Oxidising agents in sub-arc mantle melts link slab devolatilisation and arc magmas

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Subduction zone magmas are more oxidised on eruption than those at mid-ocean ridges. This is attributed either to oxidising components, derived from subducted lithosphere (slab) and added to the mantle wedge, or to oxidation processes occurring during magma ascent via differentiation. Here we provide direct evidence for contributions of oxidising slab agents to melts trapped in the sub-arc mantle. Measurements of sulfur (S) valence state in sub-arc mantle peridotites identify sulfate, both as crystalline anhydrite (CaSO4) and dissolved SO4^2− in spinel-hosted glass (formerly melt) inclusions. Copper-rich sulfide precipitates in the inclusions and increased Fe^{3+}/ΣFe in spinel record a S^6+-Fe^{2+} redox coupling during melt percolation through the sub-arc mantle. Sulfate-rich glass inclusions exhibit high U/Th, Pb/Ce, Sr/Nd and δ³⁴S (+7 to +11‰), indicating the involvement of dehydration products of serpentinised slab rocks in their parental melt sources. These observations provide a link between liberated slab components and oxidised arc magmas.
he oxidation state of magmas represents the sum of the electron exchange balance between multivalent atoms including major (Fe), minor (Mn), trace (Cr and V) and volatile (S, C and H) elements. The redox conditions, expressed in terms of oxygen fugacity ($f_{O_2}$), control the evolution and degassing of magmas in volcanic arcs above subduction zones and the formation of ore deposits. In practice, the $f_{O_2}$ during the generation and evolution of magmas can be estimated on the basis of Fe$^{3+}/\Sigma$Fe (Fe$^{3+}/(\text{Fe}^{3+} + \text{Fe}^{2+})$) in quenched melts and olivine-pyroxene-spinel assemblages in crystal-rich rocks, or alternatively from $S^2+/(S^2+ + S^6+)$ in quenched melts.

In subduction zones, the $f_{O_2}$ of the different rocks varies over several log units above the fayalite-magnetite-quartz (FMQ) reference buffer assemblage. Mid-ocean ridge basalts (MORBs) and abyssal peridotites are representative of the oceanic lithosphere that ultimately undergoes subduction (slab) and are relatively reduced, with $f_{O_2}$ close to and below FMQ. However, before being subducted, the oceanic lithosphere can be altered and oxidised on or near the seafloor by hydrothermal and metamorphic processes. Arc lavas, generated by interactions between agents derived from the oxidised slab and the relatively reduced mantle wedge, generally display higher $f_{O_2}$ than MORB, with values above FMQ.

The oxidised nature of arcs compared with mid-ocean ridges has been largely attributed to the addition of volatile-rich slab agents to the asthenospheric mantle source in arcs before or during melting. Slab-derived $S^6+$, generally linked with oxygen to form reactive sulfate ($SO_4^{2-}$) ions, has been proposed as a key player in mantle wedge oxidation, as it is a powerful oxidising agent able to convert 8 mol of Fe$^{2+}$ into Fe$^{3+}$ per mole of $S^6+$ according to the reaction:

$$SO_4^{2-} + 8\text{Fe}^{2+} \rightarrow S^4+ + 4\text{Fe}_3\text{O}_4$$

Mounting evidence from stable isotope measurements on deeply subducted rocks supports the idea that fluids released from these rocks could be enriched in $SO_2^-$.

![Fig. 1](image-url) **Sulfur valence state at oxygen fugacities prevailing at mid-ocean ridges and subduction zones and the origins of the glass (formerly melt) inclusions (MI) in Kamchatka and West Bismarck sub-arc mantle peridotites.**

(a) $S^6+/\Sigma S$ equilibrium (thin black curves) in silicate melts and the range of $\Delta logf_{O_2}$ measured for subduction zone rocks and melts expressed relative to FMQ: orange, abyssal peridotites (MORB mantle); white bars, sub-arc mantle rocks; yellow, arc lavas. The $S^6+/\Sigma S$ equilibrium curves are shown for Fe-poor (Fe/S $\leq$ 2) and Fe-rich (Fe/S $\geq$ 2) silicate melts at low-pressure ($\leq$ 0.2 GPa) conditions and for 1 GPa. The $S^6+/\Sigma S$ determined by XANES and inferred from Raman spectrometry for Kamchatka LT inclusions, MP, and vein MI and West Bismarck MI are respectively shown in cyan, green, pink and blue. The upper-bound Fe$^{3+}/\Sigma$Fe in spinel measured by EPMA (i.e., in halos next to the inclusions) for the percolated harzburgite samples Av33 (Kamchatka) and 67-02D(7) (West Bismarck) is indicated with a grey horizontal bar (Supplementary Tables 5 and 6). The range of $\Delta logf_{O_2}$ calculated for the percolated harzburgite samples Av33 and 67-02D(7), using the EPMA data on spinel (away from the inclusions and their halos) reported in this study and earlier, is indicated with a grey vertical bar (Supplementary Tables 9 and 10). Also shown are the calculated Fe$^{3+}/\Sigma$Fe in spinel in equilibrium with the parental melts of LT inclusions and MP at 0.2, 1 and 1.5 GPa (bold black curves), using the Fe$^{3+}/\Sigma$Fe equilibrium in silicate melts and partitioning coefficients for Fe$^{3+}$ and Fe$^{2+}$ between Cr-bearing spinel and melt (Supplementary Table 1).

(b) A subduction zone cross-section showing the original position of the studied peridotite xenoliths (sub-arc mantle peridotites) from Kamchatka and West Bismarck in the shallow mantle lithosphere before their ascent in arc magmas. Also indicated are the stability fields for subducted serpentinite (antigorite, dark blue line) and the geochemical features of the inferred fluids derived therefrom (dark blue arrows). DMM (orange) and erupted arc magmas (yellow triangle). The inclusions in this study allow probing the redox conditions in and sulfur isotope compositions of the deep mantle wedge (‘fluxed melting’, red field).
in arc melts and volcanic gases interpreted as the result of S recycling from the slab18–21 (Fig. 1b). However, it remains unclear if the released slab fluids are sufficiently abundant and oxidised to travel tens of kilometres to the zones of arc melt generation without being reduced by the ambient mantle (Fig. 1b). Indeed, direct evidence for the presence of recycled, slab-derived sulfate in sub-arc mantle melts sampled at their earliest stages of evolution remains to be found.

The need for identifying such a missing link also stands out, because the oxidised nature of the sources of arc magmas has been disputed on the grounds that the similar V/Sc and Fe/Zn ratios in ridge- and arc-associated basalts may imply compostions (MI) and pockets, which record the in situ oxidation state of primitive arc melts as they ascend to the overlying crust. The results show that large quantities of S(IV) are transferred from the slab to magma generation zones in the mantle wedge, and that sulfate contributes to the oxidation of Fe in sub-arc mantle minerals and the formation of magmatic Cu-rich sulfide.

Results

Samples. The investigated samples are all spinel harzburgite xenoliths from the sub-arc mantle lithosphere; these peridotites record relatively low temperatures ranging from 650 to 1000 °C, as calculated using olivine-spinel thermometry25–27 (Fig. 1b). The mantle xenoliths were brought to the surface by recent volcanic activity at the Avacha (samples Av24, Av25 and Av33) and Ritter (sample 67-02D(7)) volcanoes, respectively, located in the Kamchatka (Russia) and West Bismarck arcs (Papua New Guinea)26–29.

As originally described in detail in Ionov et al.28 and Bénard et al.29, Cr-bearing spinel in Kamchatka xenoliths contains glass MI s with compositions spanning omphacite-dacite (‘LT inclusions’, where LT stands for low temperature), magnesian omphacite (melt pockets, ‘MP’) and dacite-rhyolite of boninitic affinity (‘vein MI s’). Spinel in West Bismarck xenoliths contains magnesian omphacite glass (‘West Bismarck MI s’, Supplementary Fig. 1). The Mg# (Mg/(Mg + Fe)) of Fe, where Fe0.4 means all Fe is treated as Fe2+) of the inclusion glasses is generally ≥ 0.6 in MP, vein MI and West Bismarck MI but is <0.4 in LT inclusions (Supplementary Table 1). High concentrations of slab agents in the inclusion parental melts were inferred from lithophile trace element signatures and very high volatile abundances in the glasses26–31; the second compositional feature (e.g., up to ~1 wt% H2O and ~1 wt% CO2, ref. 29) also indicates that melt entrapment occurred at high pressure in the sub-arc mantle lithosphere (Fig. 1b). The inclusion parental melts are ‘exotic’ liquids (i.e., they were trapped on their way to the surface and not formed in situ), which were confined in spinel in the sub-arc mantle lithosphere during a percolation process, either pervasive (LT inclusions, MP and West Bismarck MI) or along channels (vein MI)28,29 (Figs. 1b and 2a). More detail on the spinel-hosted MI investigated in this study is provided in the Supplementary Discussion.

In contrast with earlier works on Kamchatka inclusions26–31, we have not used experimentally treated (i.e., heated) MI and their host spinel grains to investigate S and Fe valence states in this study. This choice was made considering the possibility of an Fe3+ + Fe2+ exchange reaction during experiment between melt and spinel, in which Fe3+ is compatible32, or Fe3+ oxidation in melt triggered by H+ loss from the inclusions through either diffusion33 or leakage. Instead of using treated MI, we have investigated unheated inclusions that are naturally free of daughter silicate phases28,29 (Supplementary Figs 2–4 and Discussion).

Sulfur abundances and valence state. The full dataset supporting this study is given in Supplementary Tables 1–13. Micro X-ray fluorescence (XRF) mapping combined with micro X-ray absorption near-edge structure (XANES) spectroscopy show that sulfur is heterogeneously distributed in LT inclusions and vein MI, while MP have more homogeneous S concentrations (Fig. 2a–d). The ‘bulk’ glasses in Kamchatka and West Bismarck MI contain 150–6000 p.p.m. S (Supplementary Tables 1–3). The molar Fe/S of the inclusion glasses, an important feature regarding S dissolution mechanism in hydrous silicate melts16, mostly ranges from 8 to 20 in MP, vein MI and West Bismarck MI, but only from 1 to 2 in LT inclusions (Supplementary Tables 1–3).

All spinel-hosted inclusions contain S6+ present as SO42− within the glass structure (Fig. 2e–g). The LT inclusions contain almost solely S6+ in the glass (S6+/ΣS always close or equal to 1) and often exhibit the contribution of S8+ from crystalline anhydrite (CaSO4, Fig. 2d and Supplementary Fig. 5). The MP glass contains a homogenous mixture of dissolved S6+ and S2+ with S6+/ΣS=0.57 (Fig. 2e). In addition to S6+, some XANES spectra of vein MI indicate the presence of S2− that is heterogeneously distributed as a S-bearing solid phase (i.e., an immiscible sulfide, Fig. 2d, g and Supplementary Fig. 5). Depending on the contribution of the immiscible sulfide to the overall XANES spectral measurement, the calculated S6+/ΣS for ‘bulk’ vein MI are variable and can be as low as 0.24–0.44 (Fig. 2d, g and Supplementary Fig. 5). The highest S6+/ΣS for vein MI range from 0.62 to 0.88 in glassy areas displaying a more homogeneous S distribution (Fig. 2d, g and Supplementary Fig. 5), which indicate the presence of dissolved S2− in the glass of these inclusions as well. Further characterisation of multiple inclusions using Raman spectrometry reveals that anhydrite is systematically present in LT inclusions (Fig. 2h) and West Bismarck MI (Fig. 2i).

Imaging and mapping. The presence of sub-micrometre anhydrite crystals in LT inclusions and West Bismarck MI is one of the most important results of this study and is further documented by imaging and mapping using electron probe micro-analysis (EPMA) and scanning electron microscope (SEM) techniques (Supplementary Figs 2–4). Although not evidenced by any XANES measurement, rare sulfide blebs sometimes occur in LT inclusions (Supplementary Figs 2–4, 6 and 7). An important observation is that these sulfides may contain as much as 20 wt% Cu (Supplementary Table 4).

Iron valence state. Measurements of Fe valence state in the MI-hosting spinel using EPMA calibrated with secondary (Fe3+, Fe2+) bearing spinel standards3 reveal Fe3+ zoning in irregular halos28 next to the inclusions (Fig. 3a–d and Supplementary Tables 5–7). The highest Fe3+/ΣFe in spinel is found adjacent to anhydrite-bearing inclusions and decreases away from the MI, typically from 0.34 to 0.30 and 0.33 to 0.27 for LT inclusions and West Bismarck MI34, respectively (Fig. 3d and Supplementary Tables 5 and 6). The halos are also characterised by significantly lower Cr and higher Al concentrations (by up to
Fig. 2 Spinel-hosted glass (formerly melt) inclusions (MI) from the mantle lithosphere beneath the Kamchatka and West Bismarck arcs and their sulfur distribution and valence state. a A reflected-light image of a spinel grain containing many LT inclusions and MP. Coloured inlay in a shows the elemental distribution of S in the spinel, LT inclusions and MP determined by S Kα X-ray fluorescence imaging (red, high S concentration; blue, low S concentration). Note the presence of a LT inclusion in an orthopyroxene (Opx) from the host harzburgite, which supports the formation of these inclusions by pervasive percolation of their parental melts in the sub-arc mantle lithosphere. Scale bar length is ~200 μm. b–d Uncalibrated S Kα X-ray fluorescence maps of b LT inclusions, c MP and d vein MI. The LT inclusions and vein MI are characterised by a heterogeneous distribution of sulfur. The S-free spinel appears in dark blue. Scale bar lengths are respectively ~10 μm in b and ~20 μm in c, d. e–g S K-edge XANES spectra of e LT inclusions, f MP and g vein MI. Spectra numbers refer to the spot positions shown in b–d. Vertical black lines indicate energies for specific S valence states: 2482.8 eV for S6+, 2478 eV for S4+ and 2472.5 eV for S2− in crystalline Fe-S compounds. The additional feature at ~2486 eV is typical for crystalline anhydrite (CaSO4). Some S4+ is generated during XANES measurements of glasses by photo-reduction of S6+ but also show varying contributions of S2− from immiscible sulfides (Supplementary Table 1). h, i Raman spectra for h multiple LT inclusions and an MP, and i West Bismarck MI, compared with their host spinel (grey spectrum) and an anhydrite (CaSO4) reference (black spectrum). All these inclusions, with the exception of the MP, contain anhydrite. Note that all the inclusions for which data are presented here are unheated

Oxygen fugacity estimates. The fO2 values (expressed as the deviation from FMQ in log units, ∆logO2) inferred from the S6+/$\Sigma$S equilibrium in ‘Fe-poor’ silicate melts (Fe/S ≤ 2) at ≤ 0.2 GPa are range from FMQ + 0.5 to FMQ + 1.5 for LT inclusions. The ∆logO2 values inferred from the S6+/$\Sigma$S equilibrium in ‘Fe-rich’ silicate melts (Fe/S > 2) at ≤ 0.2 GPa range from FMQ + 1 to FMQ + 1.5 for MP and vein MI, and correspond to ca. FMQ + 2 for West Bismarck MI (Fig. 1a). It is noteworthy that as anhydrite saturation is evidenced in all LT inclusions and West

0.10–0.25 at%, but comparatively little variations in Fe2+, Mg and Mg# (by only 0.01–0.04) than in spinel away from the inclusions (Supplementary Tables 5 and 6); these halos are very similar to those around MP reported by Ionov et al. (Supplementary Fig. 8 and Supplementary Table 8). Further EPMA measurements reveal that the Fe3+/ΣFe increase can be also restricted to the LT inclusion-bearing rims of some spinel grains that are only partially impregnated with melt (Supplementary Fig. 7 and Supplementary Table 5).
Bismarck MI investigated in this study (Fig. 2c, i and Supplementary Fig. 5), the ΔlogO2 inferred from the S6+/ΣS equilibrium for these inclusions may constitute only lower-bound estimates. Calculations at 1.5 GPa with a thermometer5 and an oxybarometer9 for the MI-bearing harzburgite samples, using the stable compositions of spinel measured away from the inclusions and their halos34 (Supplementary Tables 5 and 6) and those of coexisting silicate minerals previously reported by Bénard et al.26, yield ΔlogO2 ranging from FMQ + 1.0 to FMQ + 1.4 (±0.2–0.3, Fig. 1a and Supplementary Tables 9 and 10).

**Sulfur isotope compositions.** From the absence of an immiscible S-bearing phase, and the homogeneous elemental distribution and valence state of S dissolved in their glasses (Fig. 2c, f), it appears that MP are the best suited for the determination of pristine δ34S using secondary ion mass spectrometry (SIMS). Furthermore, the other types of inclusions are much smaller than MP in size28 (Fig. 2a), which render SIMS analysis very difficult. We have further selected bubble-free MP found in the harzburgite spinel for these measurements. The δ34S (see Methods for the usage of delta notation) measured by SIMS ranges from +7 to +11‰ (±1–1.6, 2σ) in the glass of MP (Supplementary Table 11).

**Discussion**

Before interpreting further the origins of elevated fO2 in sub-arc mantle melts and harzburgites, it should be considered if post-entrapment processes affected this feature in the studied inclusions or not. One of these processes is H2 loss from the inclusions, which can displace the equilibrium:

\[2\text{FeO} + \text{H}_2\text{O} \leftrightarrow \text{Fe}_2\text{O}_4 + \text{H}_2\]  

(2)

to the right side as H2O dissociates according to:

\[\text{H}_2\text{O} \leftrightarrow \text{H}_2 + 1/2\text{O}_2\]  

(3)

and H2 escapes from the system. The very low totals of EPMA analyses in Kamchatka MI (down to 88 wt% for LT inclusions, 98 wt% for MP and 92 wt% for the vein MI, Supplementary Table 1) indicate bulk volatile contents close to the maximum H2O abundances previously determined by SIMS analysis, with up to ~12 wt% and ~3 wt%, respectively, in LT inclusions and MP.30,31 and ~10 wt% H2O in the vein MI.29 The EPMA setup used in this study has been previously demonstrated to provide deficiency of totals of analyses in good agreement with SIMS volatile data.29 Therefore, the inclusions in this study are among the most volatile-rich identified in these sub-arc mantle xenoliths so far and, as such, unlikely suffered appreciable H2O loss.

Insignificant H2O loss from the inclusions is further suggested by the fact that solid-state diffusion of H+ within spinel is also two to three orders of magnitude slower than in olivine.35,36 With the relatively low temperatures recorded in the percolated harzburgites in this study (950–1020 °C, Supplementary Table 10) and prevailing in the shallow mantle below the Kamchatka and West Bismarck arcs,25–27 H+ diffusivities of \(\leq 10^{-14} \text{m}^2 \text{s}^{-1}\) are expected in spinel.36 Only 30 min were inferred for the ascent from the sub-arc mantle of West Bismarck peridotite xenoliths from the same sampling sites as in this study.37 Several hours have been calculated for the ascent of mantle xenolith-bearing magmas at convergent margins with thicker continental crust,38 such as is the case for the Kamchatka arc. We conclude that volatile loss has not significantly affected the H2O-rich inclusions during the fast ascent of the xenoliths to the surface.

The calculated fO2 for the inclusions and their host harzburgites in this study fall within the range typically observed for subduction zone lavas and mantle rocks, respectively (Fig. 1a). All ΔlogO2 estimated above for the inclusions may be shifted even further up if one considers that increasing pressure has a significant effect on the S6+/ΣS equilibrium in silicate melts.39,40 However, quantifying this pressure effect remains difficult in the present state of knowledge, as it likely interplays in a complex way with those imposed by the variations in melt composition (e.g., Fe/S, ref. 16). For instance, Moretti and Baker39 have modelled a shift of the S6+/ΣS equilibrium of only ca. +0.5 log units in fO2 for hydrous tholeiite melts, whereas Matjuschkin et al.40 have experimentally inferred a shift of ca. +1.5 log units for hydrous trachydacite melts (Fig. 1a), both with a pressure increase of ~1 GPa.

The magnitude of the pressure effect on the S6+/ΣS equilibrium for the inclusions in this study can be tested independently using the Fe5+/ΣFe equilibrium in silicate melts and the experimentally determined partitioning coefficients for Fe5+ and Fe2+ between Cr-bearing spinel and melt.32 The upper-bound Fe5+/ΣFe measured in sub-arc mantle spinel adjacent to the MI (0.34–0.37, Supplementary Tables 5 and 6), correspond to those
calculated for $\Delta \log O_2$ ranging from FMQ + 1 to FMQ + 1.5 at 1–1.5 GPa in spinel in equilibrium with the parental melts of LT inclusions and MP (Fig. 1a and Supplementary Table 12). As this $\Delta \log O_2$ range corresponds well to the results of oxybarometric calculations for the host sub-arc mantle harzburgites in this study (Fig. 1a and Supplementary Table 10), we conclude that it constitutes the best estimate for the formation of their inclusions. Furthermore, the calculated Fe$^{3+}$/ΣFe in spinel provides additional evidence that the formation of the inclusions occurred at ≥ 1 GPa, i.e., in the sub-arc mantle (Fig. 1a, b). This test based on our EPMA data does not preclude an effect of pressure on the S$^{6+}$/ΣS equilibrium in silicate melts, but rather suggests that it is within the error of the $\Delta \log O_2$ estimates (typically ± 0.5, Supplementary Table 10) for the samples in this study.

In situ observations demonstrate that sulfate is present in melts from the mantle below the Kamchatka and West Bismarck arcs, recording $\Delta \log O_2$ of at least ca. FMQ + 1 (Fig. 1a). The mantle source protoliths (i.e., considered before fluxing by slab agents occurs in the mantle wedge, Fig. 1b) of the inclusion parental melts must be more depleted than the MORB source mantle (DMM), as inferred from their relatively low heavy and middle rare-earth element and Y abundances (Fig. 4a). For instance, ~15% melting of a DMM source containing 1000 p.p.m. S at ≥1.5 GPa and 1000 p.p.m. S as sulfate (with an assumed S$^{6+}$/ΣS equilibrium in silicate melts, but rather suggests that it is within the error of the $\Delta \log O_2$ estimates (typically ± 0.5, Supplementary Table 10) for the samples in this study.

Furthermore, 15% melting of a DMM source containing 90–150 p.p.m. S (ref. 46) and the formation of a basalt dissolving ≥1000 p.p.m. S at ≤1.5 GPa and ≥1200 °C (ref. 47) is also unlikely to leave significant amounts of residual sulfides. However, all inclusion types in this study are particularly enriched in S and other volatiles (Fig. 4a, Supplementary Tables 1–3 and Discussion). The high $\delta^{34}S$ measured in the MP are not intrinsic to the upper Earth’s mantle such as DMM (46,48,49), but are inevitably related to recycled components (Fig. 4b). It has been recently shown that subducted serpentine is a possible carrier of large amounts of sulfate with elevated $\delta^{34}S$ to sub-arc mantle depths15,17,18. A contribution from subducted serpentine is further consistent with the very high U/Th, Pb/Ce and Sr/Nd of the inclusion parental melts in this study50 (Fig. 4a and Supplementary Table 13). Mixing models show that the high $\delta^{34}S$ contents and $\delta^{34}S$ in MP (i.e., representative of the composition of the volatile fraction dissolved in their parental melts, Fig. 4b) require the involvement of subducted serpentine-derived agents carrying ≥1000 p.p.m. S as sulfate (with an assumed $\delta^{34}S$ of 14.5%) in the original agents15). Therefore, high S, S$^{6+}$/ΣS and $\delta^{34}S$ in melts percolating through the mantle below the Kamchatka and West Bismarck arcs must result predominantly from the addition of S-rich, oxidised slab agents to their depleted source protoliths in the mantle wedge (Fig. 1b). As the results in this study link the presence of sulfate recycled from the slab and elevated $\delta^{34}S$ in sub-arc mantle melts, by extension, they also support the idea that high $\delta^{34}S$ in primitive, un-degassed lavas from global arcs19–21,51 (Fig. 1b) can serve as a reliable proxy for the presence of oxidising slab agents in their mantle wedge sources.

The lower-bound $\Delta \log O_2$ inferred for the MP in this study (ca., FMQ + 1, Fig. 1a) precisely corresponds to previous
estimates based on the Fe$^{3+}$/ΣFe in spinel from primitive arc lavas\textsuperscript{11}. In this context, it is interesting to note that the major element compositions of the original parental melts of MP and vein MI (respectively, magnesian andesite\textsuperscript{25} and high-Ca boninite\textsuperscript{25}) are close to those of mantle-derived liquids typically found at subduction zones, whereas LT inclusions rather resemble low-temperature hydrothermal melts produced in partial melting experiments of slab rock analogues\textsuperscript{29,34} (Supplementary Table 1). This dichotomy in the apparent origins of the inclusion parental melts is directly illustrated by the variable Mg$^+$ of their glasses, which are close to those for melts in equilibrium with the mantle in MP and vein MI but much lower in LT inclusions (Supplementary Table 1). Note that, as variations in the Mg$^+$ of spinel next to these inclusions are very limited (Supplementary Tables 5 and 8), it is improbable that this parameter was significantly modified in the included melts by post-entrapment processes (e.g., re-equilibration through solid-state diffusion in spinel). Therefore, the results in this study suggest that slab agents transporting recycled sulfate ions can not only maintain their oxidising capacity during kilometre-scale percolation in the mantle wedge, but this oxidised sulfur can be effectively transferred to primitive arc magmas during mantle melting (Fig. 1b).

Considering the percolated harzburgite samples in this study, their calculated equilibrium $f_0_2$ fits within the upper range previously reported for sub-arc mantle peridotites\textsuperscript{13,34} (Fig. 1a). Recently, elevated $\Delta$log$O_2$ and orthopyroxene contents in SiO$_2$-rich, sub-arc mantle harzburgite xenoliths have been both related to fluxed melting processes involving oxidised slab agents during their formation\textsuperscript{26,34}. In this study, it is shown that ≥1000 p.p.m. of sulfate from subducted serpentinite can contribute to the volatile fraction in the mantle-derived parental melts of MP (Fig. 4b), while SiO$_2$-rich liquids resembling hydroxal slabs melt in LT inclusions contain ~3400 p.p.m. sulfate on average (Supplementary Table 1). On the one hand, a SiO$_2$-rich melt is required to explain the generation of an orthopyroxene-rich sub-arc mantle through the reaction:

\[
\text{Olivine + SiO}_2 \leftrightarrow \text{orthopyroxene}
\]

(4)

during fluxed melting\textsuperscript{26}. On the other hand, ~3000 p.p.m. sulfate are required to elevate $\Delta$log$O_2$ from FMQ – 0.5 to FMQ + 1.5 through reaction (1) in a primary melt containing ~10 wt% total FeO (ref. 15). An elevation of $\Delta$log$O_2$ from FMQ-0.5 to FMQ + 1.5 overlaps with the shift between the average upper-bound oxidation states recorded in abyssal and sub-arc mantle peridotites, respectively\textsuperscript{13,34,43,44} (Fig. 1a).

Detailed characterisation of the percolated harzburgite samples in this study allows further insights into melt-rock interaction processes occurring in the sub-arc mantle. Ionov et al.\textsuperscript{28} originally attributed the formation of LT inclusions and MP to the pervasive percolation of ‘exotic’ melts in the sub-arc mantle lithosphere. This is in line with the generally (Cr, Fe$^{3+}$, Fe$^{2+}$)-rich nature of spinel in the percolated harzburgites samples, in comparison with those recognised as ‘pristine’ residues and found at the same sampling sites\textsuperscript{25,29,34}. The observation that the Cr, Fe, and Fe$^{3+}/$ΣFe increase is sometimes restricted to the LT inclusion-bearing rims of some spinel grains further shows that this mineral experienced oxidation because of reactions with sulfate-bearing melts originally percolating at grain boundaries (Supplementary Fig. 7 and Supplementary Table 5). Therefore, melt-peridotite interactions in the sub-arc mantle lithosphere have partially or entirely modified the chemistry of spinel grains, likely through dissolution and re-precipitation of this mineral (Supplementary Discussion). This process is consistent with the inferred redox equilibrium between the percolated harzburgite samples and the inclusion parental melts at $\Delta$log$O_2$ ranging from FMQ + 1 to FMQ + 1.5 (Fig. 1a and Supplementary Discussion).

Melt-peridotite interactions in the sub-arc mantle lithosphere were constrained by diffusion to occur only several months before eruption in the case of some West Bismarck peridotite xenoliths from the same sampling zones as in this study\textsuperscript{35}. However, it is unlikely that these timescales are short enough to fully prevent post-entrapment Fe$^{2+}$-Mg re-equilibration between the included melts and spinel, for instance during cooling\textsuperscript{24,35}. The small extent of this process, however, is traced by the presence of irregular halos with very limited variations in Fe$^{2+}$, Mg and Mg$^+$ around the inclusions in this study (Fig. 3d, Supplementary Tables 5, 6 and Discussion). The LT inclusions and MP analysed in this study do not contain daughter silicate phases; the former only host anhydrite and rare sulfo-rides\textsuperscript{28} (Figs. 2, 3 and Supplementary Fig. 4). Therefore, if chemical variations in spinel halos are related to post-entrapment crystallisation from the inclusion parental melts, they can only involve these S-bearing phases. Simple chemical exchange reactions between a sulfate-bearing melt and spinel can be inferred from the variations in atomic concentrations within the EPMA profiles around the inclusions (Supplementary Tables 5, 6 and Discussion). From these exchange reactions, it appears that higher Fe$^{2+}$/ΣFe in the halos can only originate from the oxidation of small amounts of Fe$^{2+}$ from the host spinel by $S^{6+}$-present in the inclusion parental melts through reaction (1), or a similar one involving H$_2$SO$_4$ and FeS compounds (Supplementary Discussion). We conclude that the (Cr, Fe$^{3+}$, Fe$^{2+}$)-rich nature of spinel in the percolated harzburgite samples, further substantiated by the presence of Fe$^{3+}$-rich halos, primarily traces $S^{6+}$-Fe$^{2+}$ redox coupling during melt-rock interactions within the sub-arc mantle lithosphere. Therefore, it is directly shown in this study that sub-arc mantle oxidation can proceed during melt-rock interactions involving SiO$_2$-rich and $S^{6+}$-bearing melts (Fig. 3d & Supplementary Fig. 7). These observations, made here in xenoliths from the sub-arc mantle lithosphere, provide an analogue for the fluxed melting reactions typically occurring throughout the mantle wedge\textsuperscript{6,34} (Fig. 1b).

Melt-rock interactions involving $S^{6+}$-Fe$^{2+}$ redox coupling can eventually lead to the formation of sulfo-ride species according to reaction (1) (Supplementary Figs 2–4, 6 and 7). These sulfo-rides, when present as an immiscible phase in LT inclusions, are typically enriched in Cu at the contact with the enclosed, sulfate-bearing silicate melts (Supplementary Fig. 4 and Supplementary Table 4), which is consistent with the composition of sulfo-rides formed at high $f_0_2$ in experiments\textsuperscript{56}. This compositional feature of sulfo-rides trapped in the inclusions contrasts with those found disseminated in the host spinel harzburgite, which are dominated by (Fe, Ni)-bearing mono-sulfo-ride solid solution, pyrrhotite and pentlandite species with systematically <1 wt% Cu (ref. 57). A similar metal enrichment process in sulfo-rides formed under oxidised conditions has been suggested for some other precious metals such as gold\textsuperscript{58}. Therefore, our results provide in situ evidence for the role of oxidised conditions in the concentration of metals of economic interest in immiscible, $S^{2-}$-bearing phases at subduction zones.

Overall, as this study directly documents the oxidised nature of melts from the Kamchatka and West Bismarck arcs at mantle conditions (Fig. 1b), it rules out melt differentiation in the arc crust as a cause for this oxidation. Instead, slab-derived sulfate originating from $S^{34}$S- and (U, Pb, Sr)-rich subducted serpentinites\textsuperscript{13,50} is demonstrated to be a potentially oxidising agent added to mantle wedge magma sources. Inevitably, this implies that slab agents can maintain their oxidising capacity during migration through the lower mantle wedge (Fig. 1b), and hence they are able to deliver oxidised volatile species to the source regions of arc magmas and affect the ‘redox budget’ in subduction zones.
Methods
XRF imaging and XANES. XRF maps and XANES spectra at the S K-edge were collected at the European Synchrotron Radiation Facility (ESRF; Grenoble, France) using the scanning X-ray microscope of the ID21 beamline and a micro-focused beam. The beamline uses a Si (111) double-crystal mono-chromator and the energy was calibrated to the position of the white line of gypsum (2482.94 eV). The incident beam intensity was measured using a photodiode. All measurements were performed in fluorescence mode with a focused beam of 0.4 × 0.8 μm because of the small size of most of the melt inclusions (≤ 50 μm) investigated in this study. A focused beam in combination with a high photon flux may cause damage to the sulfur-bearing glass samples, generating S4+ by photo-reduction. In order to minimise the focussed beam damage, an attenuator of Al foil with 6 μm thickness was applied to reduce the incident flux on the sample. Before each XANES measurement, the melt inclusion was localised within the spinel by simultaneous Si, Al and S Kα XRF imaging with step sizes of 1 or 2 μm and counting times of 1 s per step. Results of the S Kα X-ray maps are shown in Fig. 2 and Supplementary Fig. 5.

The XANES spectra were acquired by continuously scanning the monochromator and changing the gap of the undulator with a step size of 0.23 eV. One to 10 quick scans (with the acquisition time fixed at 0.1 s per energy step) were collected and stacked to reduce signal-to-noise ratio. The background of the spectra was subtracted by fitting the energy region below the edge with a quadratic function and subtracting this from the spectra. The edge jump was normalised to unity by fitting an arctangent and a Gaussian function to the spectra. The S0/2S was calculated using integrated intensities collected on energy windows corresponding to S2− and S6+ following the method of Jugo et al. and Wilke et al. The XANES spectra and calculated S0/2S are shown in Fig. 2 and Supplementary Fig. S5, and given in Supplementary Table 1.

Raman spectrometry. Raman spectra were collected with a Renishaw micro-Raman spectrometer (RM-1000) using the 532 nm line of a NaYAG laser at the Goethe University (Frankfurt am Main, Germany). The spectrometer was equipped with a Leica DMLM optical microscope and a Peltier-cooled, charge-coupled device detector. All spectra were collected from polished (~120 μm thick) sections and separated spinel grains mounted into epoxy in the wavenumber range 100–3000 cm−1. The spectral resolution was 2 cm−1 and a quasi-backscattering geometry was employed. Exposure times were 60 s with the laser power fixed at 10–20%. No effect of laser beam exposure (i.e., beam damage) on the qualitative results was observed with these analytical conditions; for instance, only variations in signal-to-noise ratio are observed for lower acquisition times. The system was calibrated using the 519 cm−1 peak of pentaerythritol crystals, with increased sample currents and counting times.

Data were collected with normal mode using three spectrometers (respectively with a pentaerythritol and two large quartz) equipped with a Leica DMLM optical microscope and a Peltier-cooled, charge-coupled detector. Matrix effects were corrected using the Phi (r) z modelling available on PeakSight© software from Cameca.

EMPA analyses of the inclusion glasses. The major element compositions and sulfur contents of the inclusion glasses were determined by EMPA at the Research School of Earth Sciences (RSES) of the Australian National University (ANU; Canberra, Australia). The instrument used was a Cameca SX 100 operating at an accelerating voltage of 15 kV, defocused beams of 5–20 μm in diameter and reduced beam currents of 2–10 nA. Counting times were 5–10 s on background and 20–30 s (Cr and Ni), 15 s (Ca and Ti) and 10 s for all other elements on peaks, with Na and K analysed first. Sulfur was independently analysed in peak integral mode using three spectrometers (respectively with a pentaerythritol and two large pentaerythritol crystals), with increased sample currents and counting times. Matrix effects were corrected using the Phi (r) z modelling available on PeakSight© software from Cameca.

The analytical conditions allowed minimising alkali metal losses and/or migration from the analysed area; this setup was previously used to report Na2O concentrations of up to 6.4 wt% in Kamchatka sub–arc mantle Mi10,29. In addition, this setup has been previously demonstrated to provide deficiency of totals in good agreement with SIMS volatile data.18

EMPA and SEM imaging and mapping. EMPA and SEM maps and quantitative analyses were respectively acquired at RSES and the Centre for Advance Microscopy at ANU. The instruments used were the Cameca SX 100 (EMPA) and operating at an accelerating voltage of 15 kV and a beam current of 40 nA) and a Schottky Field Emission Hitachi 4300 SE/N (SEM, operating at the same conditions as the EMPA).

EMPA analyses of spinel with Mössbauer standards. The Fe3+/2Fe of spinel was determined by EMPA at the Goethe University using a set of secondary standard glasses following the procedure outlined by Wood and Virgo.18 The analyses were performed on a JXA-8900 superprobe, using six spinel standards for which Fe3+/2Fe had been previously determined by Mössbauer spectroscopy by Wood & Virgo.18 Measurements were conducted with an accelerating voltage of 15 kV, a ~3 μm spot diameter and a beam current of 20 nA. Data were collected with normal counting times of 15–45 s on backgrounds and 200 ms peaks (depending on the element considered). In this study, corrections to the Fe3+/2Fe calculated by stoichiometry were small and ranged from 0 to −0.02 (i.e., overestimated value).

The error on the corrected Fe3+/2Fe in spinel is ±0.025. The corrected Fe3+/2Fe in sample spinel are displayed in Supplementary Tables S5 and S6, whereas standard analyses during EMPA runs are given in Supplementary Table 7.

Sulfur isotope measurements. The S isotope compositions (δ34Smeasured, see below for usage of delta notation) of the MP were determined by SIMS using the Cameca IMS 1280 (mono-collector) of the Northeast National Ion Microprobe Facility (NENMF) at Woods Hole Oceanographic Institution (WHOI; USA). The measurements were conducted using a 10 μm Ca2+ primary beam, an accelerating voltage of 10 kV and a beam current of 1–2 nA. The secondary ions were collected at an accelerating voltage of 10 kV, with a 150 μm field of view and a mass resolution power (MRP; M/AM) of 4000–5500, using an electron multiplier. The energy slit was centred and opened to 40–60 V. Each measurement consisted of fifty cycles of δ34S and δ32S, respectively. By operating the Cameca IMS 1280 at a MRP of 5500, it becomes possible to avoid interferences from 31P-H and 32S-H (ref. 46). With this analytical setup, in situ δ34S measurements on a 15 × 15 μm area can be conducted with a precision of 0.4–0.6‰ in silicate glasses containing about 500–1600 p.p.m. S (ref. 46), i.e., overlapping the range measured in the MP in this study.

The SIMS analysis is based on the measurement of S-bearing glass standards with known S isotope composition to account for the instrumental mass fractionation (IMF)45. In-house glass standards at WHOI with major element compositions ranging from basaltic to SiO2-rich glasses were used for this calibration.45 The S isotope composition of these glass standards (δ34Smeasured) covers a range from about −5.3‰ up to about +12‰ and was typically determined by KIBA reagent extraction method or calculated on the basis of the isotope composition of the source of S used for the glass synthesis. The nearly 1:1 linear correlation between the KIBA and SIMS results reported earlier48 confirms the high analytical accuracy of the independent determination of δ34Smeasured.

The y axis intercept of the linear correlation between KIBA and SIMS results reflects the IMF, which was typically ranging between 0.9935 and 0.995 during our analytical session (Supplementary Table S1). The nearly 1:1 correlation also indicates that the IMF is largely independent of matrix effects related to bulk glass compositions (i.e., major elements and δ34S) within the ranges defined by the standards.45 In addition, variations in the S valence state in silicate glasses are not expected to produce a detectable IMF. This is because the energy involved in the sputtered ion formation process (10–12 keV) completely overwhelms the bond energies in silicate glasses, as was demonstrated by δ34S recently determined on experimental glasses equilibrated at variable sulfur pressures (ref. 45). The δ34S of the raw SIMS data (to give (34S/32S)corrected) were realised to account for the variations of IMF during a 50-cycles measurement. In order to monitor short- and long-term variations of IMF and to allow a correction of the raw δ34S, at least two measurements on a selected standard (JDF 46N basaltic glass) were conducted every 2–3 unknown sample (Supplementary Table S1). The δ34Scorrected were then calculated relative to the Vienna Canyon Diablo Troilitte (V–CDT) isotope reference standard as follows:

\[
\delta^{34}S_{\text{measured}} = \left( \frac{34S}{32S} \right)_{\text{corrected}} \times \frac{\text{IFM}}{0.04416375} \times 1000
\]  

where 0.04416375 is the 34S/32S for V–CDT having δ34S = 0‰. The 2σ errors associated with the δ34Smeasured in this study (0.6–1.6‰, Supplementary Table S1) were propagated from the signal count statistics and the uncertainty in the regression of the SIMS calibration curve. Recent replicate analyses of a MORB glass standard (892-1) have revealed an almost perfect reproducibility of SIMS analysis of ±0.32‰ (n = 13, 2σ)56. More detail on SIMS calibration materials for in situ S isotope analyses of silicate glasses and the processing procedures of raw SIMS data can be found in Fiege et al.45

Data availability
The authors declare that the data generated or analysed during this study are included in this published article and its Supplementary Information files.

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Author contributions

A.B. and K.K. originated the project and wrote the manuscript with contributions from A.B.W., R.J.A., M.W., R.E.B., O.N., N.S. and D.A.I. A.B. prepared the samples, collected Raman spectra, acquired EPMA and SEM data, performed Fe valence state measurements with A.B.W., sulfur isotope measurements with N.S. and all calculations reported in this article. K.K. collected XRF maps and XANES spectra with M.W., R.E.B. and C.R. Xenoliths from Avacha (Kamchatka arc) and Ritter (West Bismarck arc) volcanoes were provided by D.A.I. and R.J.A., respectively.

Additional information

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