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Mantle wedge oxidation due to sediment-infiltrated deserpentinisation

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2476 words/Summary (219 words)

The Earth's mantle is oxygen-breathing through the sink of oxidised tectonic plates at convergent margins^{1,2}. Ocean floor serpentinisation increases the bulk oxidation state of iron relative to dry oceanic mantle and results in a variable intake of other redox-sensitive elements such as sulphur^{2,3}. The reversibility of seafloor oxidation in subduction zones during high-pressure dehydration of serpentinite (“deserpentinisation”) at subarc depths and the capacity of the resulting fluids to oxidise the mantle source of arc basalts are highly contested⁴⁻¹⁵. Thermodynamic modelling^{8,10,15}, experiments^{6,12,14}, and metaperidotite study in exhumed high-pressure terrains^{4,15,16} result in differing estimates of the redox state of deserpentinisation fluids, ranging from low to highly oxidant. Here we show that although intrinsic deserpentinisation fluids are highly oxidant, the infiltration of small fractions of external fluids equilibrated with metasedimentary rocks strongly modulates their redox state and oxidation-reduction capacity explaining the observed discrepancies in their redox state. Infiltration of fluids equilibrated with graphite-bearing sediments reduces the oxidant, intrinsic deserpentinisation fluids to oxygen fugacities similar to those observed in most graphite-furnace experiments and natural metaperidotites. However, infiltration of CO₂-bearing fluids equilibrated with modern GLOSS generates sulphate-rich, highly oxidising deserpentinisation fluids. We show that such GLOSS-infiltrated deserpentinisation fluids can effectively oxidise the mantle wedge of cold to hot subduction zones potentially accounting for the presumed oxidised nature of the source of arc basalts.

37 **Main (701 words)**

38 Interaction of seawater with the oceanic lithosphere results in alteration of the oceanic crust and
39 hydration of mantle peridotite to serpentinite. Serpentinisation substantially increases the amount of
40 water and the ferric iron over total iron ratio ($\text{Fe}^{3+}/\Sigma\text{Fe}$)^{1,2,13,17,18} (Fig. 1a; 0.4–1.0 with a median and an
41 average value of 0.60 and 0.58, n = 601) relative to that of the Depleted MORB Mantle (DMM, 0.015–
42 0.04)¹⁹ (Fig. 1a), placing serpentinite among the most oxidised rocks of the altered oceanic lithosphere.
43 Seafloor serpentinisation furthermore increases the content of redox-sensitive, multivalent elements,
44 particularly sulphur, whose abundance varies by up to three orders of magnitude relative to DMM (Fig.
45 1b), reflecting a large variability of oxygen fugacity ($f\text{O}_2$) and S intake processes.

46 Subduction of altered oceanic lithosphere triggers the high-pressure (high-P) dehydration of
47 serpentinite at intermediate slab depths of subduction zones, a process usually referred to as
48 deserpentinisation. Deserpentinisation is considered the main volatile source of arc magmatism and
49 likely plays an important role in the recycling of redox-sensitive elements^{8,10,11,13} and the genesis of ore
50 deposits²⁰. More controversial is the potential role of deserpentinisation aqueous fluids as oxidation
51 agents of the mantle wedge source of arc magmatism, accounting for the more oxidised nature of arc
52 basalts relative to MORBs^{5–8,12,14}. While there is a consensus that water is mostly recycled back to the
53 crust and atmosphere by deserpentinisation, the oxidation of seafloor serpentinites (Fig. 1a) is generally
54 thought to be irreversible. While pure molecular species in aqueous fluids have a limited oxidising
55 capacity²¹, the redox capacity of deserpentinisation electrolytic fluids highly depends on their content
56 in oxidised species bearing multivalent elements, particularly sulphur^{8,22,23}. Sulphur species with a high
57 oxidising capacity—such as sulphates—are thermodynamically predicted during deserpentinisation at
58 $f\text{O}_2$ near or above the hematite–magnetite oxygen buffer⁸. Most deserpentinisation experiments,
59 however, yield significantly lower $f\text{O}_2$ ^{12,14}. Rare metaperidotite formed by high-P dehydration of
60 subducted serpentinite, now exhumed in metamorphic paleo-subduction terranes—Cerro del Almirez
61 (CdA) and Cima di Gagnone (CdG)—also records lower oxidising conditions than those predicted by
62 thermodynamic models^{4,15,24}. High-P serpentinite (metaserpentinite) and metaperidotite from CdA have
63 a rather narrow range of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio (0.60–0.64, first and third quartile, n=27 and 0.24–0.33, n = 21
64 respectively, Fig. 1a) and magnetite content (3–4 wt.%, n=19 vs. 0.3–1.1 wt.%, n=11, Supplementary
65 Fig. 1), and the transition from metaserpentinite to metaperidotite results in a 40 % decrease of its redox
66 budget (from 0.7 to 0.4 mol/kg, Methods and Supplementary Fig. 4 and Table 1). The trend of
67 decreasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ content from metaserpentinite to metaperidotite in CdA has been ascribed to
68 deserpentinisation¹⁶ suggesting the reversibility of seafloor serpentinisation oxidation during
69 subduction (Fig. 1a), yet the ultimate cause for such reversal has not been provided. Alternatively, this
70 trend is ascribed to different extents of oceanic serpentinisation of their protoliths^{4,15,24}, implying the
71 irreversibility of seafloor oxidation serpentinisation during subduction (Fig. 1a). This interpretation is
72 however at odds with numerous textural and geochemical evidence for the provenance of CdA and CdG

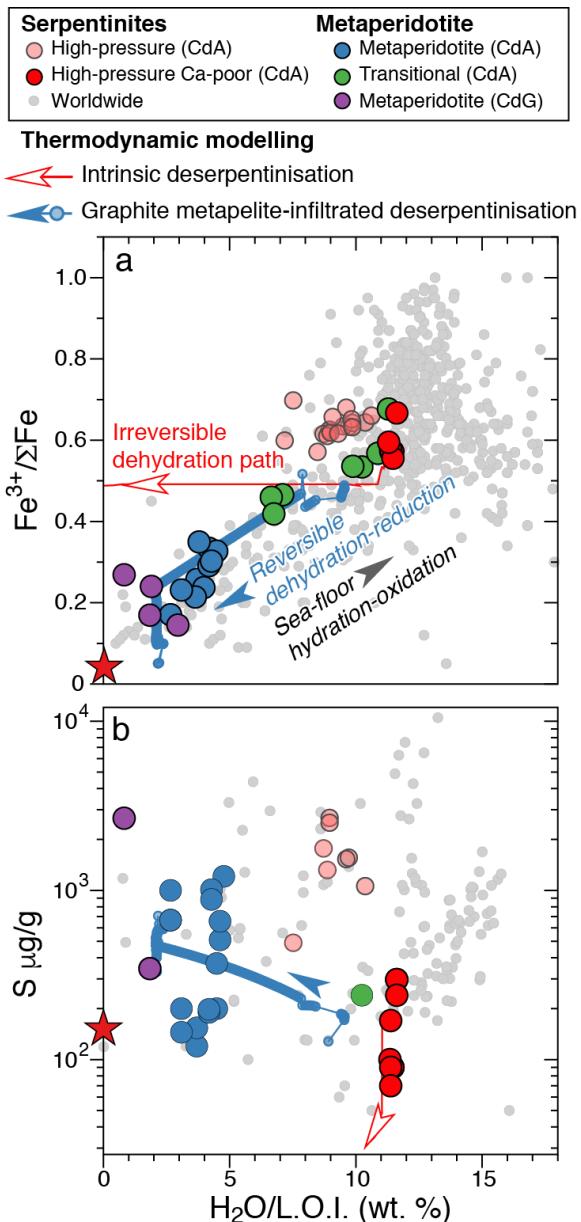


FIGURE 1a. The cycle of hydration-oxidation of mantle peridotite (serpentinites, grey arrow) at the Earth's ocean floor relative to the nominally anhydrous mantle (red star, Depleted MORB Mantle⁹) and two possible deserpentinisation paths either reversing or preserving the oxidation set at the Earth's surface. The directions of the arrows for the thermodynamically modelled intrinsic and graphite metapelitic-infiltrated deserpentinisation evolutions indicate the direction of H_2O loss during subduction (depicted also in Fig. 2a). The only known rock samples from high-pressure terrains recording the deserpentinisation (metaperidotites from the Cerro del Almirez, CdA, and Cima di Gagnone, CdG, localities) match the reversible path requiring an external influx of reduced fluids during dehydration. Worldwide serpentinites also include partially serpentinized orogenic peridotites (< 9.0 wt.% H_2O , see Methods). **b.** The observed increase in total S content in the CdA and CdG metaperidotites compared to serpentinites is also reproduced by the graphite metapelitic-infiltrated deserpentinisation model (blue arrow), in contrast to the intrinsic deserpentinisation model (red arrow).

74 metaperidotites from highly serpentinised peridotite protoliths metasomatised by crustal fluids^{25–27}.
75 CdA metaperidotite is also characterised by a moderate increase in S relative to its putative Ca-poor
76 serpentinite protolith —with a low S content (< 300 µg/g) similar to DMM; an opposite trend to that
77 predicted from thermodynamic modelling (Fig. 1b). Furthermore, subducted serpentinite has lower and
78 narrower S contents than average oceanic serpentinite (Fig. 1b), thus limiting the capacity of
79 deserpentinisation fluids to oxidise the mantle wedge. Thermodynamic modelling, experiments and
80 natural samples thus provide seemingly contradictory views on the role of deserpentinisation fluids as
81 potential agents for the oxidation of the mantle source of arc basalts.

82 The pervasiveness of subducted-sediment geochemical signatures is the hallmark of arc
83 magmatism²⁸, an attribute increasingly ascribed to the interaction of slab crustal lithologies with slab
84 fluids sourced from deserpentinisation. There is also overwhelming geochemical evidence on the role
85 of infiltration of fluids equilibrated with metasedimentary rocks in the genesis of natural serpentinite-
86 derived metaperidotite^{25–27,29–33}. However, it has not yet been investigated how the interaction of
87 sediment-derived fluids modify the $f\text{O}_2$ and the cargo of multivalent elements in the deserpentinisation
88 fluids, compared to those sourced from the intrinsic (i.e. without external fluid infiltration)
89 deserpentinisation.
90

91 **Intrinsic deserpentinisation (396 words)**

92 Figure 2a shows the thermodynamic modelling of the intrinsic prograde evolution a serpentinite
93 subducted along the geothermal gradient of high-P metamorphic terrains. At constant bulk O_2 (red
94 arrows in Fig. 1a and 2a, Supplementary Fig. 2), this evolution implies a dramatic increase of the
95 $\Delta\log_{10}f\text{O}_2[\text{FMQ}]^{7,10,34}$ from +2.2 (450 °C, 0.9 GPa), where olivine is first produced, to +4.6 (660 °C,
96 1.7 GPa), where antigorite serpentinite dehydrates to metaperidotite. The rise in $f\text{O}_2$ is due to the
97 formation of hematite after magnetite to maintain the bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ constant (Fig. 1a; red line) since
98 the $X_{\text{Mg}} [\text{Mg}/(\text{Fe}^{2+}+\text{Mg})]$ of olivine and orthopyroxene reaction products is lower than that of reactant
99 antigorite (Supplementary Fig. 3 and 4). In agreement with previous models for a similar
100 $\Delta\log_{10}f\text{O}_2[\text{FMQ}]^8$, our model shows that S and C of serpentinite are fully dissolved in the
101 deserpentinisation fluid , with $\text{HSO}_4^{-\text{(aq)}}$ and, to a lesser extent, $\text{SO}_4^{2-\text{(aq)}}$ as the dominant sulphur species
102 (Supplementary Table 2).

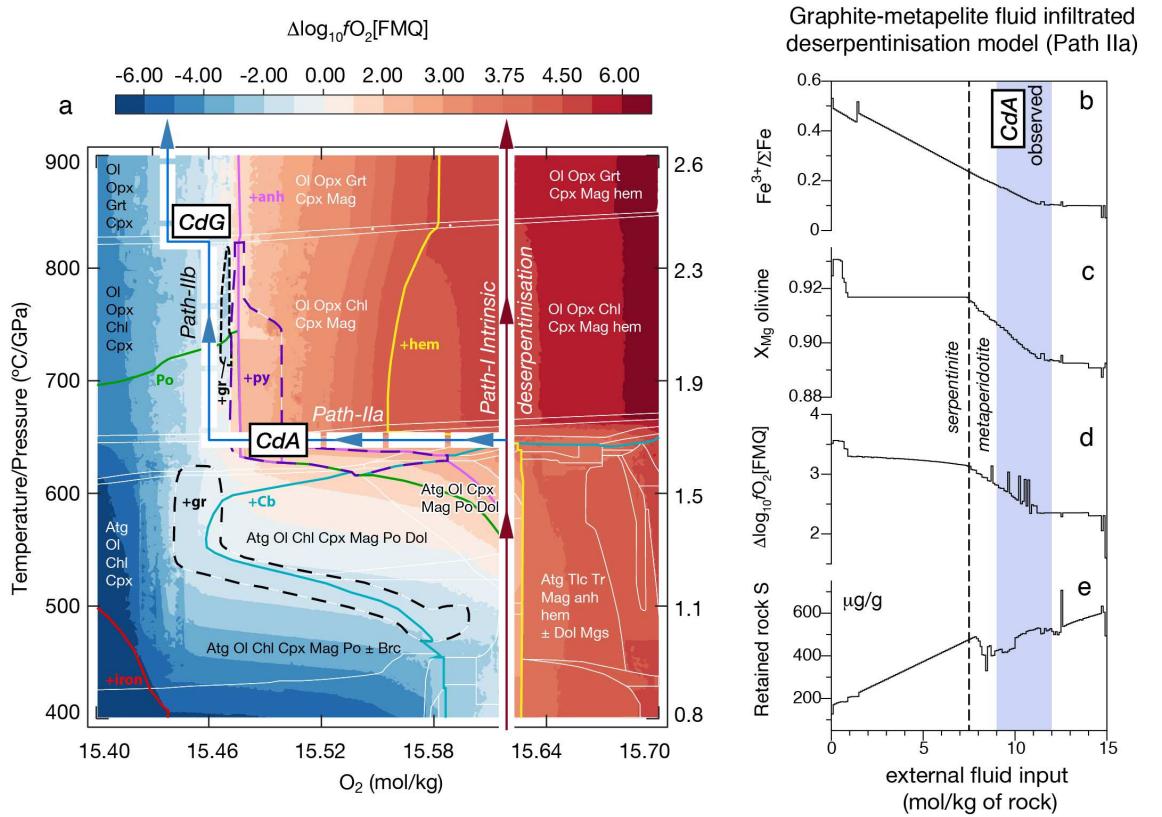


FIGURE 2a. Two potential evolutions of the oxygen fugacity fO_2 for the subducting serpentinite slab (expressed as relative to the FMQ buffer; see Methods) for a geothermal gradient crossing the antigorite ($660\text{ }^\circ\text{C}/1.7\text{ GPa}$) and chlorite dehydration ($820\text{ }^\circ\text{C}/2.4\text{ GPa}$) as observed at CdA and CdG computed for a representative fully serpentinized peridotite containing 5 wt.% magnetite, 11.6 wt.% H₂O, 170 ppm S, and 200 ppm C (Figure 1 and Supplementary Table 1). Stability fields highlighting some key mineral assemblages are superimposed as thick lines (see Supplementary Figure 2). Path-I (“Intrinsic deserpentinisation”) corresponds to the conventional, closed system, prograde metamorphism where the rock imposes the fO_2 and shows a dramatic increase in the $\Delta \log_{10} fO_2 [FMQ]$ of up to +4.5. Here we show that, alternatively, externally-derived fluid infiltration can induce complete antigorite dehydration at isobaric-isothermal conditions (horizontal Path-IIa, graphite-metapelite infiltrated deserpentinisation) with a decrease in the relative fO_2 and in the redox budget if the infiltrating fluid is derived from a sediment (pyrite and graphite-bearing metapelite) with a high reducing capacity⁴⁶. **b-e.** Isothermal and isobaric evolution ($650\text{ }^\circ\text{C}/1.7\text{ GPa}$) along the computed, dehydration-driven infiltration path. The vertical dashed line marks the complete deserpentinization (for the Path-I intrinsic evolution see Supplementary Figure 4): **b.** Bulk-rock ferric to total iron content ($Fe^{3+}/\Sigma Fe$). **c.** X_{Mg} in olivine. **d.** $\Delta \log_{10} fO_2 [FMQ]$. **e.** Total sulphur content retained in the reacting rock during the external infiltration. The blue-shaded range shows the extent of fluid-rock reaction necessary to induce full dehydration of serpentinite and reproduce the observed $Fe^{3+}/\Sigma Fe$ and X_{Mg} in the CdA exhumed high-pressure terrain (metaperidotite).

104 The intrinsic deserpentinisation thermodynamic model fails to explain many features of natural
105 serpentinite and metaperidotite, such as the decrease of the bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ ^{4,16,35} and the relative increase
106 in S content in metaperidotite³⁶ (Fig. 1); its magnetite content and lack of hematite^{4,16,24,35}
107 (Supplementary Fig. 1); and the lower olivine X_{Mg} ^{4,35} (Supplementary Fig. 4). Nor does it explain the
108 substantially lower $\Delta\log_{10}f\text{O}_2[\text{FMQ}]$ ($+2.1 \pm 0.3$; at 800 °C, 1GPa) found in most high-P serpentinite
109 dehydration experiments^{12,14,37–39} that obtain olivine —coexisting with magnetite^{6,14,40}— with an X_{Mg}
110 that perfectly matches that of natural metaperidotite^{4,15,35,41}. Although these lines of evidence might
111 point to the non-validity of the thermodynamic model of intrinsic deserpentinisation, it is well known
112 that the $f\text{O}_2$ is externally buffered and biased towards lower $f\text{O}_2$ in high-T, long-run, graphite-furnace
113 experiments¹⁴. Interestingly, deserpentinisation experiments conceived to maintain high $f\text{O}_2$ using
114 LaCrO_3 instead of graphite furnace⁶ obtain high X_{Mg} olivine (0.94–0.97) coexisting with hematite and
115 magnetite, and $\Delta\log_{10}f\text{O}_2[\text{FMQ}]$ ranging from +3.1 to +4.1, in excellent agreement with our
116 thermodynamic model predictions (Fig. 2 and Supplementary Fig. 4). As serendipitously attained in
117 graphite-furnace experiments^{12,14,37–39}, many natural metaperidotite features would be matched if the
118 bulk O₂ of the system was open, externally imposed and shifted towards lower bulk O₂ values (blue
119 lines for CdA and CdG, respectively in Fig. 2a). This hypothesis would reconcile the seemingly
120 contradictory $f\text{O}_2$ stemming from thermodynamic modelling, some experiments, and natural samples.
121

122 **Sediment-fluid infiltration driven by deserpentinisation (553 words)**

123 The infiltration of fluids equilibrated with metasedimentary rocks —well documented in the genesis of
124 natural metaperidotite^{25,33,42,43}—is a potential mechanism for modifying the $f\text{O}_2$ and multivalent element
125 cargo of deserpentinisation fluids. Lowering the $f\text{O}_2$ relative to the oxidising conditions of intrinsic
126 deserpentinisation (Fig. 2a) requires the infiltration of fluids in equilibrium with metasedimentary rocks
127 with a highly reducing capacity, such as graphite-bearing sediments^{44,45}. Graphite-bearing sediments
128 and calc-silicates subducted to eclogite facies conditions during the Alpine orogeny are widely
129 associated with the few known natural occurrences of metaperidotite derived from high-P
130 deserpentinisation^{33,46–48}. Figures 2b–e show the results of thermodynamic modelling of the infiltration
131 of fluids equilibrated with graphite-bearing metapelite at a temperature 10 °C colder than the intrinsic
132 deserpentinisation conditions in the CdA (650 °C, 1.7 GPa). At these conditions, serpentinite releases 2
133 wt.% of H₂O and generates sufficient permeability for external fluid infiltration. The metapelite-derived
134 infiltrating aqueous fluid is rich in CH₄ and H₂S with minor H₂ (Supplementary Table 2). At the onset
135 of its infiltration into dehydrating serpentinite, CH₄ is oxidised to CO₂, and the H₂S and H₂
136 concentrations decrease at the expense of more oxidised HSO₄^{−(aq)} and SO₄^{2−(aq)} species that increase
137 compared to those in the intrinsic deserpentinisation fluid (Supplementary Table 2 and Fig. 5a).
138 Sediment-fluid infiltration gradually decreases the bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 2b), thus decreasing its bulk rock
139 and olivine X_{Mg} (Fig. 2c) due to a lower $f\text{O}_2$ (Fig. 2d), and increases the bulk S content of metaperidotite

140 and fluid (Fig. 2e and Supplementary Fig. 5a and Table 2). Complete dehydration occurs at isobaric
141 and isothermal conditions with an infiltration as low as 7.4 mol/kg of a fluid equilibrated with a
142 graphite-bearing metapelite (vertical dashed line in Fig. 2b–e).

143 For an infiltration extent of 9–12 mol/kg (ca. 0.2 fluid/rock mass ratio, Fig. 2b–e), sediment-
144 equilibrated fluid infiltration driven by deserpentinisation fully succeeds in explaining many features
145 of natural CdA serpentinite and metaperidotite, such as the trend of decreasing bulk $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 1a;
146 0.17–0.10 in Fig. 2b), the relative increase in metaperidotite bulk S content (ca. 400–500 $\mu\text{g/g}$ S, Fig.
147 1b and 2e) relative to its metaserpentinite protolith (c. 170 $\mu\text{g/g}$), and the modal magnetite content
148 (Supplementary Fig. 1) and lack of hematite in metaperidotite. It also predicts an olivine X_{Mg} (0.91–
149 0.89, Fig. 2c) and $\Delta\log_{10}/\text{O}_2[\text{FMQ}]$ (+2.7 to +2.3, Fig. 2d), in excellent agreement with the olivine X_{Mg}
150 of CdA metaperidotite^{4,15,35} and the $f\text{O}_2$ and olivine X_{Mg} obtained in graphite-furnace serpentinite
151 dehydration experiments¹². Compared to the intrinsic deserpentinisation, the infiltration of 9–12 mol/kg
152 of sediment-equilibrated fluids does not significantly modify the bulk major element contents, silicate
153 mineral assemblage or modal proportions of metaperidotite. This petrological similarity likely explains
154 why sediment-fluid infiltration has only been considered responsible for the cryptic geochemical
155 signature of natural metaperidotite but largely passed unnoticed as a mechanism to modulate the redox
156 state and cargo of redox-sensitive elements during deserpentinisation. For an external fluid infiltration
157 of > 11 mol/kg, the rise of H_2S and $\text{HS}^{-}_{(\text{aq})}$ in the fluid results in pyrite precipitation (Supplementary
158 Fig. 5b)—occasionally found in CdA metaperidotites—while maintaining an elevated concentration
159 of $\text{HSO}_4^{-}_{(\text{aq})}$, accounting for the observed increase of the $\text{SO}_4/\Sigma\text{S}$ ratio allied to a decrease in total $\delta^{34}\text{S}$
160 in metaperidotite relative to its serpentinite protolith reported in CdA³⁶.

161

162 Implications for the redox state of the subarc mantle (607 words)

163 The interaction of slab fluids with the subarc mantle wedge source is increasingly recognised^{40,41} as the
164 cause of the more oxidised nature of arc basalts relative to MORBs. Deserpentinisation is the main
165 source of slab fluids at subarc depths and thus a possible mantle wedge oxidation agent. While the
166 extent of serpentinisation of fast-spreading mid-ocean lithosphere is largely unconstrained, serpentinite
167 is widespread in subducted slow-spreading, mid-ocean ridge lithosphere and at the slab interface of
168 subduction zones. At the slab interface of hot to cold subduction zones, modelling shows that
169 serpentinite intrinsically dehydrates between 2.4–3.4 GPa and 650–660 °C under relatively oxidising
170 conditions (+2.9 to +3.7 $\Delta\log_{10}/\text{O}_2[\text{FMQ}]$), particularly in hot subduction zones (see ID in Fig. 3a) due
171 to the negative pressure dependence of $\Delta\log_{10}/\text{O}_2[\text{FMQ}]$ for metaperidotites (Supplementary Fig. 6).
172 The dominant fluid sulfur species in all thermal regimes is $\text{HSO}_4^{-}_{(\text{aq})}$, which is slightly more abundant
173 in deserpentinisation fluids from—relatively more oxidant—hot subduction zones (Fig. 3a). At the
174 slab interface, serpentinite coexists with fluid-saturated metasedimentary rocks in

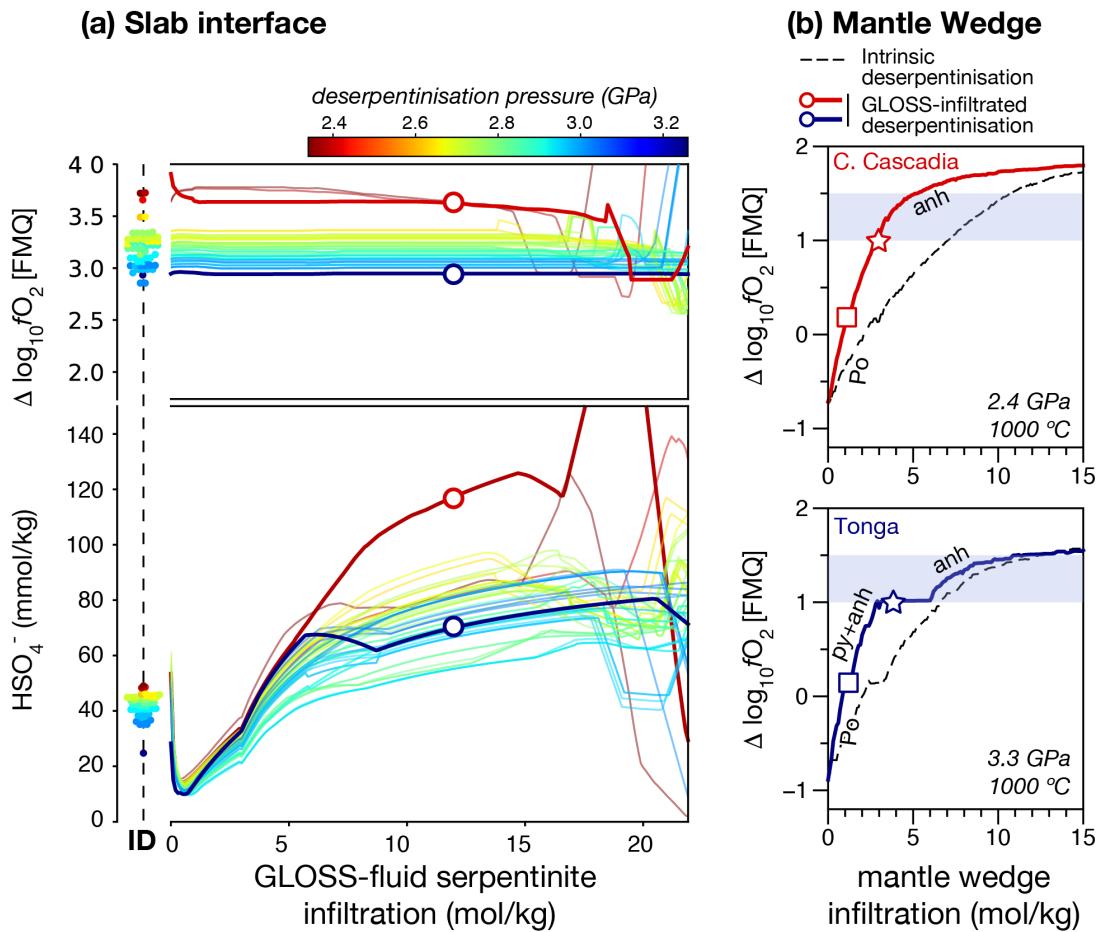


FIGURE 3a. Modification of the $\Delta \log_{10} f\text{O}_2 [\text{FMQ}]$ and the concentration of the main oxidising fluid species (HSO_4^-) relative to the intrinsic dehydration (ID) serpentinite fluid when serpentinites are infiltrated by sediment-derived fluids with low reducing capacity (GLOSS) for a worldwide compilation of subduction zones (color-coded for the pressure at which the serpentinite dehydrates at the slab surface, Methods). **b.** The capacity of these modified, serpentinite-derived fluids (empty dots in a) to oxidise the mantle wedge on top of the slab at near wet-solidus conditions is computed for the hottest (Central Cascadia) and coldest (Tonga) subduction zones. A minimum value range of $\Delta \log_{10} f\text{O}_2 [\text{FMQ}]$ inferred for oxidised IAB source and recorded by high-pressure metasomatized mantle atop of the slab^{52,53} is given as a horizontal blue-shaded range. Sediment (GLOSS)-serpentinite derived fluids are more than two-fold more efficient (3 mol/kg) to oxidise the mantle wedge than the intrinsically-released serpentinite dehydration fluids (7 mol/kg). The metasomatized mantle wedge has an initial depleted composition. Squares and stars on the red and blue lines indicate the condition range limits at which pyrrhotite (Po), pyrite (py) or anhydrite (anh) are the stable minerals hosting S in the rocks. For an ultradepleted MORB mantle see Supplementary, Fig. 7. For an interaction with sediments with high reducing capacity (blackshale-like sediments) see Supplementary Fig. 8.

melange zones⁴⁹ and sediment-fluid infiltration driven by deserpentinisation is favoured. Modelling shows that for an extent of infiltration of 12 mol/kg —similar to that inferred from natural CdA (Fig. 2b-e)— infiltration of fluids equilibrated with modern Global Subducting Sediments (GLOSS)^{21,42} during deserpentinisation does not greatly modify their fO_2 relative to intrinsic deserpentinisation whatever the subduction thermal regime (Fig. 3a). However, the abundance of dominant sulphate fluid species $\text{HSO}_4^-_{(\text{aq})}$ increases notably in warm and hot subduction zones (Fig. 3a), boosting the redox capacity of deserpentinisation slab fluids relative to those produced by intrinsic dehydration.

Figure 3b shows the modelling of the fO_2 evolution of a DMM mantle wedge —at the near-vapour-saturated solidus temperature⁵⁰— infiltrated by deserpentinisation fluids for a hot (Central Cascadia) and cold (Tonga) subduction zone. Infiltration of at least 7 mol/kg of slab fluids produced by intrinsic deserpentinisation is required to oxidise the mantle wedge within the minimum range of $\Delta\log_{10}fO_2[\text{FMQ}]$ inferred for the mantle source of arc magmas (FMQ +1.0^{51,52}). In contrast, GLOSS-infiltrated deserpentinisation fluids have a greater oxidising capacity; the interaction of about 3 mol/kg of these slab fluids drastically increases the $\Delta\log_{10}fO_2[\text{FMQ}]$ of the mantle wedge in hot and cold subduction zones (Fig. 3b). Therefore the effectiveness of rock deserpentinisation required to oxidise the mantle wedge is increased by a factor of more than two compared to intrinsic deserpentinisation. In both thermal regimes, slab fluids can attain the inferred fO_2 of the mantle source of arc magmas by precipitating anhydrite, thought to be the main sulfur host at these fO_2 mantle wedge conditions⁵¹. Our results demonstrate that metasomatism of the mantle wedge with GLOSS-infiltrated deserpentinisation fluids is a viable mechanism to account for the oxidised nature of the mantle source of arc magmas in hot and cold subduction zones. Similar conclusions are obtained when considering a more depleted and reduced —due to dependence of the fO_2 on the peridotite bulk composition⁵³— mantle wedge (Supplementary Fig. 7), indicating that the extent of mantle wedge depletion has a subsidiary role compared to the redox capacity of the incoming slab fluids.

As attested by natural metaperidotite, the oxidising capacity of sediment-infiltrated deserpentinisation fluids depends on the redox capacity of subducted sediments. This capacity has changed throughout Earth's geological history linked to the oxidation state of the atmosphere–ocean system and varies from oxidant GLOSS^{28,54} to highly reducing black shales^{44,45}. Modelling of deserpentinisation infiltrated by fluids equilibrated with graphite-bearing metapelite shows that in hot subduction zones the oxidant capacity of fluids is as high as for intrinsic deserpentinisation but is significantly lower for cold subduction zones (Supplementary Fig. 7 and 8).

207

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- 337
- 338

339 **Methods**

340 **Abundance of redox-sensitive elements.** We extended a previous compilation¹⁷ of ferric and ferrous
 341 iron contents in serpentinite from different geologic settings (n=758) (Fig.1a) to include alpine
 342 serpentinite from Malenco (N. Italy, n=42)^{55,56} and 33 new analyses from CdA analysed by
 343 potentiometric titration. Bulk Fe³⁺/ΣFe ratios are in excellent agreement with mineral mode estimates
 344 based on the measured amount of magnetite by saturation magnetization corrected for the paramagnetic
 345 fraction¹⁶ and using the Fe³⁺/ΣFe content of antigorite measured by XANES spectroscopy in selected
 346 samples⁵⁷. Magnetite contents (Supplementary Fig. 2) comprise serpentinites from mid-ocean ridges
 347 (ODP Leg 153 MARK^{18,58,59}), passive margins (ODP Leg 173 Iberia^{58,59}), Puerto Rico Trench
 348 (NWPRT)⁵⁹, forearc (ODP Leg 125 Marianas^{58,59}), alpine serpentinites^{16,35,57}, and prograde
 349 metaperidotite from CdA^{4,35,57} and CdG⁴¹. Late-stage weathering of prograde metaperidotite may cause
 350 re-oxidation during hydration, therefore we only consider samples with < 4.5 wt.% H₂O for comparison
 351 with the thermodynamic predictions (Fig.1). Bulk carbon and sulphur contents are from this study and
 352 ref^{2,11,36,41,60}.

353

354 **Computation of redox budget.** The redox budget⁶¹ is an extensive variable quantifying the ability of
 355 a rock–fluid system to potentially induce oxidation or reduction relative to an arbitrary reference redox
 356 state of interest. The specific redox budget (RB) is normalized to units of mol/kg and it is defined as,

$$357 RB = \sum_j n_j \cdot v_j$$

358 where v_j is the number of electrons required to take one mole of the element in the redox state j to the
 359 reference redox state, and n_j is the number of moles per kg of the element in the redox state j present in
 360 the system (rock and fluid). Here (Supplementary Table 1 and Fig. 3), we consider the redox budget of
 361 the solid rock as this is the only variable that can be measured after fluid extraction. For the whole
 362 mantle reference redox state², the oxidation state of iron, carbon and sulphur are Fe²⁺, C⁰ and S²⁻,
 363 respectively, resulting in v_j of 1, -2, 4, 1 and 8 for Fe³⁺, Fe⁰, C⁴⁺, S⁻ and S⁶⁺. In the modelled system,
 364 the RB is computed based on the number of moles per kg of rock of the phases containing Fe³⁺, Fe⁰,
 365 C⁴⁺, S⁻ or S⁶⁺ (hematite, native iron, magnesite, dolomite, calcite, pyrite, pyrrhotite, pyroxenes, garnet
 366 and anhydrite, Supplementary Fig. 3) multiplied by the number of redox-sensitive atoms in their
 367 structural formulae. For mineral phases having ferric iron in solid solution, the RB is weighted by the
 368 molar proportion of the ferric iron endmember (magnetite in spinel⁶², Fe_{0.875}S in pyrrhotite⁹, magnesium
 369 ferri-tschermak's in orthopyroxene modified by J.A.D. Connolly from ref⁶³, and khoharite in garnet⁶⁴) .
 370

371 **Phase equilibria.** Phase equilibria and electrolyte fluid speciation were computed by Gibbs energy
 372 minimization using the PerpleX algorithm^{65,66}. Forward thermodynamic modelling has been performed
 373 in the CFMACrSHCSO system using elements as thermodynamic system components (Ca–Fe–Mg–
 374 Al–Cr–Si–H₂–C–S₂–O₂) for metaserpentinite and metaperidotite and in the NKCFMASHCSO system

(Na–K–Ca–Fe–Mg–Al–Cr–Si–H₂–C–S₂–O₂) for the graphite-bearing metapelite^{33,46} and GLOSS⁵⁴, as well as for the metasomatic infiltration models derived from them (bulk composition used are in Supplementary Table 1). Fluid saturation conditions were not imposed during the computation. Element components are preferred over oxide components when modelling electrolytic fluid speciation because C–O–H–S solvents in the fluid have a strong tendency to order for certain bulk compositions at low temperature⁶⁷. Thermodynamic data for endmembers are taken from ref⁶⁸. Considered solid solutions models were olivine (Ol), orthopyroxene (Opx), clinopyroxene (Cpx), chlorite (Chl), dolomite (Dol), magnesite (Mgs), epidote (Ep), staurolite (St), all of them from ref^{69,70}, pyrrhotite (Po)⁶⁸, amphibole (Amph(DHP))⁷¹, garnet (Grt(WPH))⁶⁴, antigorite (Atg)³⁷, white mica (mica(CF))⁷², biotite (Bi(WPH))⁶⁴, feldspar⁷³, Cr-bearing spinel (Mag)⁶², talc (Tlc, ideal), brucite (B, ideal), anthophyllite (Anth, ideal), and pure endmembers hematite (hem), pyrite (py), anhydrite (anh), graphite (gr), quartz (q) and iron. We used models Chl(W)⁷⁴ and Cpx(HGP)⁷⁵ for graphite-bearing metapelite and GLOSS, whereas for the mantle wedge metasomatism modelling we used solid solution models specifically calibrated for the mantle⁶². The systems considered in our work allow the investigation of redox reactions among the Fe–C–S-bearing solid phases (pyrrhotite, pyrite, anhydrite, magnetite, hematite, iron, carbonates and graphite) and species (e.g. HS⁻, SO₄²⁻, CaSO_{4(aq)} among many others) in an electrolyte aqueous C–O–H–S fluid. Non-modelled components (Ti, Mn and Ni) typically represent less than 0.5 wt.% (expressed as oxides) of the bulk rock composition. The absence of titanium and nickel prevents the modelling of phase assemblages containing ilmenite and pentlandite which typically occur in excess in high-pressure serpentinite and metaperidotites. The initial oxidation state of the redox-sensitive elements (Fe–C–S₂) is specified by the amount of O₂ in the system and requires a knowledge of the oxidation state of iron, carbon and sulphur (Supplementary, Table 1). However, the oxidation state of iron, carbon and sulphur are not imposed but are set by the stable phases obtained by Gibbs energy minimization (Supplementary Fig. 2 and 3). The geothermal gradient used to compute Fig. 2 and Supplementary Fig. 2-4) (P[bar] = -18057 + 37.9357 * T[K]) follows the P–T path inferred for CdA⁷⁶, and also applies for peak metamorphic conditions estimated for the CdG metaperidotite⁴¹.

Solvent and speciation in the aqueous fluid. The neutrally charged solvent molecules considered in the fluid were H₂O–CO₂–CH₄–H₂–H₂S (thermodynamic data from ref.⁶⁸) described by a generic hybrid fluid EoS with non-linear subdivision (COH-Fluid+ from ref⁶⁷). The EoS for H₂O and CO₂ is PSEoS⁷⁷, whereas for other solvents is the MRK⁷⁸. All other species are taken as solutes following the approach of ref.^{67,79} (see Supplementary Table 2). Thermodynamic data for aqueous species are taken from the latest version of the DEW model⁸⁰. The species CO_(aq) and SO_{2(aq)} are considered as solute species in the fluid, although they occur at very low concentrations (Supplementary Table 2). Organic species from the DEW model were excluded from the computation following ref⁶⁷. The Mg(SiO₂)(HCO₃)⁺ and H₂CO_{3(aq)} species were also excluded as they were found to result in unrealistically high concentrations.

411 Back- and lagged-computation methods⁶⁷ give similar results at temperatures cooler than the complete
412 serpentinite breakdown, but only the lagged method correctly models the complete loss of sulphur at
413 higher temperatures because this method imposes mass balance conservation.

414

415 **Infiltration models.** The fluids in equilibrium with the graphite-bearing metapelite were first computed
416 by Gibbs energy minimization at the P–T conditions of interest (650 °C, 1.7 GPa, Supplementary Table
417 2) using MEEMUM from the PerpleX package⁶⁶ and the lagged calculation method⁶⁷. This composition
418 (renormalized to two hydrogen moles) was then equilibrated with the model serpentinite at the same P–
419 T conditions at steps of 0.1 mol of fluid aliquot along 150 nodes (0-d infiltration mode), without
420 fractionation of the fluid at each node. Additional computations fractionating the fluid at each node do
421 not significantly modify the results. An example of the reequilibrated composition after interaction of
422 12 mol/kg with a fluid equilibrated with graphite-bearing metapelite is presented in the Supplementary
423 Table 2. To model global subduction zones, the same procedure was repeated for all s 56 subduction
424 zone segments at the P and T of the intersection of the antigorite breakdown with the slab surface based
425 on the numerical model D80 from ref.⁸¹ The intersection was found by solving the polynomial fitting
426 of the antigorite dehydration curve from this study and the slab trajectories at the surface⁸¹ as
427 documented in ref.⁸². MEEMUM was then computed for the 56 P–T conditions for the two different
428 fluid sources (graphite-bearing metapelite and GLOSS sediment) resulting in 112 different fluid
429 compositions. Once these fluids were retrieved, 112 infiltration models were run with VERTEX at the
430 specified P–T conditions. These computations generate multigrid outputs for all available properties
431 accessible with WERAMI, including, mineral and fluid modes, dependent chemical potentials (used to
432 compute $\Delta\log_{10}f\text{O}_2[\text{FMQ}]$) and the amount of solvents in the fluid (as mole fraction) and species
433 concentration (as molalities, mol/kg). We provide a global dataset (source data) including
434 $\Delta\log_{10}f\text{O}_2[\text{FMQ}]$, bulk fluid composition and solvent-solute fluid composition for the intrinsic and the
435 two sediment-infiltrated deserpentinisation models (using high and low reducing capacity fluids) for
436 the 56 subduction transects and an extent of interaction of 12 mol/kg. A Python notebook is provided
437 under request to generate the dataset for any desired extent of interaction.

438

439 **Mantle wedge redox conditions.** Two end-member bulk compositions were considered to compute the
440 $f\text{O}_2$ of the mantle wedge before fluid infiltration (Fig. 3 and Supplementary Fig. 6): depleted MORB
441 mantle source (DMM)⁸³ with a $\text{Fe}^{3+}/\Sigma\text{Fe}$ equal to 0.035, taken from the Primitive Upper Mantle, and
442 adding S content of 119 µg/g; and a highly depleted mantle (sample PHN5239 from ref.⁸⁴) with a
443 $\text{Fe}^{3+}/\Sigma\text{Fe}$ equal to 0.021 and a 50 µg/g of S, taken as the lowest possible bound based on the Cu–S
444 covariance in MORBs⁸⁵. We chose fluids from the hottest and coldest subduction zones after 12 mol/kg
445 interaction of the two fluids (graphite-bearing metapelite and GLOSS) with the reference serpentinite.

446 The aqueous fluid was fractionated at each node for mantle wedge infiltration models to reflect the low
447 instantaneous fluid–rock ratio expected for pervasive fluid flow at mantle conditions.

448

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455

456 **Author contributions**

457 J.A.P.N. conceived the project, processed the data, acquired funding and wrote the original manuscript.
458 V.L.S-V. contributed to the conceptualization, performed the computations, organized the raw data and
459 contributed to the writing of the manuscript. M.D.M. computed the global deserpentinisation conditions
460 and assisted computations. M.T.G-P. contributed to the writing of the manuscript. C.J.G contributed to
461 the conceptualization, acquired funding, t and writing of the manuscript.

462

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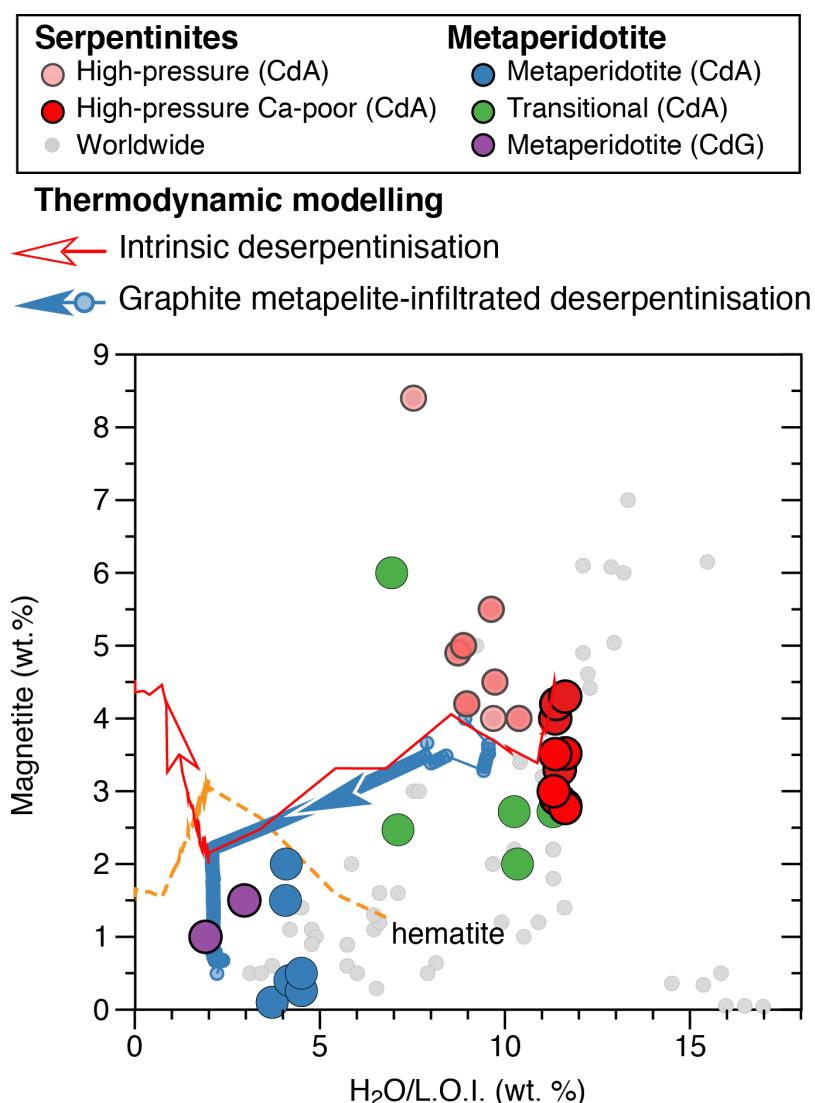
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541 **Supplementary figures and tables**

542 **Figure 1.** Global compilation of magnetite content in serpentinite and metaperidotite (Chl-
 543 harzburgite) against the water content (measured for CdA, this work and ref³⁶) or loss of ignition
 544 (L.O.I.) as a proxy for water content for samples from the literature (see Methods). The observed
 545 decrease in magnetite content relative to common magnetite-bearing serpentinite is reproduced by
 546 deserpentinisation infiltrated with highly reducing fluids equilibrated with graphite-bearing
 547 metapelite. The decrease in magnetite for the intrinsic deserpentinisation model is coeval with the
 548 precipitation of hematite (dashed red line) which is not observed in natural samples.

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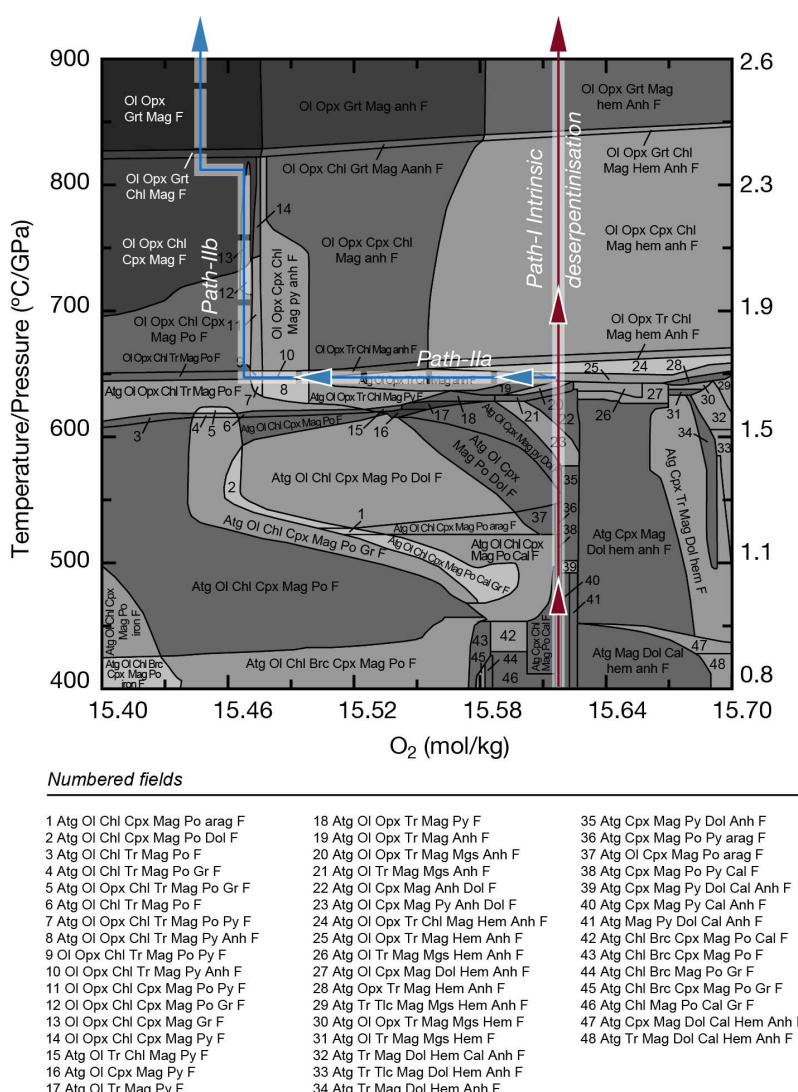
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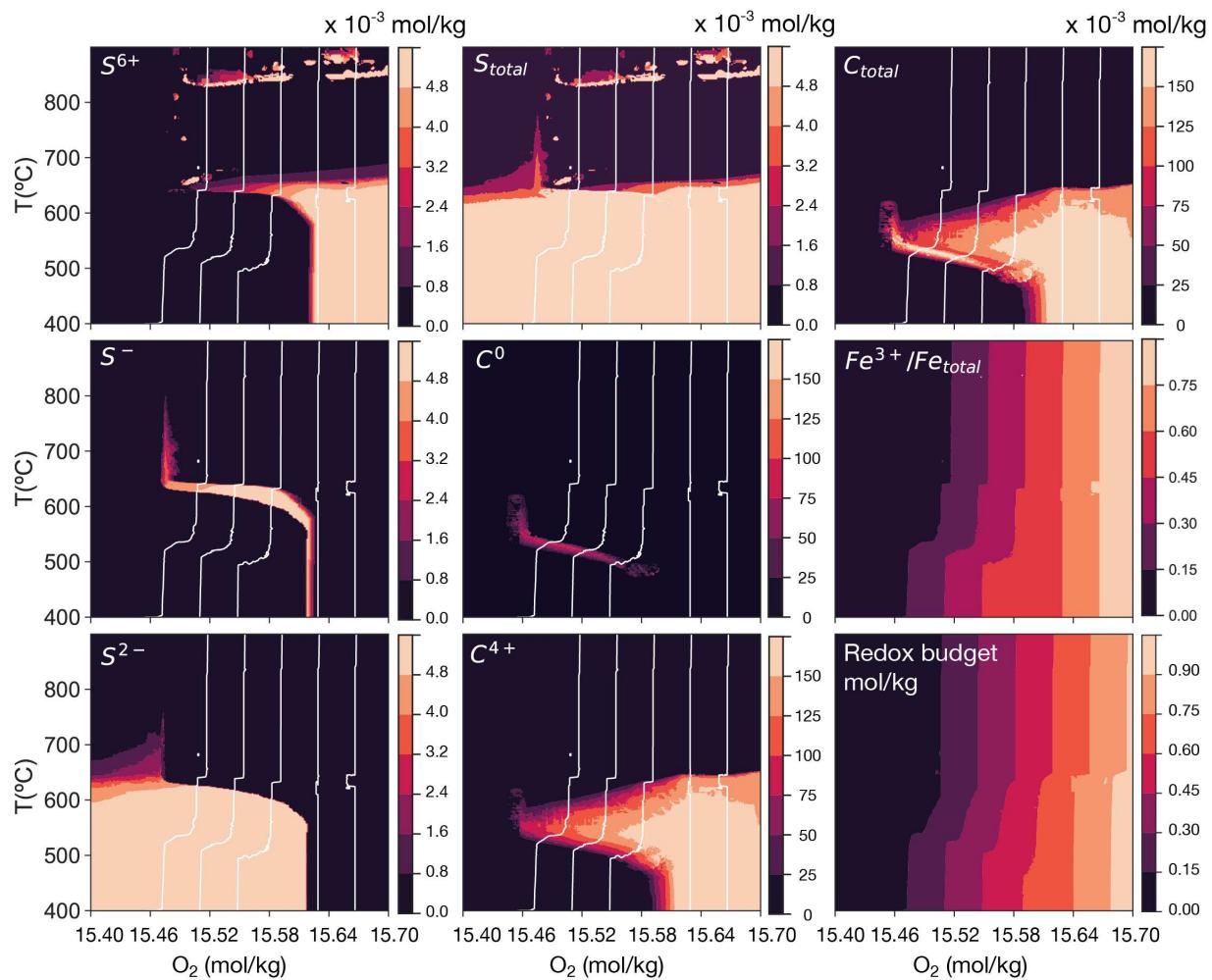
554 **Figure 2.** X(O₂)-P/T (along a thermal gradient, see Methods) pseudosection¹⁰ for a representative Ca-
 555 poor serpentinite from CdA (sample Al98-05a²⁵) with sulphur and carbon content from ref³⁶ (these
 556 values were confirmed by new, duplicate analyses) and ferric iron from this work (see Supplementary
 557 Table 1). The vertical line represents the intrinsic deserpentinisation for a fixed O₂ content of the
 558 system (Path I), corresponding to the bulk O₂ for sample Al98-05a (15.602 mol/kg is used instead of
 559 the measured 15.672 mol/kg for better agreement with the observed sequence of mineral assemblages
 560 at CdA; it likely reflects the amount of ferric iron in antigorite, not accounted for in the available solid
 561 solution models⁸⁶). The horizontal path (IIa) shows schematically the evolution if the system is
 562 externally infiltrated by fluids equilibrated with metasedimentary rocks with a high reducing capacity
 563 (graphite-bearing metapelite). The quantitative evolution along path IIa is shown in Figure 2b in the
 564 main text (see also Supplementary Figure 5 for the evolution of the speciation in the fluid). The path
 565 IIb corresponds to the prograde evolution after the graphite metapelite-infiltrated deserpentinisation
 566 potentially followed by CdG.
 567



568

569 **Figure 3.** Absolute concentration of oxygen-sensitive components in the solids (expressed as mol/kg
 570 of rock A198-05a) for the pseudosection shown in Supplementary Figure 2 (see also Figure 2 in the
 571 main text for the contouring of oxygen fugacity relative to the buffer FMQ). All panels were
 572 computed from the absolute amounts of mineral phases containing oxygen-sensitive components and
 573 their concentration in pure and solid solution endmembers from WERAMI outputs. Computations
 574 used the back-calculated method for fluid speciation in PerpleX, except for pannel S^{6+} that was
 575 computed using the lagged speciation method that allows mass balance constrains in the region below
 576 the complete serpentinite dehydration. The last panel shows the redox budget referred to the whole
 577 mantle reference redox state (Methods).

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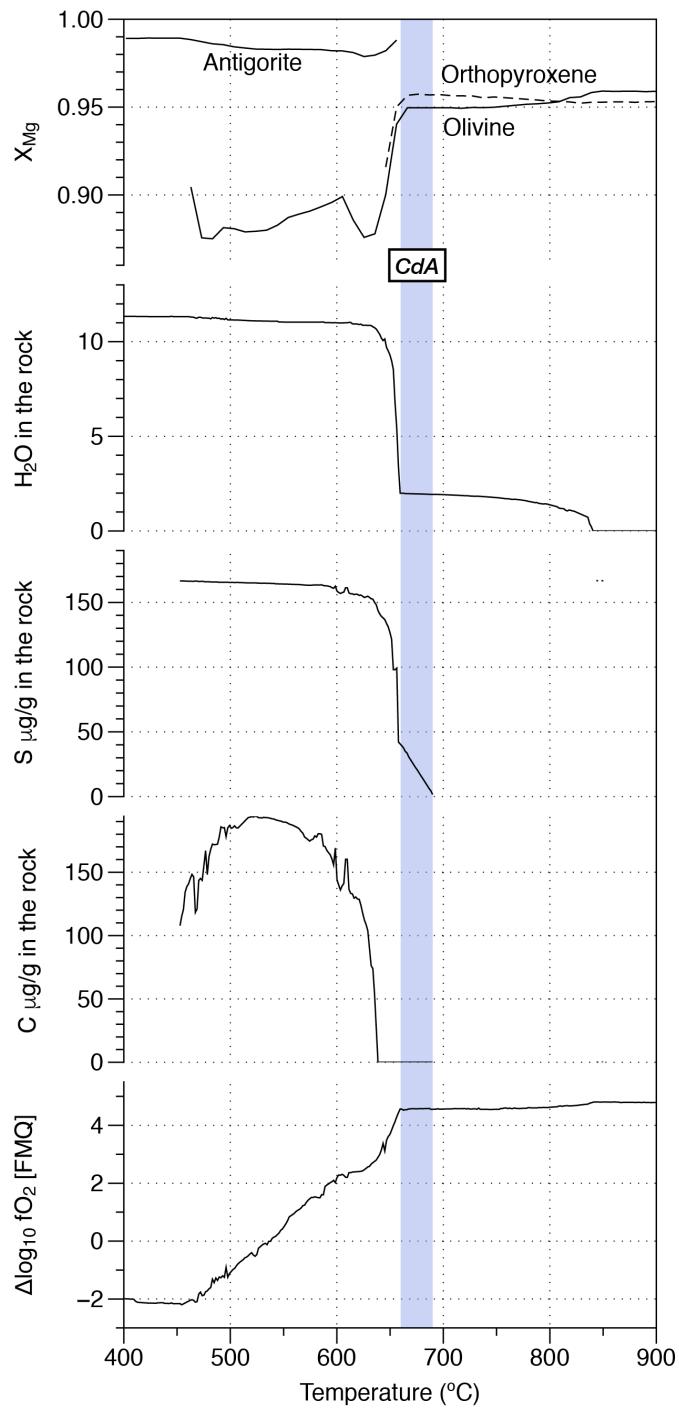


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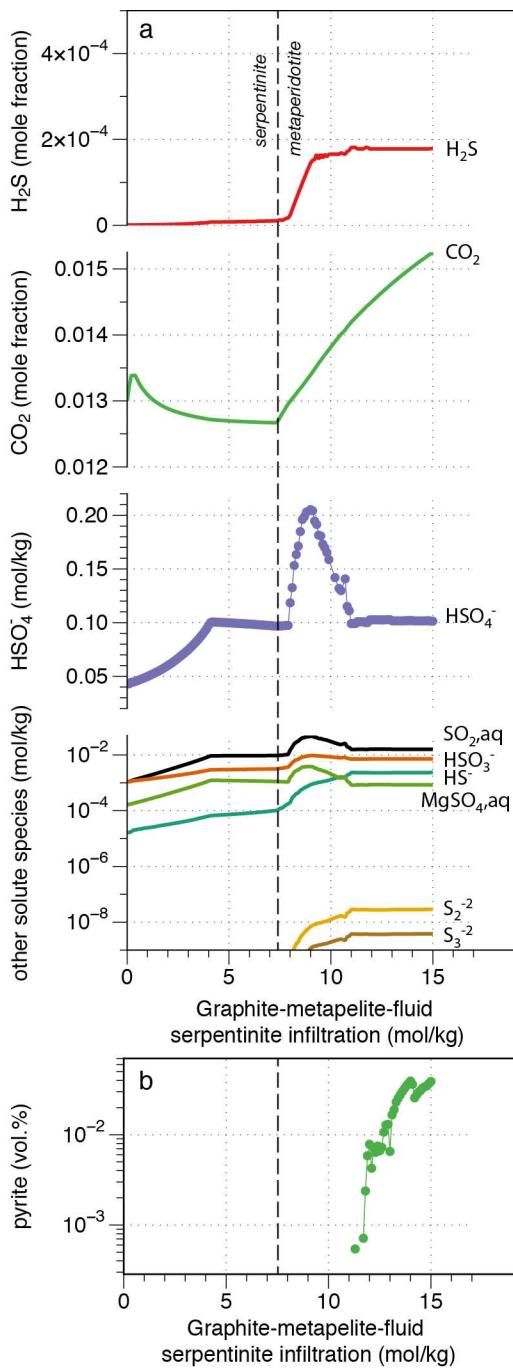
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582 **Figure 4.** Evolution of key parameters along intrinsic deserpentinisation (intrinsic path I in Figure 2,
 583 red vertical line). (a) X_{Mg} in antigorite and their dehydrated product olivine and orthopyroxene; (b)
 584 H_2O content hosted in the solid phases; (c) and (d) bulk sulphur and carbon contents retained in the
 585 solid phases; (e) evolution of the oxygen fugacity relative to the FMQ buffer. The blue region
 586 corresponds to the temperature conditions of dehydration in Cerro del Almirez (CdA). Note that none
 587 of the observables (X_{Mg} , S and C content, see Fig. 2b in the main text) agrees with the model
 588 predictions along with the intrinsic deserpentinisation model.



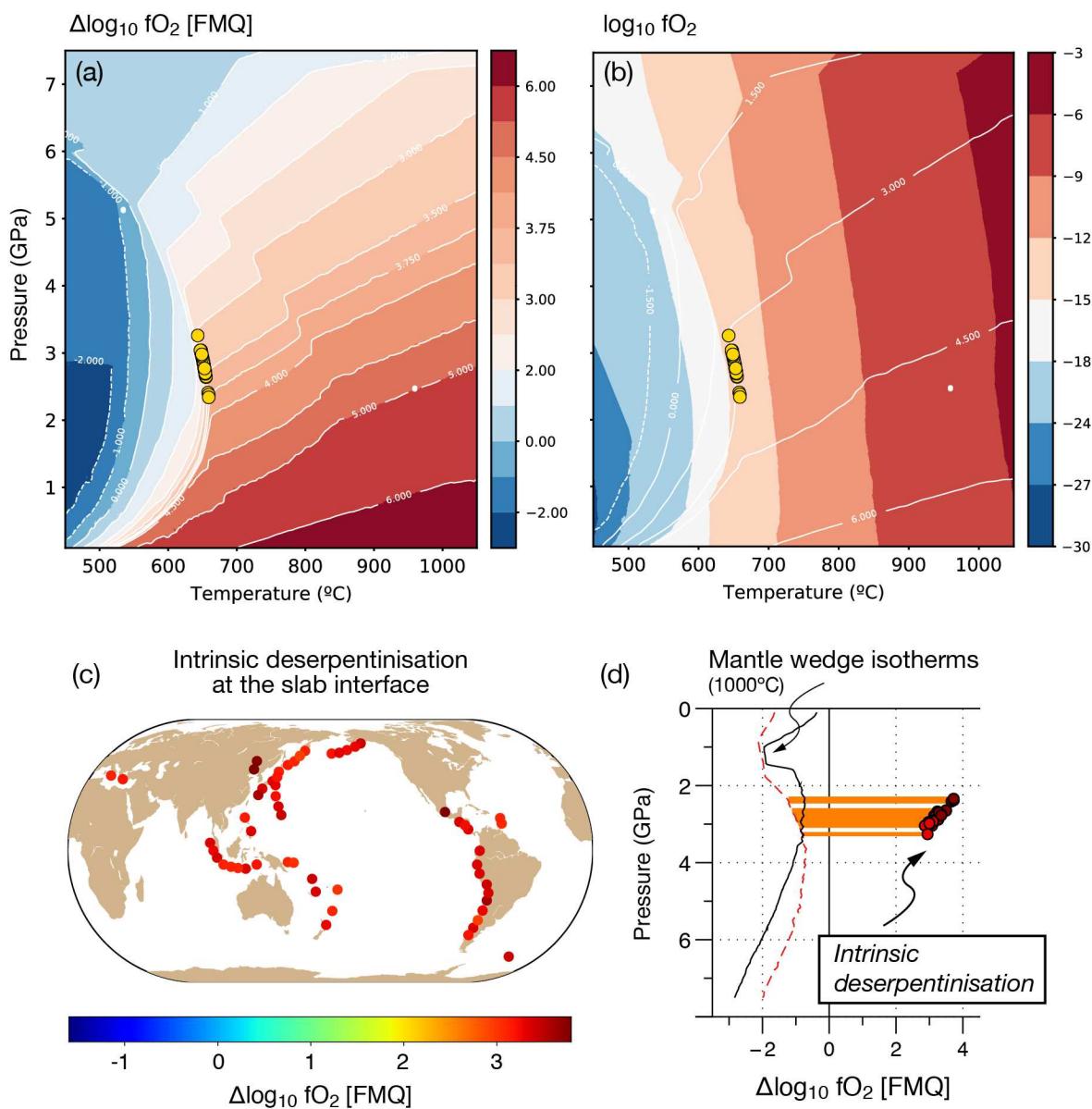
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591 **Figure 5.** a. Fluid speciation evolution during the infiltration of a partially dehydrated
 592 serpentinite with a fluid equilibrated with a graphite-bearing metapelite at 650 °C and 1.7
 593 GPa. The solvent species H₂S and CO₂ are expressed as mole fraction, whereas the solute
 594 species are expressed as molality (mol/kg). The main oxidising species (HSO₄⁻) is
 595 represented on a linear scale whereas other less abundant species are on a logarithmic scale.
 596 b. Modal (vol.%) pyrite abundance in the metaperidotite induced by graphite metapelite fluid
 597 infiltration.



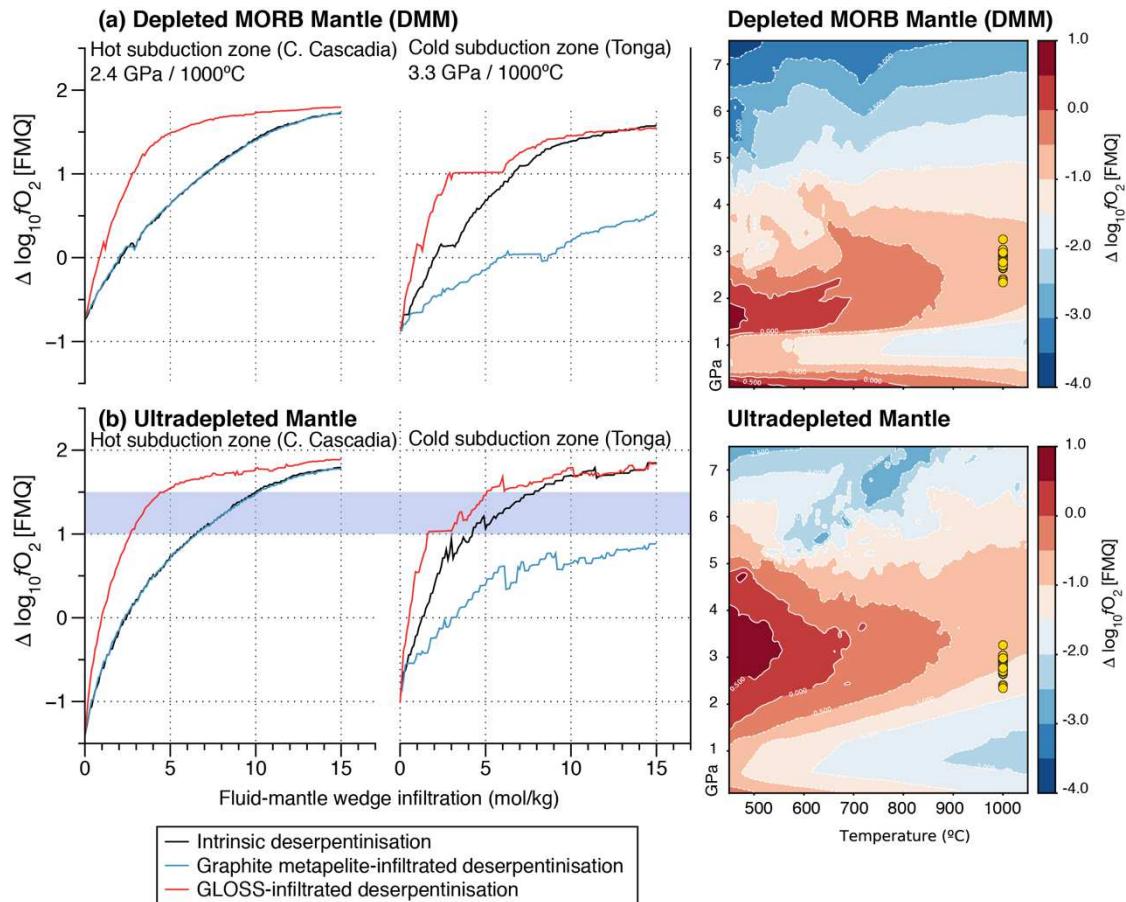
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600 **Figure 6.** Intrinsic deserpentinization oxygen fugacity conditions (a) relative to the FMQ
 601 buffer, $\Delta\log_{10}f\text{O}_2[\text{FMQ}]$ and in absolute values (b) for a representative metaserpentinite
 602 (sample A198-05a, see Supplementary, Table 1) in a pressure-temperature space. Yellow dots
 603 are pressure-temperature deserpentinisation conditions at the slab surface for a worldwide
 604 compilation of subduction zones^{81,82}, geographically located in (c), (d) Difference between the slab
 605 surface intrinsic deserpentinisation and the mantle wedge oxygen fugacity (expressed as
 606 $\Delta\log_{10}f\text{O}_2[\text{FMQ}]$) along the 1000°C isotherm.
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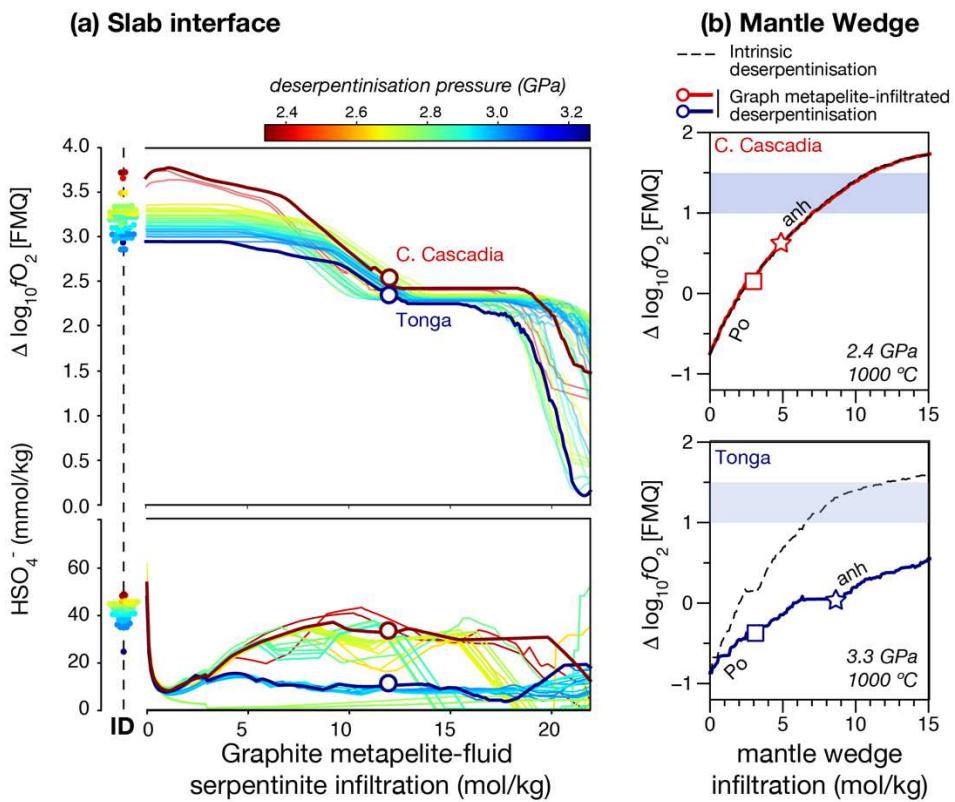
611 **Figure 7.** Effect of peridotite mantle wedge depletion on the $\Delta \log_{10} f\text{O}_2[\text{FMQ}]$ evolution during
 612 fluxing by different types of deserpentinisation slab fluids. The left panel shows the results
 613 for (a) a depleted MORB mantle wedge source⁸³ (DMM) and (b) an ultradepleted mantle
 614 wedge source⁸⁴, both for a hot (Central Cascadia) and a cold (Tonga) subduction zone. The
 615 mantle wedge $\Delta \log_{10} f\text{O}_2[\text{FMQ}]$ evolution of the mantle wedge fluxed by fluids sourced from
 616 intrinsic deserpentinisation and sediment-infiltrated deserpentinisation fluids produced by the
 617 infiltration of 12 mol/kg of fluids equilibrated with GLOSS and graphite-bearing metapelite.
 618 Right panels are the contours of the initial $\Delta \log_{10} f\text{O}_2[\text{FMQ}]$ of the mantle wedge for a DMM
 619 (upper panel) and ultradepleted source (lower panel) before fluxing with slab fluids; shown as
 620 yellow dots are the initial $\Delta \log_{10} f\text{O}_2[\text{FMQ}]$ conditions at the 1000 °C of the mantle wedge for a
 621 worldwide compilation of dehydration conditions in hot to cold subduction zones. Central
 622 Cascadia (hot subduction) and Tonga (cold subduction) correspond, respectively, to a
 623 minimum (2.4 GPa) and maximum pressure (3.3 GPa) for the dehydration of serpentinisation
 624 at the slab surface. Note that the initial $\Delta \log_{10} f\text{O}_2[\text{FMQ}]$ conditions depend on the thermal
 625 regime of the subduction zone and the depletion of the mantle wedge source, but have a
 626 subsidiary effect on the $\Delta \log_{10} f\text{O}_2[\text{FMQ}]$ evolution of the mantle wedge during fluxing of
 627 different types of deserpentinisation fluids.



628

629 **Figure 8.** (a) Evolution of the $\Delta \log_{10} f\text{O}_2[\text{FMQ}]$ and the concentration of HSO_4^- —relative to
 630 the intrinsic deserpentinisation fluid (ID)—during infiltration of fluids equilibrated with
 631 metasedimentary rocks with a high reducing capacity (graphite-bearing metapelite) for a
 632 worldwide compilation of subduction zones^{81,82} (colour-coded for the pressure at which the
 633 serpentinite dehydrates at the slab surface, Source Data). (b) The capacity of these modified,
 634 serpentinite-derived fluids (empty dots in a) to oxidise the mantle wedge on top of the slab at
 635 near wet-solidus conditions is computed for the hottest (Central Cascadia) and coldest
 636 (Tonga) subduction zones. A minimum value range of $\Delta \log_{10} f\text{O}_2[\text{FMQ}]$ inferred for oxidised
 637 IAB source and recorded by high-pressure metasomatized mantle atop of the slab^{52,8752,87} is
 638 given as a horizontal blue-shaded range. Sediment (graphite-bearing)-serpentinite derived
 639 fluids have a variable capacity to oxidise the mantle wedge for hot and cold subduction
 640 zones, a variable potential that is directly related to the contrasting solubility of HSO_4^- for the
 641 two extreme thermal cases. The metasomatized mantle wedge has an initially depleted
 642 composition⁸³. Squares and stars on the red and blue lines indicate the condition range limits
 643 at which pyrrhotite (Po), or anhydrite (anh) are the stable minerals hosting S in the rocks. For
 644 an ultradepleted MORB mantle, see Supplementary, Fig. 7. For interaction with sediments
 645 with low reducing capacity (GLOSS), see Fig. 3 in the main text.

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649 **Supplementary Tables**

650 **Supplementary Table 1.** Bulk rock compositions used for thermodynamic modelling.

651 **Supplementary Table 2.** Fluid composition and speciation for CdA peak metamorphic
652 conditions at intrinsic dehydration and after interaction (12 mol/kg) with sediment with high
653 reducing capacity

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655 **Source data**

656 Supplementary file (csv). Worldwide subduction zone database⁸¹ used to compute the
657 pressure and temperature conditions for the slab surface deserpentinisation⁸². These pressure
658 and temperature conditions are used to compute the intrinsic fluid chemistry and the fluid
659 composition for high and low-reducing capacity sediments (graphite and GLOSS
660 respectively) that are used for infiltration at the same serpentinite dehydration pressure and
661 temperature conditions. Main species are given for the three cases: intrinsic (_intr) and for
662 infiltration of 12 mol/kg for the cases of graphite-bearing and GLOSS sediments derived
663 fluids (_graph and _gloss). Fluid bulk compositions are given in mol per formula unit of fluid
664 and species concentrations are given in mol/kg. This database can be generated for other
665 degrees of infiltration using a Jupyter notebook available upon request.

Supplementary Files

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