}$ ). The conversion from the redox budget to the “specific redox budget” was accomplished with the following passages:

$$\begin{aligned} E(\text{mol}) \cdot \text{molar weight } E \left( \frac{\text{g}}{\text{mol}} \right) &= E(\text{g}) \\ \left[ \frac{E(\text{g})}{\sum E_{fluid}(\text{g})} \right] \cdot 1000 &= E \left( \frac{\text{g}}{\text{kg}_{fluid}} \right) \\ \left[ \frac{E(\text{g})}{\sum E_{fluid}(\text{g})} \right] \cdot 1000 &= E \left( \frac{\text{g}}{\text{kg}_{fluid}} \right) \\ E \left( \frac{\text{mol}}{\text{kg}_{fluid}} \right) \cdot (v_{sample} - v_{reference}) &= RB \left( \frac{e^- \text{mol}}{\text{kg}_{fluid}} \right) \end{aligned}$$

Sulfur RB was calculated for atomic S and not diatomic  $S_2$ . The mineral abbreviations are after [62].

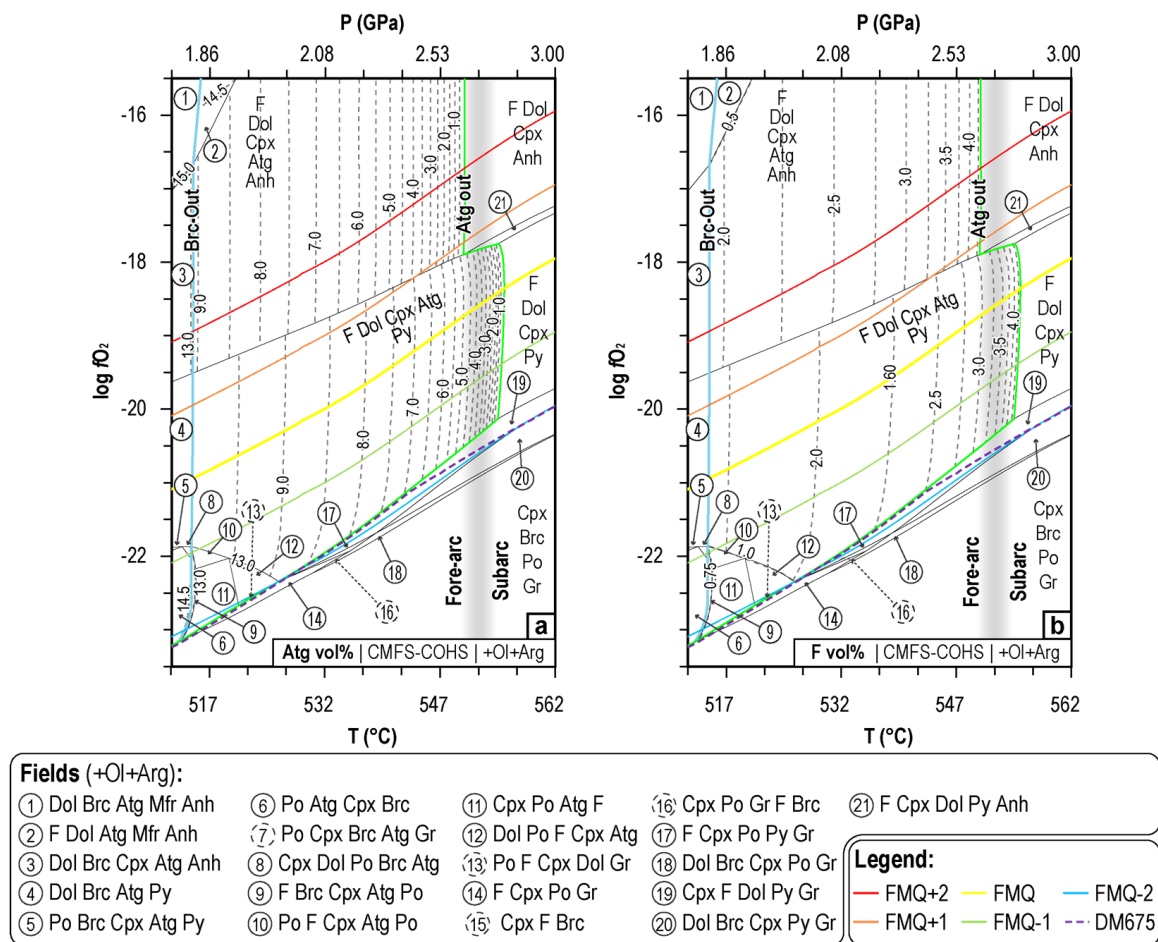
## 4. Results

### 4.1. $P$ - $T$ - $fO_2$ Mineral Phase Relationships during $CaCO_3$ + Antigorite Dehydration Reaction

To investigate the role of the  $CaCO_3$ +antigorite dehydration reactions in influencing the redox state of the released fluid, the system's pressure, temperature, and oxygen fugacity ( $fO_2$ ) have to be monitored.  $fO_2$  is an intensive variable, expressed as log units of  $fO_2$ , commonly used in petrology to investigate the redox character of an investigated system. To moderate the dependence of  $fO_2$  on  $P$  and  $T$ ,  $fO_2$  values are usually expressed as a deviation from the  $fO_2$  of a reference buffer under the same  $P$ - $T$  conditions. The most commonly used buffer is Fayalite–Magnetite–Quartz (FMQ). Thus, in the present work,  $fO_2$  is expressed as values of  $\Delta FMQ$ , with positive values referring to oxidised conditions and negative values indicating reduced conditions, both relative to the FMQ.

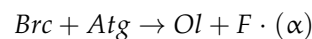
For the BIU impure marble DM675, the calculated redox state changes under varying *P-T* conditions (Figure 1c). At 512 °C and 1.82 GPa, the redox state is at  $\Delta\text{FMQ}-2.15$ ; it increases to a maximum of  $\Delta\text{FMQ}-1.87$  at 543 °C and 2.39 GPa, and then it decreases to  $\Delta\text{FMQ}-2.01$  at 559 °C and 2.91 GPa. These negative values indicate that the sample DM675 is a reduced impure marble.

Using the DM675 as a natural proxy, the equilibrium phase relations (Figure 2) and fluid chemistry for the corresponding CM(F)S-COHS system were modelled along the prograde BIU *P-T* path in the ranges of 1.82–3.00 GPa and 512–562 °C (Figure 1b), as well as in an  $f\text{O}_2$  range relevant for monitoring the  $\text{CaCO}_3$ -buffered reaction at redox states between  $\Delta\text{FMQ}+2$  and  $\Delta\text{FMQ}-2$ .

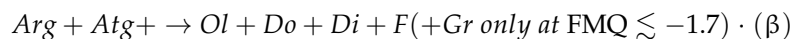


**Figure 2.** *T(P)*– $f\text{O}_2$  phase diagram calculated for the Atg dehydration reaction. Isomodes showing the variation of Atg vol% (a) and fluid (F) vol% (b) in the system during reactions  $\alpha$  and  $\beta$ . The DM675 *T(P)*– $f\text{O}_2$  path is the same as that plotted in Figure 1b.

The antigorite dehydration reactions are the two major reactions controlling fluid production in the modelled CM(F)S-COHS system as *T* and *P* increase, i.e., during deep subduction (Figures 1b and 2). The first reaction is the discontinuous (univariant) brucite-breakdown reaction that involves the dehydration of both brucite and antigorite, without carbonates involved, up to complete brucite consumption (brucite-out):



The second reaction is the continuous antigorite-breakdown reaction that starts as soon as reaction  $\alpha$  is completed and that progressively consumes antigorite up to its whole destabilisation (antigorite-out; Figure 2a):



While the  $P$ - $T$  conditions of the brucite breakdown are not influenced by the redox conditions of the system (514 °C and 1.8 GPa; Figures 1b and 2), those of the antigorite breakdown are moderately influenced. Above  $\Delta\text{FMQ}+0.7$  conditions, complete antigorite consumption occurs at constant  $T$  and  $P$  (550 °C and 2.64 GPa, respectively). These  $P$ - $T$  values are lower than those (555 °C and 2.80 GPa) under redox conditions between  $\Delta\text{FMQ}+0.7$  and  $\Delta\text{FMQ}-1.7$ . Below  $\Delta\text{FMQ}-2$ , antigorite is substituted by brucite as the major hydrous phase of the system. Under such  $P$ - $T$ - $f\text{O}_2$  conditions, the topology of the boundary between the antigorite-bearing and antigorite-free fields becomes almost parallel to that of  $\Delta\text{FMQ}-2$ .

As shown in Figure 2, aragonite and dolomite are always stable under the investigated conditions. On the contrary, graphite is stabilised under reduced conditions, below  $\Delta\text{FMQ}-1.7$ . Regarding sulfur-bearing phases, anhydrite substitutes pyrite under oxidised conditions between  $\Delta\text{FMQ}+1.5$  and  $\Delta\text{FMQ}+0.5$ . Because the modelled bulk composition is Fe-poor, the predicted silicates (Mg-rich olivine, Mg-rich clinopyroxene, antigorite, and brucite) do not play any significant role in buffering oxygen fugacity by hosting potential  $\text{Fe}^{3+}$ . Instead, carbon-bearing minerals (carbonate and graphite) and sulfur-bearing minerals (sulphates and sulphides) are the solid phases that primarily control the oxygen-buffering capacity of the system.

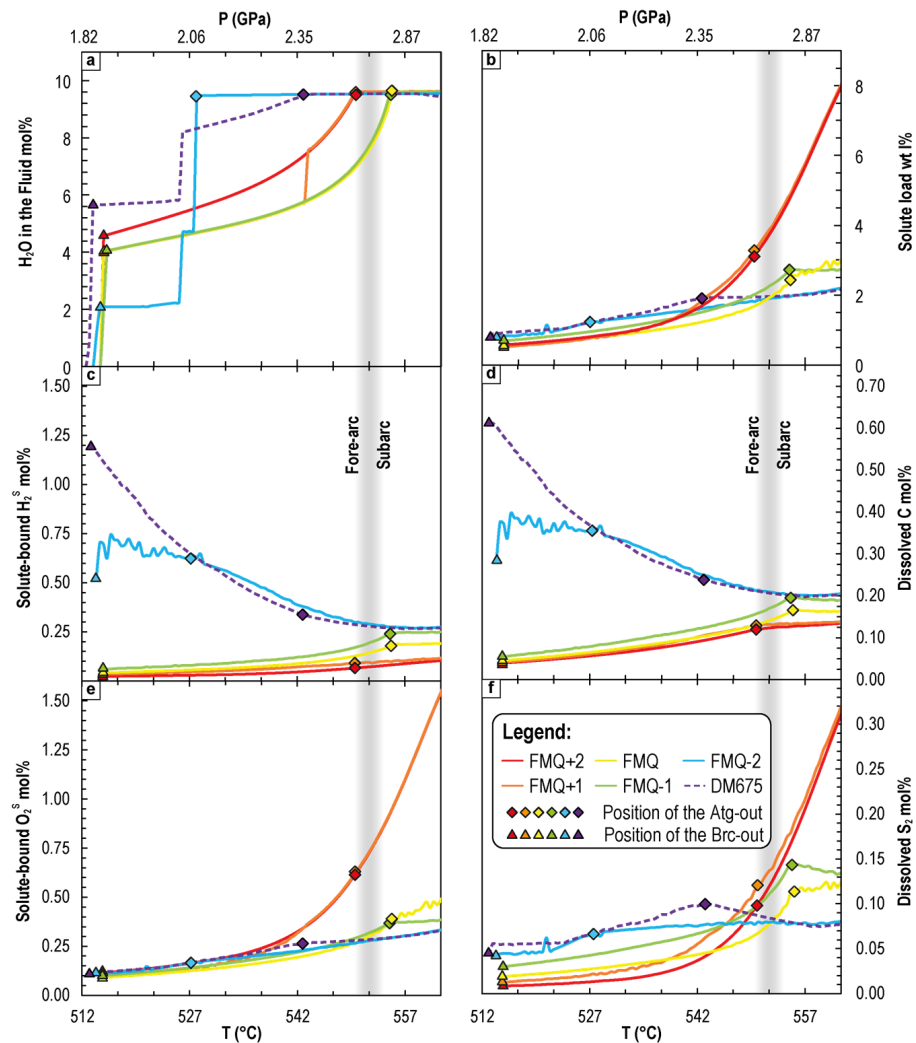
#### 4.2. $P$ - $T$ - $f\text{O}_2$ Fluid Phase Relationships during $\text{CaCO}_3$ +Antigorite Dehydration Reactions

As prograde dehydration reactions under high-pressure conditions produce fluids during subduction, the mineral dissolution of the surrounding rock-forming minerals (e.g., [63]) progressively changes the fluid chemistry (e.g., [64]). To better understand how the dissolution process influences the redox state of the resulting fluid, it is essential to evaluate the variations of the dissolved redox-sensitive elements, the average valence state of C and S, and the variations of the fluid pH during prograde mineral dehydration and rock dissolution in the fluid.

##### 4.2.1. Variation of Dissolved Redox-Sensitive Elements

During reaction  $\alpha$ , ca. 1.7–2 vol% of fluid, equivalent to 4–4.5 mol% of  $\text{H}_2\text{O}$ , is instantaneously produced above  $\Delta\text{FMQ}-2$ . In contrast, only 0.86 vol% (equivalent to 2 mol% of  $\text{H}_2\text{O}$ ) is produced at  $\Delta\text{FMQ}-2$ , and up to 2.54 vol% (equivalent to 5.7 mol% of  $\text{H}_2\text{O}$ ) is produced in the DM675 (Figures 2b and 3a). The remaining fluid is produced during reaction  $\beta$ , reaching 4.25–4.50 vol% (corresponding to 9.5 mol% of  $\text{H}_2\text{O}$ ) at antigorite-out regardless of the redox conditions (Figures 2b and 3a). The concomitant mineral dissolution gradually decreases the  $\text{H}_2\text{O}$  content in the fluid. Because of the redox-neutral character of  $\text{H}_2\text{O}$  (e.g., [65]), any redox capacity held by the fluid is due to the dissolved element load.

As dehydration reactions proceed, the produced fluid is characterised by an increase in the solute load that can reach up to 8 wt% under oxidised conditions (Figure 3b). The amount of solute is due to the progressive dissolution of carbonate minerals and anhydrite under oxidised conditions or carbonate and sulphides (pyrrhotine and, then, pyrite) under more reduced conditions (Figure 2). These minerals exert primary control on the solute composition, especially on the redox-sensitive elements H, O, C, S, and Fe.



**Figure 3.** (a) Amount of solvent H<sub>2</sub>O as mol% constituting the fluid (composed of solvent and solutes) as a function of  $P$ ,  $T$ , and  $fO_2$ . (b) Evolution of total dissolved load (wt%) as a function of  $P$ ,  $T$ , and  $fO_2$ . (c,e) Molar variation of H<sub>2</sub><sup>S</sup> and O<sub>2</sub><sup>S</sup> bound to solute and not to H<sub>2</sub>O as a function of  $T$ ,  $P$ , and  $fO_2$ . (d,f) Dissolved C and S<sub>2</sub> in the fluid phase as a function of  $T$ ,  $P$ , and  $fO_2$ .

In particular, the amount of hydrogen and oxygen not bound to H<sub>2</sub>O can be considered to explore whether a bulk-fluid composition has a more reducing or oxidising character. Hydrogen and oxygen can also constitute gaseous phases (H<sub>2</sub> and O<sub>2</sub>) or can be bound to solutes (H<sub>2</sub><sup>S</sup> and O<sub>2</sub><sup>S</sup>; from here forward, the superscript “<sup>S</sup>” is used to refer to the amount of H<sub>2</sub> and O<sub>2</sub> constituting the fluid phase that is bound to the solute portion of the fluid). The H<sub>2</sub><sup>S</sup> and O<sub>2</sub><sup>S</sup> abundance in the fluid (Figure 3c,e) is controlled by reactions  $\alpha$  and  $\beta$  and by the progressive dissociation of the produced H<sub>2</sub>O to H<sup>+</sup> and HO<sup>-</sup>. Thus, any variations in H<sub>2</sub><sup>S</sup> and O<sub>2</sub><sup>S</sup> are due to the redox behaviour of the reactions themselves. From oxidised to reduced conditions (from  $\Delta FMQ+2$  to  $\Delta FMQ-1$ ), the H<sub>2</sub><sup>S</sup> in the fluid progressively increases during reaction  $\beta$  (Figure 3c). Conversely, at  $\Delta FMQ-2$  during reaction  $\alpha$ , the amount of H<sub>2</sub><sup>S</sup> is the highest, and it is progressively diluted by reaction  $\beta$ . On the contrary, the amounts of O<sub>2</sub><sup>S</sup> are not affected by the redox state of the system but progressively increase as the reactions proceed, particularly under oxidised conditions (Figure 3e).

The amount of dissolved C during reaction  $\beta$  follows the same pattern shown by H<sub>2</sub><sup>S</sup> (Figure 3d). This similarity is due to the stabilisation of hydrocarbons (especially CH<sub>4</sub>) under reduced conditions (derived by dissolving carbonates and graphite) and to dominant HCO<sub>3</sub><sup>-</sup> species under the other conditions (derived by dissolving carbonates). Sulfur dissolution shows an evolution similar to that of O<sub>2</sub><sup>S</sup>. Dissolved sulfur increases



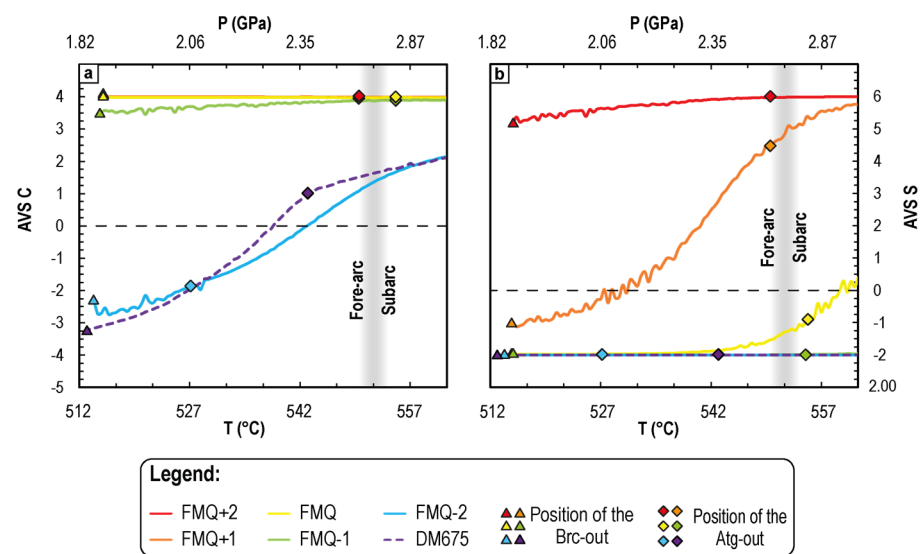
under oxidised conditions as  $P$  and  $T$  increase along a cold subduction  $P$ - $T$  path (Figure 3f). Correspondingly, sulfur is more soluble under reduced conditions (and at forearc depths, i.e., <2.5 GPa) than under oxidised conditions along a cold subduction  $P$ - $T$  path (Figure 3f).

Iron is in such low quantities in the studied system that, as shown by Maffei et al. [26], its limited dissolution leads to an abysmal dissolved load irrelevant for the  $P$ - $T$ - $fO_2$  of the system. The highest amounts of dissolved Fe ( $1.5 \times 10^{-5}$  and  $4 \times 10^{-5}$  mol%) are released in the fluid during reaction  $\alpha$ . As reaction  $\beta$  proceeds, Fe is diluted up to  $0.5 \times 10^{-5}$  mol% (Supplementary Figure S1).

#### 4.2.2. Variation of the Dissolved Average Valence State of C and S

The evaluation of the AVS, i.e., the average valence state of an element, with multiple valence states potentially present at the same time in a fluid, allows for an understanding of the potential redox role of the modelled fluid in the case where it leaves the system and interacts, for example, with an overlying mantle wedge.

The AVS of carbon under oxidised and neutral conditions is substantially constant under all  $P$ - $T$  conditions (around  $\sim+3.99$ – $+3.96$ ; Figure 4a). At  $\Delta FMQ-1$ , carbon AVS progressively increases, during reaction  $\beta$ , from  $+3.50$  up to  $\sim+3.86$ , and then it remains constant. Interestingly, carbon AVS records a considerable change in behaviour when the system is at  $\Delta FMQ-2$  (and in the DM675 redox state). As reaction  $\alpha$  ends and reaction  $\beta$  takes place, carbon AVS is very low (between  $-3.20$  and  $-2.20$ ), but it progressively increases up to  $+2$  at the end of the investigated  $P$ - $T$  portion of the path (Figure 4a).

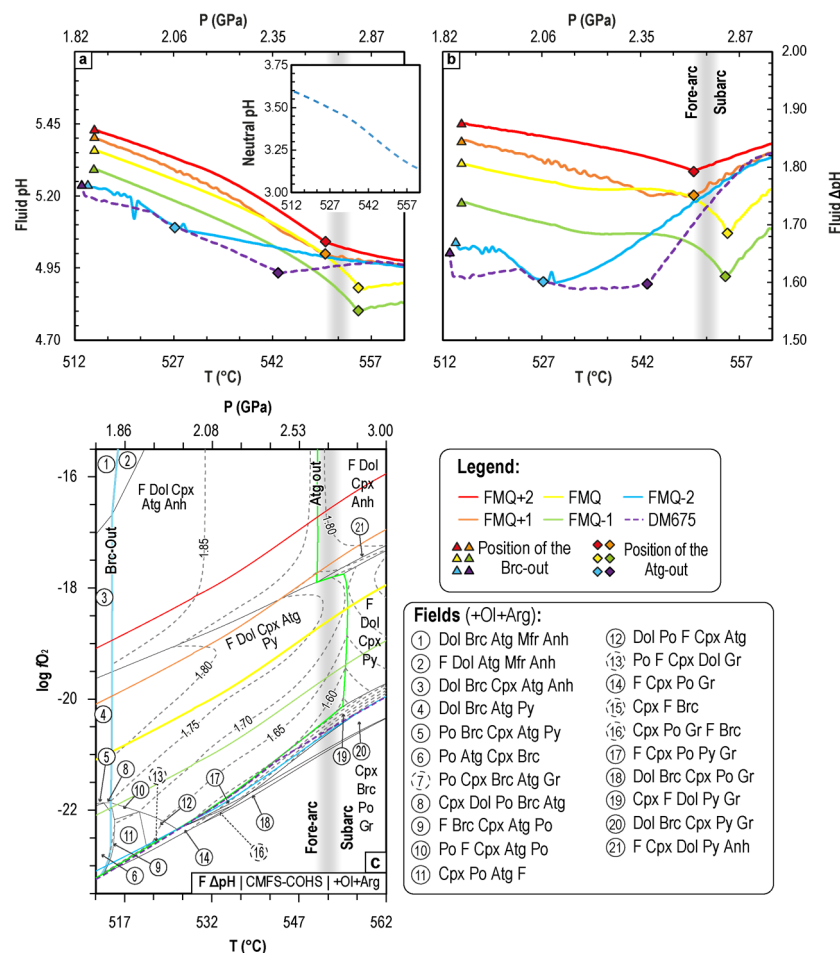


**Figure 4.** (a) Average valence state (AVS) of C dissolved in the fluid as a function of  $T$ ,  $P$ , and  $fO_2$ . (b) Average valence state (AVS) of S dissolved in the fluid as a function of  $T$ ,  $P$ , and  $fO_2$ .

Sulfur AVS shows the opposite behaviour with respect to C. At  $\Delta FMQ+2$ , even though anhydrite dissolves, the starting sulfur AVS is at  $\sim+5.50$ . It reaches  $+6$  only when antigorite is completely consumed (Figure 4b). A more extreme behaviour is observed at  $\Delta FMQ+1$  because pyrite is present under lower  $P$ - $T$  conditions and anhydrite is present under higher  $P$ - $T$  conditions (Figure 2). If pyrite is stable in the system (see  $\Delta FMQ+1$  path in Figure 2), its dissolution during reaction  $\alpha$  and part of reaction  $\beta$  leads to a sulfur AVS of  $\sim-1.10$ . As anhydrite is stabilised in the rock matrix, sulfur AVS progressively increases up to  $\sim+5.8$  at the end of the investigated  $P$ - $T$  conditions (Figure 4b). Under the neutral and reduced conditions of the system, sulfur AVS remains constant at  $\sim-1.98$  within the whole prograde path, due to continuous pyrite dissolution (Figure 4b). However, under neutral conditions, the AVS of sulfur starts to increase near the end of reaction  $\beta$ , reaching  $\sim+0.25$  at the end of the investigated  $P$ - $T$  conditions (Figure 4b).

### 4.2.3. Variation of the Fluid pH

Since the pH is representative of the activity of the ions  $H^+$  ( $a_{H^+}$ ) in the fluid, this value is indicative of the modifications of both the  $H_2O$  activity and its ionisation constant (i.e., the equilibrium constant, which is dependent on the  $P$ - $T$  conditions of the system and controls the auto-ionisation or auto-dissociation reaction of  $H_2O$  to produce  $H^+$  and  $OH^-$ ; e.g., [66,67]). Both are linked to changes in the solvent capacity of the fluid. In Figure 5a, it seems that, while both reactions  $\alpha$  and  $\beta$  occur, the fluid pH continues to decrease until complete antigorite consumption and then roughly remains stable for the rest of the prograde  $P$ - $T$  path. However, due to the decrease in the neutral pH ( $pH_{NEUTRAL}$ ) value with increasing  $T$  and  $P$  (dashed light blue curve in the inset of Figure 5a), the calculated pH of the fluid is not truly indicative of the changes in the fluid solvent capacity (i.e., it is not directly known whether the fluid becomes more acidic or basic under changing  $P$ - $T$ - $fO_2$  conditions). Therefore, to better understand the changes in the solvent ability of  $H_2O$ , the pH variation relative to neutrality ( $\Delta pH = pH - pH_{NEUTRAL}$ ; [66,68]) is more informative (Figure 5b,c). The fluid is acidic if  $\Delta pH < 0$ , and it is alkaline if  $\Delta pH > 0$ . The positive  $\Delta pH$  values ( $\Delta pH = 1.90 - 1.55$ ) indicate that the produced fluid is always alkaline, but under reduced conditions, the fluid is more acidic than under oxidised conditions.

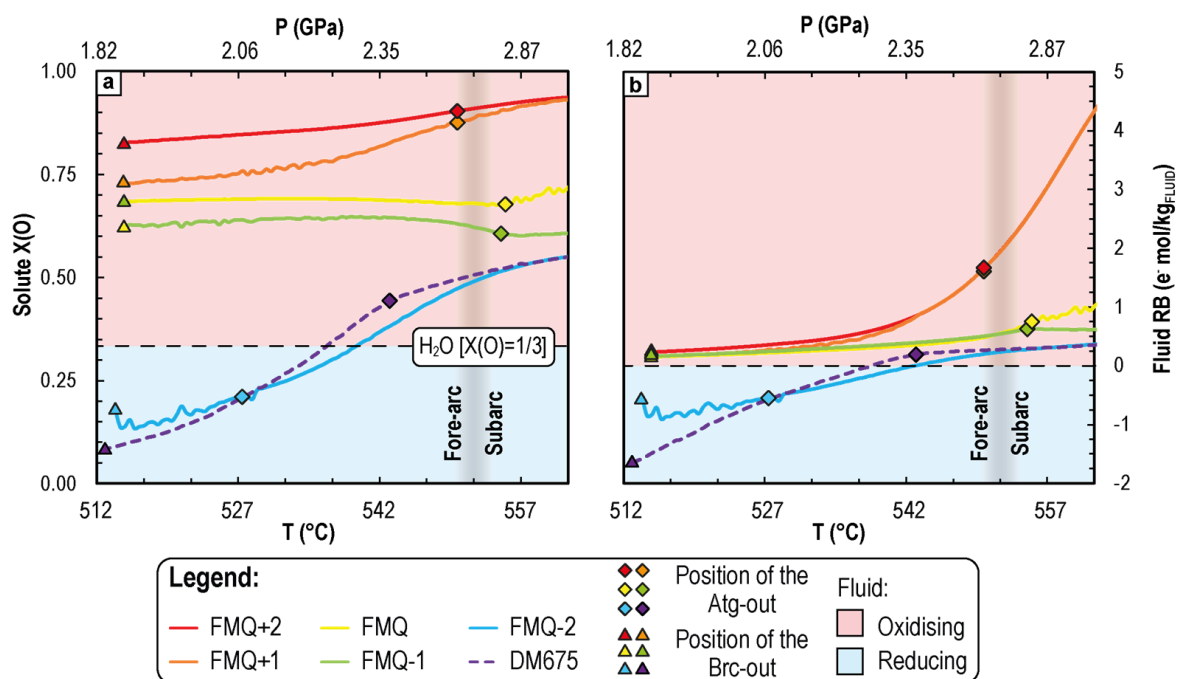


**Figure 5.** (a) Fluid pH as a function of  $T$ ,  $P$ , and  $fO_2$  with the neutral pH under the  $P$ - $T$  conditions given in the inset. (b)  $\Delta pH = pH - pH_{NEUTRAL}$  variation as a function of  $T$ ,  $P$ , and  $fO_2$ . (c) Variation of the fluid  $\Delta pH = pH - pH_{NEUTRAL}$ , first showing a progressive increase in fluid acidity, marked by a decrease in  $\Delta pH$  values, during the entire  $CaCO_3$ -buffered antigorite dehydration followed by an abrupt decrease in fluid acidity, marked by an increase in  $\Delta pH$  values, after the complete consumption of antigorite (bright light green line). Field numbers in the dashed circles are univariant reactions separating the bivariate fields.

## 5. Discussion

### 5.1. Redox-Dependent Fluid Chemistry

The preferential release of  $H_2^S$  (under progressively more reducing conditions) over  $O_2^S$  at all the examined system's redox states is better visualised with the  $X(O)$  ( $X(O) = (O_2^S / (O_2^S + H_2^S))$ ), following [65]) molar ratio of the fluid's dissolved load (Figure 6a). The threshold value of  $X(O) = 1/3$  is that of  $H_2O$  and represents the boundary between the oxidising and reducing fluids (following the definition of redox-neutral fluid in [65]) of the solutes in the investigated  $P$ - $T$ - $fO_2$  range (Figure 6a). Starting from  $\Delta FMQ+2$  down to  $\Delta FMQ-1$ , the value of the ratio shifts downward, i.e., towards the reduced field of the diagram. Under strongly reduced conditions (i.e., at  $\Delta FMQ-2$  and in the DM675 sample), the ratio is lower than  $1/3$ , thus indicating reducing fluids. The ratio becomes indicative of an oxidising fluid, even for a reduced carbonate metasedimentary composition, only above  $\sim 535$  °C and  $\sim 2.14$  GPa (Figure 6a). The shift from an oxidising to a reducing fluid shown by the  $X(O)$  ratio further proves the decoupled release of  $H_2^S$  and  $O_2^S$  under different redox conditions.



**Figure 6.** (a) Solute  $X(O)$  calculated as molar  $O_2^S / (O_2^S + H_2^S)$  and as a function of  $T$ ,  $P$ , and  $fO_2$ . (b) Calculated redox budget of the modelled fluid as a function of  $T$ ,  $P$ , and  $fO_2$ .

The fluid acidification, measured by the  $\Delta pH$  during the entire antigorite dehydration, shows that the activity of the  $H^+$  ( $aH^+$ ) in the fluid increases with the progression of the reaction. This high  $aH^+$  favours the protonation of the components of the system, i.e., the reactions between the dissociated  $H^+$  in the fluid and the chemical elements within the minerals (e.g.,  $C + 4H^+ = CH_4$  or  $FeS_2 + 4H^+ = 2H_2S + 2Fe_{\text{solution/minerals}}$ ). This protonation of the system's components due to increasing  $aH^+$ , together with the preferential release of  $H_2^S$ , suggests that  $CaCO_3$ -buffered antigorite dehydration is a reaction that favours the stabilisation of reduced species, such as  $CH_4$  and  $H_2S$ .

### 5.2. Fluid Redox Budget

As previously explained,  $fO_2$  is not an absolute variable and does not allow for a proper evaluation of the redox transfer capacity of the mobile phases (such as fluids) involved in redox processes across different rocks and environments (e.g., the transfer of the oxidising capacity from a subducting slab towards the overlying mantle wedge) [67]. Extensive variables, such as the redox budget (RB [60]), are preferable for evaluating the

redox capacity of a system (or fluid) in oxidising/reducing a reference system [60,65,69,70]. If we consider the redox transfer mediated by the fluids released from the subducting slab, the most important system that should be affected by this kind of process is the mantle wedge. The RB is the product of the amount of redox-sensitive elements and the number of electrons necessary to either oxidise or reduce a given element to another (reference) valence state [58]. For example, the C redox budget of 1 mol of CO<sub>2</sub> (C with a valence state of +4), in a subduction fluid interacting with a pristine mantle where graphite or diamond (i.e., C with a valence state of 0) can be stable, is calculated as follows:

$$RB_{Fluid} = 1 \text{ mol } C_{CO_2} \times \left( +4^{CO_2} - 0^{Gr/Dia} \right) = 1 \text{ mol } C \times 4 = +4 \text{ mol of RB}$$

To quantitatively evaluate the fluid redox transfer capacity, relative to a pre-subduction mantle, by using the specific redox budget parameter (see the Section 3 for definitions and calculation), the used reference state is that of a pristine mantle. The latter is reduced by 1–4 *f*O<sub>2</sub> log units relative to a mature and oxidised mantle wedge [1,2]. The considered redox-sensitive elements in the fluid and in the mantle are C, S, O, H, and Fe, and their mantle reference valence states are 0, –2, –2, +1, and +2, respectively. So, the specific redox budget of the fluid measures the moles of the electrons transferred, or not, by the fluid and added, or subtracted, to a pristine mantle wedge.

Due to the negligible abundance of dissolved Fe (Supplementary Figure S1) and the presence of dissolved O and H with a valence state other than –2 and +1, respectively, the contribution to the specific redox budget of these elements is completely negligible (being in the order of 10<sup>–4</sup> mol e<sup>–</sup>/kg<sub>fluid</sub> for H<sub>2</sub> and in the order of 10<sup>–18</sup> and 10<sup>–19</sup> mol e<sup>–</sup>/kg<sub>fluid</sub> for Fe and O<sub>2</sub>, respectively; see Supplementary Figure S2c–e) and is not treated further.

The specific redox budget calculated for a fluid produced during the carbonate-buffered breakdown of brucite and antigorite can have positive or negative values (Figure 6b). Positive specific redox budget values are indicative of a fluid characterised by an oxidising capacity relative to a pristine mantle. Negative specific redox budget values are indicative of a fluid characterised by a reducing capacity relative to a pristine mantle. Fluids belonging to the first case are those internally produced by a system at ΔFMQ-1 and above. Fluids belonging to the second group are those internally produced by a system at ΔFMQ-2 and by the DM675 sample below ~2.35 GPa and ~540 °C. Above such conditions, fluids equilibrated at ΔFMQ-2 and in the DM675 sample become slightly positive (Figure 6b).

In oxidised systems (i.e., at ΔFMQ+2 and ΔFMQ+1), carbonate and sulphate dissolution during antigorite breakdown can rise the specific redox budget only under *P-T* conditions close to those at which the reaction ends (Figure 6b). It is only under such conditions that carbonate and sulphate dissolution can more than double the oxidising capacity of the fluid in the span of about 10 °C (Figure 6b). In fluid internally produced by a system at FMQ or ΔFMQ-1, carbonates and pyrite dissolve during the entire rock's dehydration process, and the fluid specific redox budget retains small positive RB values (up to +0.75 mol e<sup>–</sup>/kg<sub>fluid</sub>; Figure 6b). Finally, for fluid internally produced by a system at ΔFMQ-2, the fluid's specific redox budget reduces after the brucite breakdown (Figure 6b). However, as soon as the antigorite is completely destabilised, the fluid's specific redox budget grows, reaching positive and oxidising values. The same trend is observed in the fluid produced by the DM675 sample, with the only difference being that the oxidising capacity is reached before the end of the antigorite breakdown. The general trend described by the redox budget under changing *P-T-f*O<sub>2</sub> conditions shows a dehydration process that stabilises either reducing or barely oxidising fluids. Only the concomitant dissolution of redox-sensitive minerals is able to shift the fluid redox state and capacity towards a substantial oxidising character.

### 5.3. $\text{CaCO}_3$ +Antigorite Dehydration Reaction: Reducing or Oxidising?

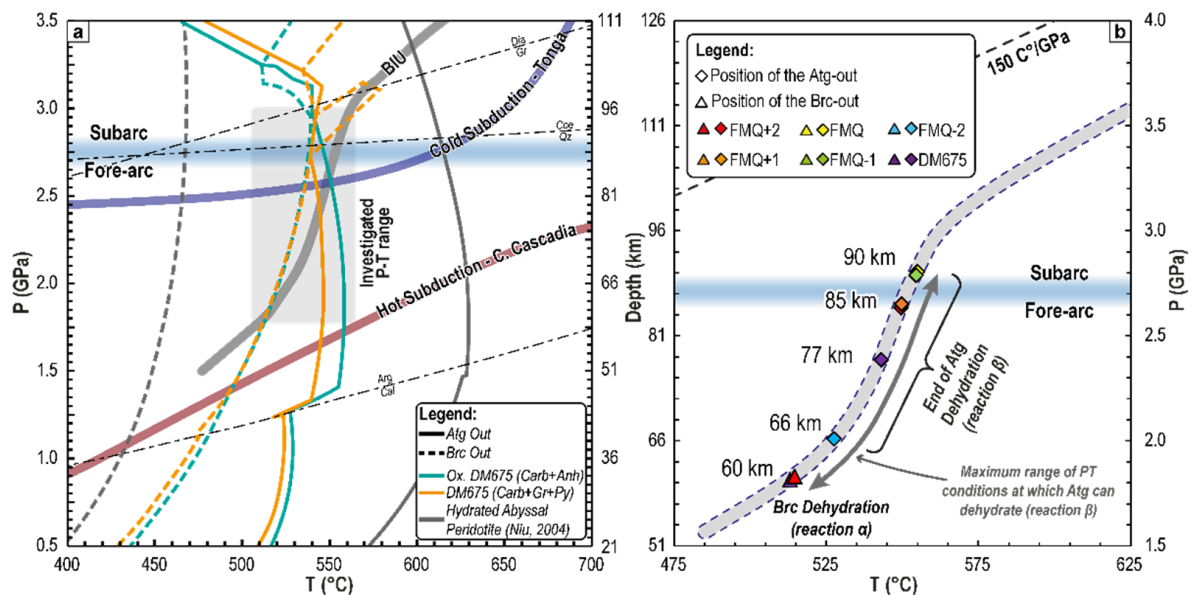
The presented data indicate that the redox of the fluid produced during antigorite dehydration in an internally carbonate-buffered system (i.e., in a CM(F)S-COHS system) is ultimately imposed by the rock's redox state and by the redox-dependent dissolving minerals (Fe oxides, carbonates, graphite, sulphates, and sulphides). A similar conclusion has been proposed by Lazar [12] and by Evans and Frost [14] for antigorite dehydration in serpentinites. In the system investigated in the present paper, the small amount of Fe and the lack of Fe oxides imply that the redox state of the released fluids is influenced by both reacting (and dissolving) carbonates and dissolving S minerals. As the  $\text{CaCO}_3$ +antigorite dehydration reaction progresses to completion—independently from the system's redox state—(i) the preferential release of  $\text{H}_2^{\text{S}}$  instead of  $\text{O}_2^{\text{S}}$ , (ii) the increase in  $a\text{H}^+$ , (iii) the increase in C and S valence states (i.e., they both start at lower values than those reached at the end of the reaction), and the progressive increase in the oxidising capacity of the fluid (as recorded by the fluid RB) highlight the contradictory aspect of the process. The reaction tends to produce a reducing fluid; however, the concomitant dissolution of redox-sensitive minerals (e.g., carbonates, graphite, sulphides, sulphates, and Fe oxides) supersedes this intrinsically reducing contribution to the fluid with, in the metacarbonate system, an overwhelmingly oxidising component. This reducing nature has also been suggested for antigorite dehydration in a carbonate-buffered system (i.e., in serpentinites) by, among others, Merkulova et al. [9] and Piccoli et al. [10]. However, the high redox-buffering capacity of the carbonatic system is testified by the increase in the fluid  $\Delta\text{pH}$  after the end of antigorite dehydration and by the positive and oxidising redox budget acquired by the fluid during mineral dissolution, regardless of the  $f\text{O}_2$  of the system. So, in metacarbonate sediments (potentially also for those with a higher metapelitic component), the HP-UHP dissolution of minerals by internally derived fluids, but also by externally derived ones, inevitably leads to the release of oxidising solute-bearing COHS fluids that are able to oxidise the overlying mantle wedge [71].

### 5.4. Linking Fluid Production Processes to Subduction Geodynamics

A recent experimental investigation of an ophicarbonite-like system (i.e., antigorite + 20 wt% of  $\text{CaCO}_3$ ) highlighted how  $\text{CaCO}_3$  depresses the  $T$  of antigorite-out compared to a  $\text{CaCO}_3$ -free serpentinite [15]. In such experiments, antigorite is consumed by 580 °C at 2.5 GPa, and even lower temperatures are predicted for increasing proportions of  $\text{CaCO}_3$ . This temperature is 100–150 °C lower than that predicted in a  $\text{CaCO}_3$ -free serpentinite [15]. Our thermodynamic modelling in a carbonate-dominated system (i.e., containing 80–90 wt% of  $\text{CaCO}_3$ ) confirms the lower  $T$  for antigorite-out with respect to a carbonate-free system. At 1.8–2.8 GPa, antigorite-out is modelled between 518 and 555 °C, depending on the system's  $f\text{O}_2$ . These temperatures are similar to those obtained for dehydration in ophicarbonite systems (e.g., [72]).

To relate such observations to subduction geodynamics, the topologies of the  $\alpha$  and  $\beta$  reactions were calculated in a  $P$ - $T$  space in which the typical  $P$ - $T$  paths of modern subduction zones were also reported [22] (Figure 7a). Reactions  $\alpha$  and  $\beta$  were calculated for (i) the original (reduced) DM675 bulk composition, characterised by carbonate+graphite+pyrite (representative of the DM675 bulk composition at  $\sim\Delta\text{FMQ}-2$ ; cyan continuous curve, Figure 7a; Table 1); (ii) for an oxidised DM675 bulk composition, characterised by carbonate+anhydrite (representative of the DM675 bulk composition at  $\sim\Delta\text{FMQ}+2$ ; orange continuous curve, Figure 7a; Table 1); and (iii) for an average composition of hydrated abyssal peridotites [41]. In Figure 7a, it is possible to assess that, in a carbonate-dominated system, reaction  $\alpha$  is exhausted at 30–70 °C higher than in a carbonate-free system, while reaction  $\beta$  is exhausted at 70–110 °C lower than in a carbonate-free system (Figure 7a). The insignificant gap of  $\sim 10$ – $15$  °C between the position of reaction  $\beta$  calculated for an oxidised and a reduced metacarbonate sediment suggests that, for modern subductions,  $f\text{O}_2$  is less important than  $T$  and the bulk-rock composition (i.e.,  $\text{CaCO}_3$ -free vs.  $\text{CaCO}_3$ -buffered systems). These differences in the reaction topology and in the location in the  $P$ - $T$  space

and, especially in cold subduction regimes, the proximity between the brucite and the  $\text{CaCO}_3$ +antigorite dehydration reactions result in remarkable differences in the dynamics and duration of fluid release from typical serpentinites or from  $\text{CaCO}_3$ -dominated lithologies belonging to the CM(F)S-COHS system. In fact, the dehydration of carbonate-free serpentinites leads to continuous fluid production, as they are subducted at forearc depths; i.e., fluid release might occur in an interval of several km of depth and of ca. 200 °C. On the contrary, antigorite-bearing metacarbonate sediments/opphicarbonate should favour a “single” pulse of fluid production and release because it occurs in an interval of a few km of depth and of an interval of ca. 10–50 °C.



**Figure 7.** (a)  $P$ - $T$  diagram showing topology and location of reactions  $\alpha$  and  $\beta$  calculated for original (reduced) and modified (oxidised) DM675 bulk compositions and for the average composition of hydrated abyssal peridotites. (b) Location of brucite dehydration and end of  $\text{CaCO}_3$ -buffered antigorite dehydration as a function of  $f\text{O}_2$  along the prograde BIU  $P$ - $T$  path.

However, the type of  $P$ - $T$  path followed by the subducting slab can amplify the role of  $f\text{O}_2$  and  $P$  in regulating fluid production and release processes for a specific rock composition (Figure 7). In the case of Alpine-like cold subductions, the depth at which dolostone- or ophicarbonate-like lithologies start to release the highest amount of fluid is almost unaffected by the redox state of the system. Assuming lithostatic conditions, a 30 km thick upper plate [73] with an average density of  $2750 \text{ kg/m}^3$ , and a mantle wedge with a density of  $3400 \text{ kg/m}^3$ , brucite dehydration occurs at a ~60 km depth (Figure 7b) regardless of the redox state of the subducted rock. On the contrary, the depth at which these lithologies finish to produce fluids is influenced by the redox state of the system (Figure 7b). Following the same assumptions used above, fluid production ends at forearc depths between 66 and 77 km for strongly reduced lithologies ( $\Delta\text{FMQ}-2$ – $\Delta\text{FMQ}-1.7$ ), at subarc depths of ca. 90 km for reduced to slightly oxidised lithologies ( $\Delta\text{FMQ}-1.8$ – $\Delta\text{FMQ}+0.7$ ), and roughly at the transition from forearc to subarc settings (ca. 85 km) for more oxidised lithologies ( $>\Delta\text{FMQ}+0.7$ ).

Although modelled along a cold subduction  $P$ - $T$  path, these results highlight the existence of a relationship between the geothermal gradient, the rock’s redox state, and fluid production, which may also be present along hotter subduction  $P$ - $T$  paths [12]. This heterogeneity in the duration of fluid release can continue within the subducting slab and can be paired with relevant differences in the chemical properties of the fluids released at distinct depths.

At forearc depths, reduced metasediments are more prone to produce fluids that are (i) richer in C and S, (ii) reducing or weakly oxidising, (iii) more acidic, due to the dissolution of carbonates, graphite, and pyrite. However, more oxidised sediments tend to release fluids that are (i) poorer in C and S, (ii) oxidising, and (iii) more alkaline, due to the dissolution of carbonates and either pyrite or sulphates.

If the metasedimentary system remains closed and fluid–rock re-equilibration—with the associated rock dissolution—persists to subarc depths, most of the fluid characteristics will be switched. Reduced metasediments will release fluids characterised by (i) a low S load, relative to that in oxidised metasediments, and a dissolved C that is lower than that at forearc depth, thus resulting in an overall lower total dissolved load; (ii) a weakly oxidising nature; and (iii) a higher pH, leading to a weaker acidic character. Finally, oxidised metasediments will release fluids characterised by (i) from two to six times more dissolved sulfur and a lower dissolved C, relative to fluids under reduced conditions, but with both being higher than fluids at forearc depths; (ii) from oxidising to strongly oxidising fluids; and (iii) heterogeneous pH depending on the metasediments' redox state. These differences in fluid abundance, chemistry, and redox capacity might contribute to explaining the difference between an oxidised and fertile subarc mantle wedge [1,2] and an inert forearc mantle.

## 6. Conclusions

Integrating data obtained using electrolytic fluid thermodynamic models into redox budget calculations allows us to indirectly explore the interplay between redox processes and mineral dissolution in HP-UHP fluids [74,75]. In this work, we investigated and decoupled the intrinsic reducing nature of the carbonate-buffered antigorite dehydration reactions in metacarbonate sediments and the redox state and capacity of the released fluids as they were subsequently modified by mineral dissolution. During subduction, strongly reduced metacarbonates are likely able to release either reducing or weakly oxidising solute-bearing aqueous COHS fluids at forearc depths. However, weakly reduced to oxidised metacarbonates are likely to release weakly oxidising to strongly oxidising solute-bearing aqueous COHS fluids, respectively, at the transition between forearc and subarc depths. Our results indicate that, ultimately, dissolving redox-sensitive minerals will impose the redox state of the released fluid. Similar behaviour is also proposed for the fluids released by subducting serpentinites and could be suggested for the fluids released by ophicarbonates. This means that the weakly oxidising to strongly oxidising fluids released in systems ranging from (C)MFS-H<sub>2</sub>O to CM(F)S-COHS are likely to metasomatise and oxidise the subarc mantle, thus recycling back C and S from the downgoing slab to the overlying mantle wedge and, then, into the arc crust and magmas. The associated volcanic degassing (both passive and explosive) of CO<sub>2</sub> and SO<sub>2</sub> (e.g., [76,77]) re-emits these climate-forcing gasses into the atmosphere. Finally, the solvent capacity of these fluids is responsible for the complexation and mobilisation of critical elements from the slab. These elements are concentrated in the arc crust through ore-forming processes (e.g., [3,4,61]), tracing the recycling pathways of the elements of economic interest.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/geosciences13050130/s1>, Figure S1: Dissolved Fe in the fluid phase as a function of  $T$ ,  $P$ , and  $fO_2$ ; Figure S2: Calculated specific redox budgets for C, S, O<sub>2</sub>, H<sub>2</sub>, and Fe as a function of  $T$ ,  $P$ , and  $fO_2$ .

**Author Contributions:** Conceptualisation, A.M. and S.F.; methodology, AM. and J.A.D.C.; software, J.A.D.C.; validation, S.F., J.A.D.C., M.L.F. and D.C.; investigation, A.M.; data curation, A.M.; writing—original draft preparation, A.M.; writing—review and editing, A.M., S.F., J.A.D.C., M.L.F. and D.C.; visualisation, A.M.; supervision, S.F.; project administration, M.L.F. and S.F.; funding acquisition, M.L.F. and S.F. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** All the data necessary for reproducing the presented data are present in the manuscript.

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