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Suggested citation referring to the original publication:
DOI https://doi.org/10.1038/s41467-018-05804-2
ISSN (online) 2041-1723

Postprint archived at the Institutional Repository of the Potsdam University in:
Postprints der Universität Potsdam
Mathematisch-Naturwissenschaftliche Reihe ; 717
ISSN 1866-8372
https://nbn-resolving.org/urn:nbn:de:kobv:517-opus4-426184
DOI https://doi.org/10.25932/publishup-42618
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 SO42− in spinel-hosted glass (formerly melt) inclusions. Copper-rich sulfide precipitates in the inclusions and increased Fe3+/∑Fe in spinel record a S6+/Fe2+ 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.

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The 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 (fO₂), control the evolution and degassing of magmas in volcanic arcs above subduction zones and the formation of ore deposits. In practice, the fO₂ during the generation and evolution of magmas can be estimated on the basis of Fe₃⁺/ΣFe (Fe³⁺/(Fe³⁺ + Fe²⁺)) in quenched melts and olivine-pyroxene-spinel assemblages in crystal-rich rocks or alternatively from S⁶⁺/ΣS (S⁶⁺/(S⁶⁺ + S²⁻)) in quenched melts.

In subduction zones, the fO₂ 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 fO₂ 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 fO₂ than MORB, with values above FMQ. Xenoliths from the sub-arc mantle lithosphere (Fig. 1b), sampled as rock fragments in volcanic deposits, record fO₂ ranging from FMQ to two log units above FMQ (Fig. 1a).

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, as slab-derived S⁶⁺, generally linked with oxygen to form reactive sulfate (SO₄²⁻) 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 Fe²⁺ into Fe³⁺ per mole of S⁶⁺ according to the reaction:

$$\text{SO}_4^{2-} + 8\text{FeO} = >S^{2-} + 4\text{Fe}_2\text{O}_3$$

Mounting evidence from stable isotope measurements on deeply subducted rocks supports the idea that fluids released from these rocks could be enriched in SO₄²⁻ (Fig. 1b). In parallel, the involvement of slab-derived S in the generation of arc magmas is supported by S isotope systematics, with elevated δ⁳⁴S values.
in arc melts and volcanic gases interpreted as the result of S recycling from the slab28–31 (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 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\(^{6+}\) 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 andesite-dacite (‘LT inclusions’, where LT stands for low temperature), magnesian andesite (melt pockets, ‘MP’) and dacite-rhyolite of boninitic affinity (‘vein MI-s’). Spinel in West Bismarck xenoliths contains magnesian andesite glass (‘West Bismarck MI-s’, Supplementary Fig. 1). The Mg\(^+\) (Mg/(Mg + Fe\(_{\text{tot}}\)) where Fe\(_{\text{tot}}\) means all Fe is treated as Fe\(^{2+}\)) 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 settings22–24. Although not evidenced by any XANES measurement, rare sulfate crystals in LT inclusions and West Bismarck MI is one of the 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 (Fe\(^{3+}\), Fe\(^{2+}\))-bearing spinel standards3 reveal Fe\(^{3+}\) zoning in irregular halos28 next to the inclusions (Fig. 3a–d and Supplementary Tables 5–7). The highest Fe\(^{3+}/\Sigma\text{Fe}\) 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 (up to...
0.10–0.25 At%), but comparatively little variations in Fe\(^{2+}\), 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.\(^{28}\) (Supplementary Fig. 8 and Supplementary Table 8). Further EPMA measurements reveal that the Fe\(^{3+}\)/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).

**Oxygen fugacity estimates.** The f\(^{O_2}\) values (expressed as the deviation from FMQ in log units, ΔlogO\(_2\)) inferred from the S\(^{6+}/\Sigma S\) equilibrium in ‘Fe-poor’ silicate melts (Fe/S ≤ 2) at ≤ 0.2 GPa\(^{16}\) range from FMQ + 0.5 to FMQ + 1.5 for LT inclusions. The ΔlogO\(_2\) values inferred from the S\(^{6+}/\Sigma S\) equilibrium in ‘Fe-rich’ silicate melts (Fe/S > 2) at ≤ 0.2 GPa\(^{16}\) 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

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**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 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 S\(^{6+}\), 2478 eV for S\(^{4+}\) and 2472.5 eV for S\(^{2−}\) in crystalline Fe-S compounds. The additional feature at ~2486 eV is typical for crystalline anhydrite (CaSO\(_4\)). Some S\(^{4+}\) is generated during XANES measurements of glasses by photo-reduction of S\(^{6+}\). The LT inclusions contain solely S\(^{6+}\) in glass and in anhydrite. The MP contain S\(^{2–}\) and S\(^{6+}\) in glass with 0.55 ≤ S\(^{6+}/\Sigma S\) ≤ 0.58. The vein MI dominantly contain S\(^{6+}\) in the glass with S\(^{6+}/\Sigma S\) up to 0.88 but also show varying contributions of S\(^{2–}\) 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 (CaSO\(_4\)) 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.
Bismarck MI investigated in this study (Fig. 2e, h, i and Supplementary Fig. 5), the $\Delta \log O_2$ inferred from the $S^6+/\sum S$ 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 $\Delta \log O_2$ ranging from FMQ + 1.0 to FMQ + 1.4 ($\pm 0.2$–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 $\delta^{34}S$ 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 $\delta^{34}S$ (see Methods for the usage of delta notation) measured by SIMS ranges from $+7$ to $+11\%_o$ ($\pm 1$–1.6, $2\sigma$) in the glass of MP (Supplementary Table 11).

Discussion

Before interpreting further the origins of elevated $fO_2$ 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 $\text{H}_2$O dissociates according to:

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

(3)

and $\text{H}_2$ 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 $\text{H}_2$O abundances previously determined by SIMS analysis, with up to $\sim 12$ wt% and $\sim 3$ wt%, respectively, in LT inclusions and MP30,31, and $\sim 10$ wt% $\text{H}_2$O in the vein MI29. The EPMA setup used in this study has been previously demonstrated to provide deficiency of totals of analyses in good agreement with SIMS volatile data29. 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 $\text{H}_2$O loss.

Insignificant $\text{H}_2$O loss from the inclusions is further suggested by the fact that solid-state diffusion of $\text{H}^+$ within spinel is also two to three orders of magnitude slower than in olivine35,36. 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 arcs25–27, $\text{H}^+$ diffusivities of $\leq 10^{-14}$ m2 s$^{-1}$ are expected in spinel36. 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 study37. Several hours have been calculated for the ascent of mantle xenolith-bearing magmas at convergent margins with thicker continental crust38, such as is the case for the Kamchatka arc. We conclude that volatile loss has not significantly affected the $\text{H}_2$O-rich inclusions during the fast ascent of the xenoliths to the surface.

The calculated $fO_2$ 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 $\Delta \log O_2$ estimated above for the inclusions may be shifted even further up if one considers that increasing pressure has a significant effect on the $S^6+/\sum S$ equilibrium in silicate melts39,40. 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 $S^6+/\sum S$ equilibrium of only ca. $+0.5 \log$ units in $fO_2$ for hydrous tholeiite melts, whereas Matjuschkin et al.40 have experimentally inferred a shift of ca. $+1.5 \log$ units for hydrous trachyandesite melts (Fig. 1a), both with a pressure increase of $\sim 1$ GPa.

The magnitude of the pressure effect on the $S^6+/\sum S$ equilibrium for the inclusions in this study can be tested independently using the $\text{Fe}^{3+}/\Sigma \text{Fe}$ equilibrium in silicate melts40 and the experimentally determined partitioning coefficients for $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ between Cr-bearing spinel and melt42. The upper-bound $\text{Fe}^{3+}/\Sigma \text{Fe}$ measured in sub-arc mantle spinel adjacent to the MI (0.34–0.37, Supplementary Tables 5 and 6), correspond to those
calculated for $\Delta \text{log}_{10} O_2$ 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 $\Delta \text{log}_{10} O_2$ 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 $S^8+/ΣS$ equilibrium in silicate melts, but rather suggests that it is within the error of the $\Delta \text{log}_{10} O_2$ 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 $\Delta \text{log}_{10} O_2$ 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. 1a). For instance, ~15% melt extraction from DMM was calculated for the mantle source protoliths of the boninitic parental melts of the vein MI$^{25}$. Studies of primary MORB show that these magmas are equilibrated in their sources at FMQ$^{1,42}$, whereas the $fO_2$ of abyssal peridotites dominantly ranges below FMQ$^{13,44}$ (Fig. 1a). Therefore, it is unlikely that the original $fO_2$ is higher than FMQ in the more depleted mantle source protoliths of the inclusion parental melts in this study, owing to the preferential decrease in Fe$^{3+}$ concentrations and Fe$^{3+}$/ΣFe in the mantle with increasing melt depletion$^{32,34,45}$. 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$^{29–31}$ (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 serpentinite is a possible carrier of large amounts of sulfate with elevated $\delta^{34}S$ to sub-arc mantle depths$^{15,17,18}$. A contribution from subducted serpentinite is further consistent with the very high U/Th, Pb/Ce and Sr/Nd of the inclusion parental melts in this study$^{50}$ (Fig. 4a and Supplementary Table 13). Mixing models show that the high 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 serpentinite-derived agents carrying ≥ 1000 p.p.m. S as sulfate (with an assumed $\delta^{34}S$ of 14.5% in the original agents$^{15}$). Therefore, high S, $S^8+/ΣS$ 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 arcs$^{19–21,51}$ (Fig. 1b) can serve as a reliable proxy for the presence of oxidising slab agents in their mantle wedge sources.

The lower-bound $\Delta \text{log}_{10} O_2$ 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$^{11}$. 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$^{25}$ and high-Ca boninite$^{26}$) are close to those of mantle-derived liquids typically found at subduction zones, whereas LT inclusions rather resemble low-temperature hydrous melts produced in partial melting experiments of slab rock analogues$^{2,8}$ (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 fO$_2$ fits within the upper range previously reported for sub-arc mantle peridotites$^{13,34}$ (Fig. 1a). Recently, elevated ΔfO$_2$ 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$^{26,34}$. 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 hydrous slab melts 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:

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

(4) during fluxed melting$^{26}$. On the other hand, ~3000 p.p.m. sulfate are required to elevate ΔfO$_2$ 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 ΔfO$_2$ 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$^{13,34,43,44}$ (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.$^{28}$ 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 harzburgite samples, in comparison with those recognised as ‘pristine’ residues and found at the same sampling sites$^{25-29,34}$. The observation that the Cr, Fe$_3$, 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 ΔfO$_2$ 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$^{37}$. 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$^{24,35}$. The small extent of this process, however, is traced by the presence of irregular halos with very limited variations in Fe$^{3+}$, 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 sulfides$^{28}$ (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$^{3+}$/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$^{6,34}$ (Fig. 1b).

Melt-rock interactions involving S$^{6+}$-Fe$^{2+}$ redox coupling can eventually lead to the formation of sulfide species according to reaction (1) (Supplementary Figs 2–4, 6 and 7). These sulfides, 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 sulfides formed at high fO$_2$ in experiments$^{56}$. This compositional feature of sulfides trapped in the inclusions contrasts with those found disseminated in the host spinel harzburgite, which are dominated by (Fe, Ni)-bearing monosulfide solid solution, pyrrhotite and pentlandite species with systematically < 1 wt% Cu (ref. 57). A similar metal enrichment process in sulfides formed under oxidised conditions has been suggested for some other precious metals such as gold$^{58}$. 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$^{13,30}$ 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.
The error on the corrected Fe\(^{2+}/Fe^{3+}\) in spinel is ±0.025. The corrected Fe\(^{3+}/Fe^{2+}\) in sample spinel are displayed in Supplementary Tables 5 and 6, whereas standard analyses during EPMA runs are given in Supplementary Table 7.

**Sulfur isotope measurements.** The S isotope compositions (δ\(^{34}S_{\text{measured}}\), 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 (NNIMF) at Woods Hole Oceanographic Institution (WHOI; USA). The measurements were conducted using a 10 μm Ca\(^+\) 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 eV. Each measurement consisted of five cycles of 7S and 34S, respectively. By operating the Cameca IMS 1280 at a MRP of 5500, it becomes possible to avoid interferences from \(^{31}\)P\(^{+}\) with \(^{32}\)S (ref. 64). With this analytical setup, in situ δ\(^{34}S\) 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. 64), 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)\(^{63}\). In-house glass standards at WHOI with major element compositions ranging from basaltic to SiO\(_2\)-rich glasses were used for this calibration\(^{63}\). The S isotope composition of these glass standards (δ\(^{34}S_{\text{std}}\)) 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 isotopic composition of the source of S used for the glass syntheses. The nearly 1:1 linear correlation between the KIBA and SIMS results reported earlier\(^{63}\) confirms the high analytical accuracy of the independent determination of δ\(^{34}S_{\text{std}}\).

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 11). 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 δ\(^{34}S\)) within the ranges defined by the standards\(^{63}\). 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 δ\(^{34}S\) recently determined on experimental glasses equilibrated at variable δ\(^{34}S\) (ref. 65).

Corrective and filtering of the calibration data (to give δ\(^{34}S_{\text{derived}}\)) 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 δ\(^{34}S\), at least two measurements on a selected standard (JDF 46N basaltic glass) were conducted to be 2–3 unknown samples (Supplementary Table 11). The δ\(^{34}S_{\text{calibrated}}\) were then calculated relative to the Vienna Canyon Diablo Tryptolite (V-CDT) isotope reference standard as follows:

\[
\delta^{34}S_{\text{measured}} = \left( \frac{\delta^{34}S_{\text{measured}}}{\delta^{34}S_{\text{true}}} \right)_{\text{V-CDT}} \times 1000
\]

where 0.04416375 is the \(^{34}S_{\text{V-CDT}}\) for V-CDT having δ\(^{34}S\) of 0‰. The 2σ errors associated with the δ\(^{34}S_{\text{measured}}\) in this study (0.6–1.6‰, Supplementary Table 11) were propagated from the signal count statistics and the uncertainty on the regression of the SIMS calibration curve. Recent replicate analyses of a MORB glass standard (892-1) have revealed an external reproducibility of SIMS analysis of ± 0.3‰ (m = 13, 2σ)\(^{65}\). 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\(^{65}\).

**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.

Received: 8 August 2017 Accepted: 24 July 2018
Published online: 29 August 2018

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Acknowledgements

We acknowledge financial support by the Australian Research Council (DE120100513 and DP120104240) and the ESRF for beam time (EC1061 and ES238). We acknowledge the ESRF for providing access to synchrotron radiation and the team ID21 for technical support. A.B. thanks L. Uenver-Thiele, R. Rapp and F. Brink for their assistance with Raman, EPMA and SEM, respectively. We thank Elizabeth Cottrell and Keiko Hattori for their constructive and helpful comments.

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

Supplementary Information accompanies this paper at https://doi.org/10.1038/s41467-018-05804-2.

Competing interests: The authors declare no competing interests.

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