

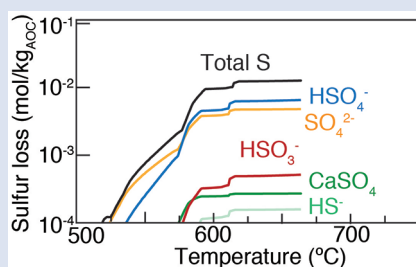
Sulfur loss from subducted altered oceanic crust and implications for mantle oxidation

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Abstract



copper porphyry deposits. The variable SO_x release predicted by our models both across and among active margins may introduce $f\text{O}_2$ heterogeneity to the upper mantle.

Oxygen fugacity ($f\text{O}_2$) is a controlling factor of the physics of Earth's mantle; however, the mechanisms driving spatial and secular changes in $f\text{O}_2$ associated with convergent margins are highly debated. We present new thermodynamic models and petrographic observations to predict that oxidised sulfur species are produced during the subduction of altered oceanic crust. Sulfur loss from the subducting slab is a function of the protolith $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio and subduction zone thermal structure, with elevated sulfur fluxes predicted for oxidised slabs in cold subduction zones. We also predict bi-modal release of sulfur-bearing fluids, with a low volume shallow flux of reduced sulfur followed by an enhanced deep flux of sulfate and sulfite species, consistent with oxidised arc magmas and associated

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Introduction

Subduction may influence the oxygen fugacity ($f\text{O}_2$) of the mantle and mantle-derived magmas through the introduction of hydrated and oxidised altered oceanic crust (AOC, Fig. 1; Evans, 2012). Mantle $f\text{O}_2$ can regulate mantle rheology and density through changes in mineralogy; for example, the H_2O content of nominally anhydrous minerals is a function of $f\text{O}_2$ (McCammon *et al.*, 2004). As a result, secular changes in mantle $f\text{O}_2$ induced by plate tectonics may drive variations in mantle circulation (Mackwell, 2008). However, the link between redox sensitive elements in subducting slabs and mantle $f\text{O}_2$ at subduction zones remains elusive.

Mounting evidence suggests that mantle $f\text{O}_2$ evolves in response to a transfer of oxidised slab components. For example, peridotite xenoliths from Mexico record $f\text{O}_2$ conditions 1.5–2.4 log units above the quartz-fayalite-magnetite (QFM) buffer (Blatter and Carmichael, 1998), whereas mid-ocean ridge peridotite overlaps with QFM (Birner *et al.*, 2018). Similarly, arc magmas are oxidised relative to mid-ocean ridge basalts (MORB; Kelley and Cottrell, 2009, 2012; Cottrell and Kelley, 2011; Brounce *et al.*, 2014). The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of arc magmas positively correlate with geochemical indicators of material addition from the slab to the magma sources, such as Ba/La ratios (Kelley and Cottrell, 2009); therefore, elevated mantle $f\text{O}_2$ along convergent margins is both spatially and chemically linked to the subducting slab.

Such a link may require the transfer of redox sensitive elements from slab lithologies, which are oxidised relative to mantle peridotite. Early studies hypothesised the introduction of slab Fe^{3+} (e.g., Lecuyer and Ricard, 1999); however, the solubility of Fe^{3+} in hydrous fluids is low (Mungall, 2002). Instead, volatiles likely play a more important role (Evans, 2012). Of these, only H, C, and S potentially occur in sufficient abundance to influence the redox state of the mantle. Sulfur and carbon are fluid mobile, exhibit an eight electron range in oxidation states, are subducted at global rates on the order of 10^{12} mol/yr, and may act as important vectors for transferring oxidation state (Evans, 2012). Significant work has focused on decarbonation during subduction, whereas sulfur loss remains less explored. This is despite the fact that the transition from S^{2-} to SO_4^{2-} occurs at more oxidising conditions relative to the C- CO_2 transition (Fig. S-1). Oxidised carbon is stable at normal upper mantle P - T - $f\text{O}_2$; therefore, slab-derived CO_2 fluxes are unable to initiate Fe oxidising reactions in the mantle wedge (see Supplementary Information S-2). In contrast, a flux of oxidised sulfur may raise $\log(f\text{O}_2)$ of the subarc mantle to $\sim\text{QFM} + 2$, consistent with the range commonly observed in subarc mantle xenoliths (e.g., Blatter and Carmichael, 1998). Sulfur thus remains the most powerful oxidising agent in subduction zones.

Recent studies have favoured either reduced (H_2S , HS^-) or oxidised (SO_4^{2-}) sulfur species in slab fluids, with the potential to reduce or oxidise the subarc mantle (e.g., Evans

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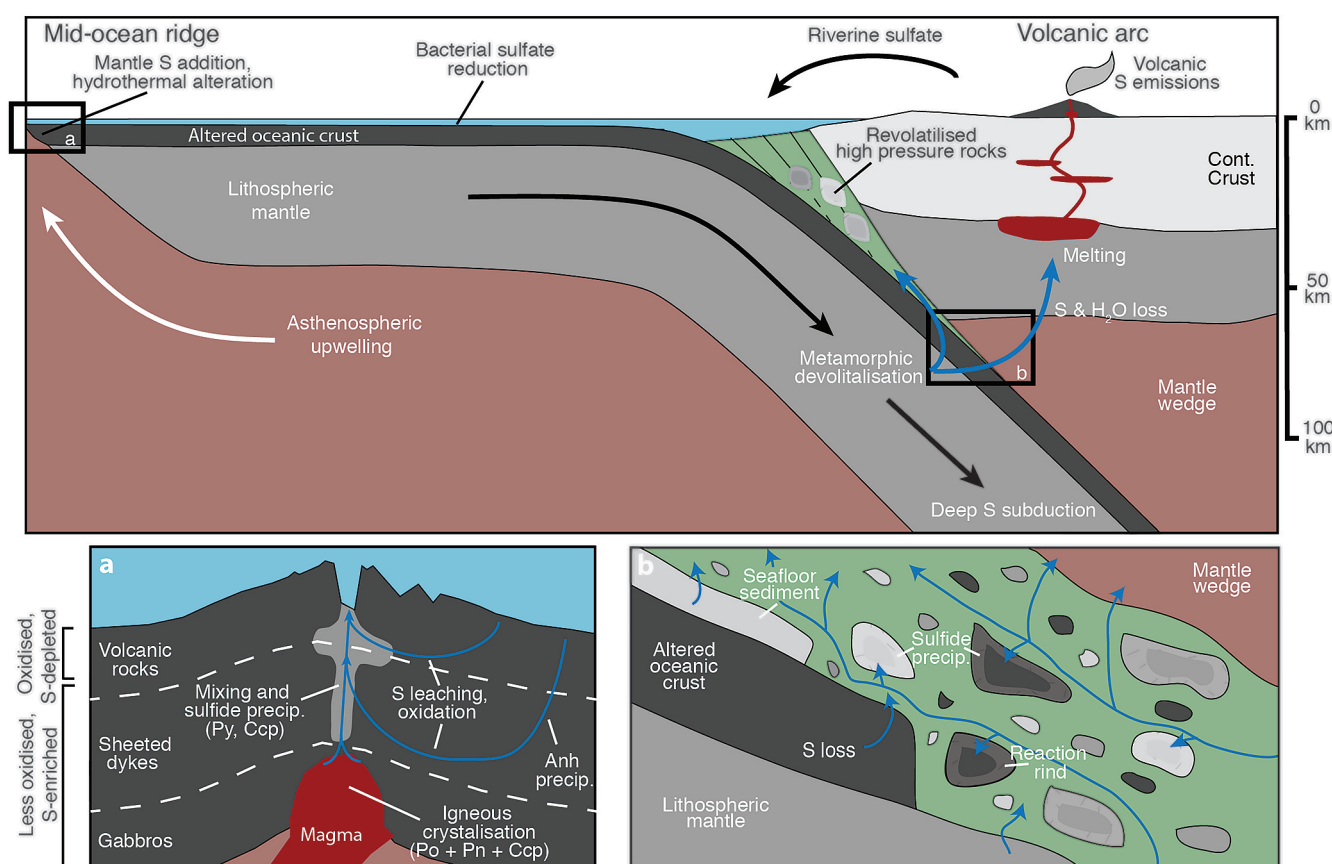


Figure 1 Schematic diagram showing the broader subduction zone system. Sulfur is introduced to the oceanic crust during crystallisation and hydrothermal circulation. **(a)** Magmatic sulfides react to form pyrite \pm chalcopyrite and iron is oxidised (see Supplementary Information S-1). Sulfur is later extracted during metamorphic devolatilisation. **(b)** Sulfides precipitate in reaction rinds formed upon exhumation of metamorphic rocks along the slab mantle interface, while the remaining sulfur infiltrates the overlying subarc mantle.

et al., 2014; Tomkins and Evans, 2015; Walters *et al.*, 2019). We address this discrepancy through thermodynamic modelling using the Gibbs free energy minimisation software *Perple_X* (Connolly, 2005) to predict sulfur speciation in AOC-derived fluids (see Supplementary Information S-3). This enables us to assess the potential of sulfur to influence mantle and arc fO_2 as a function of slab composition and subduction zone thermal structure. We predict that oxidised sulfur species are dominant in slab fluids at eclogite facies conditions and may oxidise arc magmas and the subarc mantle.

Squeezing Sulfur from the Slab

Metamorphic assemblages predicted over a P - T range of 1.5–3.5 GPa and 500–800 °C for average AOC (Fig. 2) show a change from reduced to oxidised sulfur species with increasing depth. Sulfide and sulfate minerals comprise <0.5 vol. % of the rocks, consistent with their low abundance in most high pressure rocks. Pyrrhotite is stable below 1.8 GPa and <680 °C, above which it is replaced by pyrite. Pyrite is converted to anhydrite with increasing P - T (e.g., >2.3 GPa at 650 °C). Anhydrite is the only sulfur phase at pressures above 2.8–3.3 GPa (Fig. 2). Sulfur oxidation is balanced by reduction of ferric iron, resulting in a decrease in $Fe^{3+}/\Sigma Fe$ from 0.28 to 0.13–0.17 (Fig. S-4) in the dehydrated slab residue (*i.e.* eclogite). Assemblages were also predicted for average MORB (Figs. S-6 and S-7) with an initial $Fe^{3+}/\Sigma Fe$ of 0.14. Although the compositions used here are averages, a comparison of AOC and MORB allows us to assess the degree to which alteration of the oceanic crust may influence sulfur loss. The sulfur

oxidising reactions are shifted to higher pressures and $Fe^{3+}/\Sigma Fe$ is constant with depth in the MORB model (Fig. S-10), suggesting that prograde sulfur oxidation varies as a function of pre-subduction seafloor alteration.

Sulfur concentration and speciation in slab fluids vary as a function of subduction zone thermal structure, which we demonstrate by comparing open system models in which fluids are fractionated at each P - T step along contrasting geothermal gradients (D80; Syracuse *et al.*, 2010). The Honshu ('cold') and Cascadia ('hot') models for average AOC display some similarity: fluid compositions transition from H_2S – HS^- to HSO_4^- – HSO_3^- dominant as the anhydrite-in reaction is approached with depth. Similarly, sulfur concentrations increase with depth along both paths. In the Honshu model, dissolved sulfur concentrations increase from 2.3 mmol/kg HS^- , 0.1 mmol/kg H_2S , and 0.5 mmol/kg HSO_4^- at 2.4 GPa and 500 °C to 481 mmol/kg HSO_4^- , 51.6 mmol/kg HSO_3^- , and 93.1 mmol/kg SO_4^{2-} at 2.5 GPa and 660 °C, the last P - T step before H_2O is exhausted (Fig. S-3). Concentration and speciation are similar in the high P - T region of the Cascadia model, yet at low P - T , H_2S and HS^- concentrations are two orders of magnitude greater than those in the Honshu model. In the Honshu model, sulfur loss is largely in the form of oxidised species during lawsonite breakdown at depths of 82 to 85 km (Fig. 3). In contrast, in the Cascadia model HS^- and H_2S dominate in the shallow region (<75 km), where nearly 60 % of the H_2O is lost (Fig. 3). We conclude from these models that hot subduction zones should exhibit shallow reduced and deep oxidised sulfur fluxes, whereas cold subduction zones will be dominated by the release of oxidised sulfur.

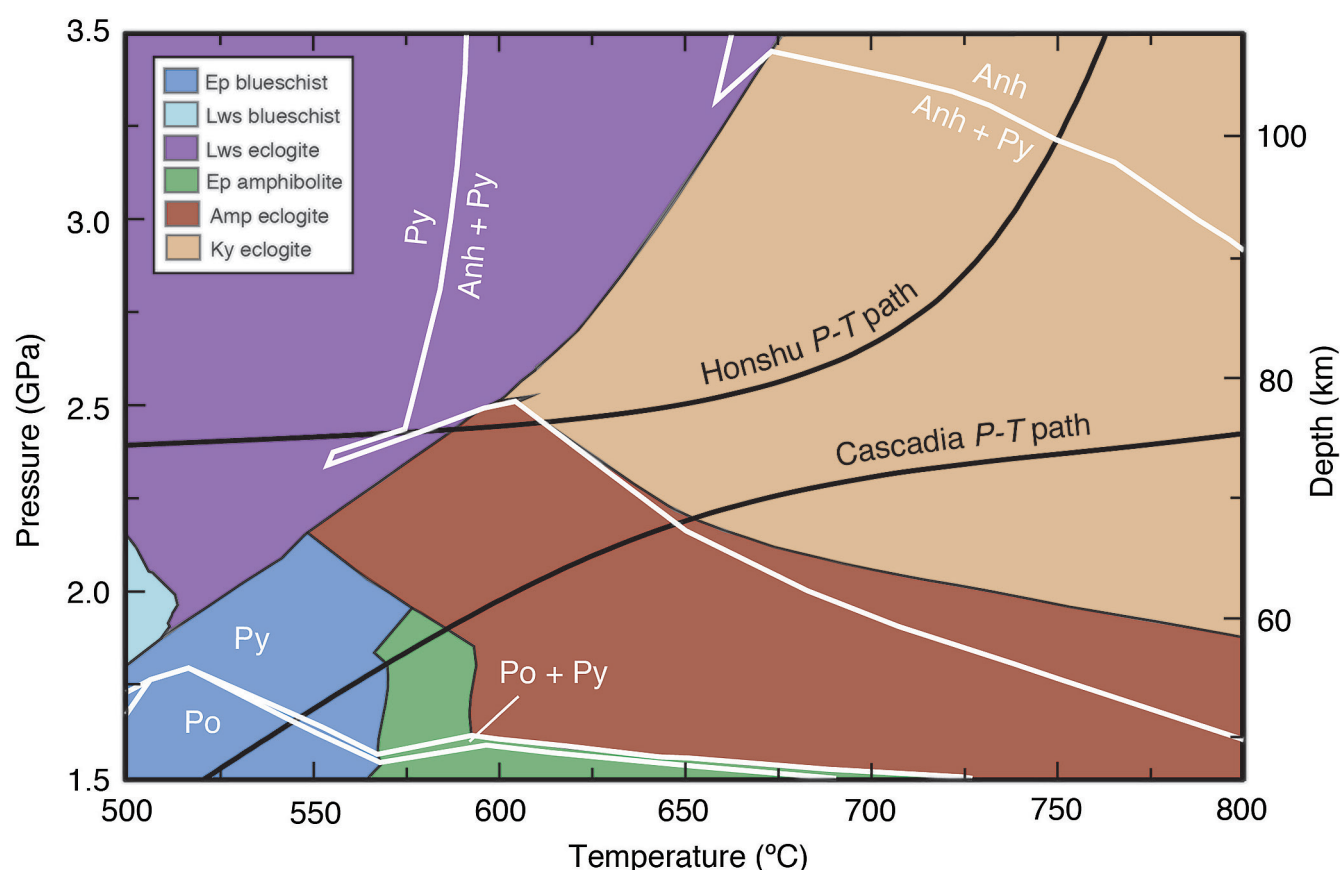


Figure 2 Closed system phase equilibrium modelling results utilising an average AOC composition from ODP hole 504B. The stability fields of common rock types are shaded (see key) and the stable solid sulfur phases are also highlighted. Honshu and Cascadia slab top *P-T* paths after Syracuse *et al.* (2010).

Oxidation of the oceanic crust enhances sulfur loss during subduction. Despite higher bulk rock sulfur and similar H_2O contents, sulfur fluid concentrations are an order of magnitude lower for MORB compared to AOC, and little oxidised sulfur is released (Figs. S-8 and S-9). These data suggest heterogeneous sulfur loss within slabs, where the oxidised volcanic section of the crust is likely to exhibit greater sulfur loss than deeper lithologies (see Supplementary Information S-1). The AOC composition modelled in this study is an average of 6.6 Ma crust formed at a fast spreading centre. More pervasively altered oceanic crust formed at slow spreading centres may exhibit greater sulfur loss. However, these effects will be balanced by the degree to which sulfur is removed during oxidative alteration (see Supplementary Information S-1).

Our results are similar to those of Debret and Sverjensky (2017) for subducted serpentinite, where SO_x species were calculated to be released at 630–660 °C and 2.0 GPa. Similarly, Tomkins and Evans (2015) predicted dissolution of seafloor anhydrite in MORB to also occur over the blueschist-to-eclogite transition modelled here, potentially enhancing the oxidised nature of slab fluids released at these depths. In contrast, Li *et al.* (2020) predicted the release of reduced sulfur species during the subduction of mafic crust; however, the reduced nature of these fluids is a result of fixing $f\text{O}_2$ at QFM to QFM – 3 along the dehydration path. We suggest that these models are similar to our MORB models but are inconsistent with the elevated $f\text{O}_2$ of AOC.

The Exhumed Rock Record

Our models are consistent with the petrographic and isotopic record from exhumed high pressure rocks. Under regional metamorphic conditions, pyrite (S^0) is commonly replaced by pyrrhotite (S^{2-}) with increasing grade (*e.g.*, Tracy and Robinson, 1988). This mechanism was adopted in earlier models of pyrite behaviour during subduction of AOC (*e.g.*, Evans *et al.*, 2014). Such reactions, balanced by the oxidation of Fe^{2+} to Fe^{3+} in silicates or oxides, would produce H_2S in the presence of water during subduction (see review in Walters *et al.*, 2019). However, our data suggest that sulfur oxidation is balanced by iron reduction. The available $\text{Fe}^{3+}/\Sigma\text{Fe}$ data for high pressure minerals combined with mass balance constraints show that eclogites are reduced relative to blueschists and AOC (see Supplementary Information S-4). Iron reduction during the blueschist to eclogite facies transition in natural rocks has to be balanced by the oxidation of another element, and we suggest that sulfur is the only possible candidate and its prograde oxidation provides the mechanism.

Further support for our model comes from a recent isotopic study of sulfides precipitated from slab-derived fluids during the exhumation of high pressure rocks. The ~36 ‰ ($\delta^{34}\text{S}$) variation among metasomatic sulfides suggests that large fractionations (10–20 ‰) were induced by precipitation from oxidised sulfur-bearing slab fluids (Walters *et al.*, 2019). In addition, a recent study of Fe isotopes in high pressure garnet from Sifnos (Greece) suggests that lawsonite dehydration is accompanied by iron reduction in low temperature eclogites, likely due to a loss of SO_x species (Gerrits *et al.*, 2019). This is consistent with the predictions of our Honshu model.

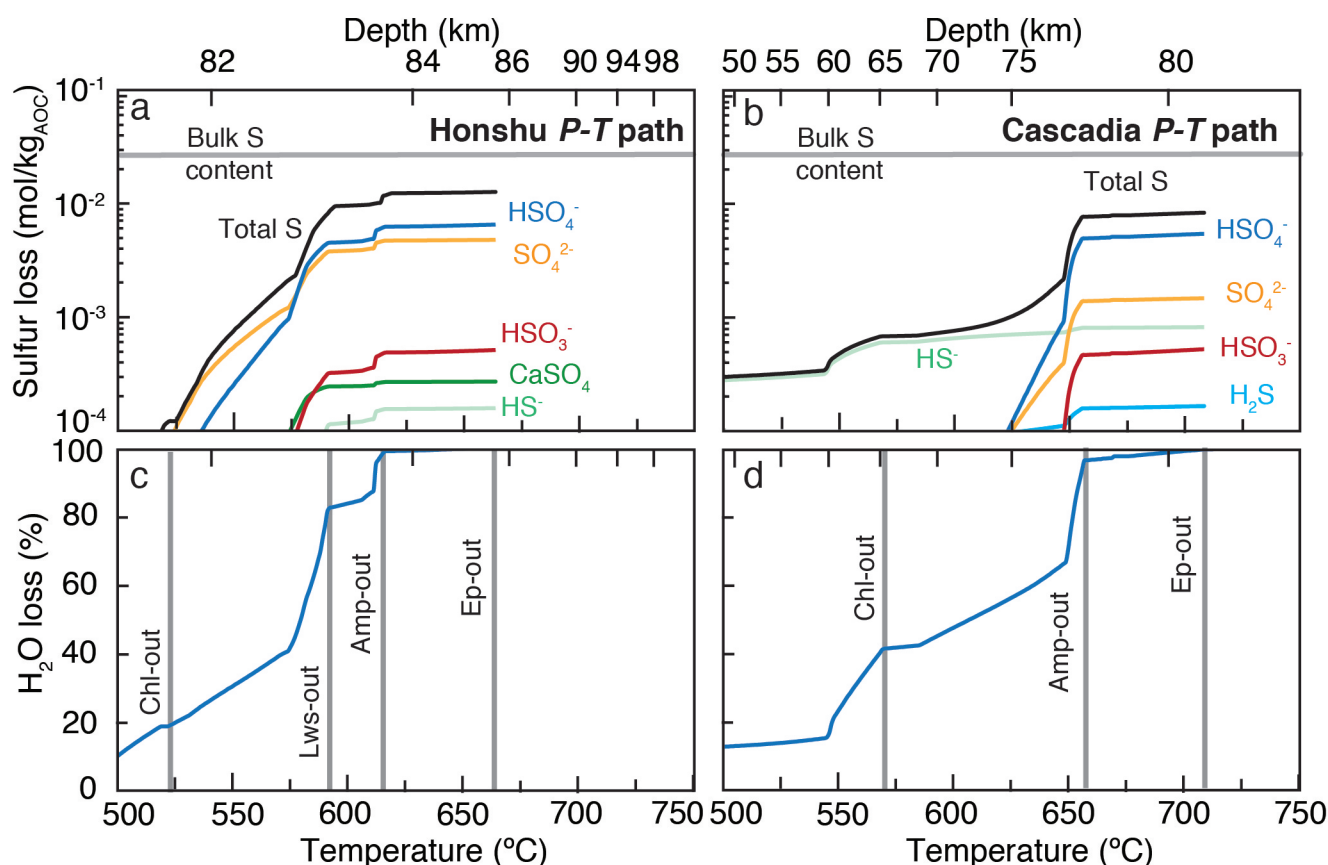


Figure 3 Cumulative sulfur (a,b) and fluid (c,d) loss diagrams for fluids fractionated along the Honshu and Cascadia P-T paths. Both temperature and corresponding slab top depth are plotted on the x-axis. Key dehydration reactions are shown for reference.

Sulfates are observed in fluid and solid inclusions in samples of subducted oceanic crust metamorphosed at relatively low pressures of 1.5–2.5 GPa (Frezza and Ferrando, 2015). This is consistent with our models for AOC, in which the sulfide-sulfate transition occurs at 2.0–2.5 GPa. In contrast, in more reduced (relative to AOC) eclogites embedded in subducted continental crust, sulfate-bearing inclusions are more commonly observed in rocks metamorphosed at pressures >3.0 GPa (Frezza and Ferrando, 2015). In agreement with these observations, we show that the sulfide-sulfate transition is shifted to >3.0 GPa in more reduced lithologies. However, there are limited observations of solid phase inclusions within subducted oceanic crust, and sample preparation with water during cutting, grinding, and polishing is likely to remove anhydrite.

Sulfides are a common trace phase found as inclusions in eclogitic minerals (Fig. 4a,b; see review in Walters *et al.*, 2019). Brown *et al.* (2014) observed prograde replacement of pyrrhotite-bearing inclusion assemblages by pyrite-bearing assemblages between 1.4–1.5 GPa and 450–500 °C and 1.9 GPa and 600 °C in New Caledonian HP rocks, consistent with the transformation of pyrrhotite to pyrite predicted by our models (Fig. 2). Matrix sulfides are commonly associated with hydrous metasomatic Fe³⁺-rich phases, such as epidote, amphibole, and chlorite (Fig. 4c,d), consistent with fluid mediated sulfur reducing reactions.

The scarcity of peak eclogite facies matrix sulfides combined with remnant prograde sulfide inclusions suggests that sulfur loss is nearly complete following dehydration of AOC; however, our models predict that 55 to 75 % of the sulfur should remain in the slab (Fig. S-4). Dissolved NaCl dramatically increases anhydrite dissolution (Newton and Manning, 2004), but is not so far incorporated into our models. Therefore,

SO_x concentrations are likely underpredicted in our models. Additional sulfur may also be mobilised by external fluids; however, fluids in these environments are likely channelised (e.g., Zack and John, 2007), such that external fluids will not liberate significant amounts of sulfur from the majority of the subducted crust. Regardless, our current models likely provide a correct estimate of sulfur speciation and a minimum estimate for the total contribution from subducting AOC to the sulfur budget of arcs.

Oxidising the Arc

The migration of sulfate-bearing fluids from dehydrating AOC will oxidise the upper mantle. Upon contact with more reduced conditions of the mantle (~QFM), sulfides are expected to precipitate from slab fluids to oxidise Fe and hydrate the mantle wedge, a process which accounts for the QFM to QFM + 2 range in *f*O₂ reported for subarc peridotite xenoliths (see Supplementary Information S-2). Metasomatism is likely to strip slab fluids of their oxidising capability before reaching melt generation regions. Fluid loss is predicted in our models at depths (60 to 80 km) less than those of the slab top directly below many volcanic arcs (~100 km; Syracuse *et al.*, 2010). However, deflection of metasomatised mantle or mélange diapirs by corner flow may carry the oxidised mantle to the region of melt generation beneath the arc (Spandler and Pirard, 2013). Bénard *et al.* (2018) identified anhydrite and SO₄²⁻-bearing inclusions in arc peridotite xenoliths, which may suggest that sulfate-bearing fluids penetrate deep into the subarc mantle. However, the input of sulfur into subduction zones is in excess of the volcanic output (Evans, 2012), suggesting that some sulfur may be stored in the mantle wedge.

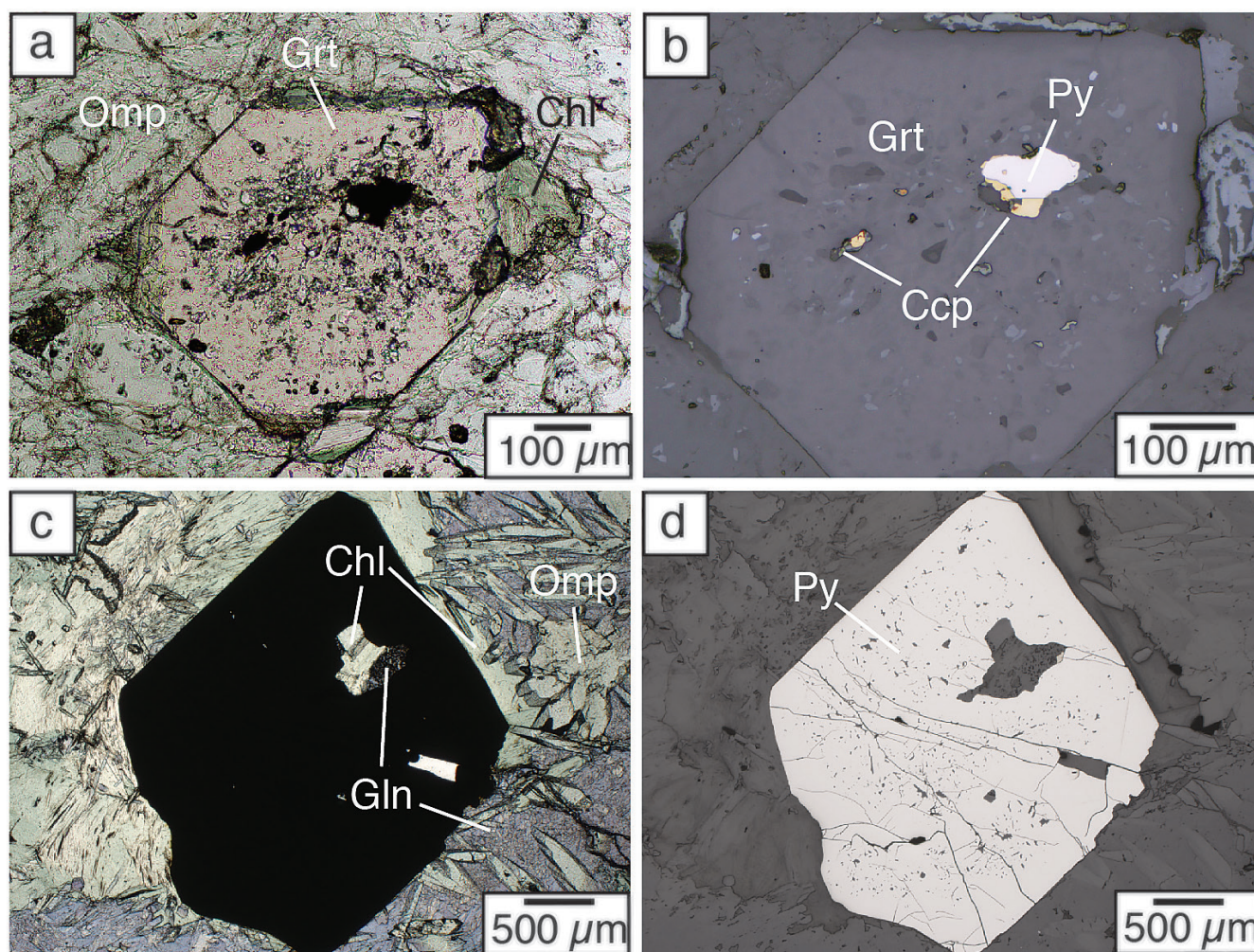


Figure 4 Transmitted (a,c) and reflected (b,d) light images of sulfides in eclogites. In (a,b), pyrite + chalcopyrite are observed as inclusions in garnet from the Junction School eclogite, Franciscan Complex, California. In (c,d), matrix pyrite is associated with retro-grade chlorite + glaucophane in a metasomatised metagabbroic eclogite from Syros, Greece.

Our models allow us to predict on a global scale the influence of sulfur loss on the redox state of volcanic arcs. During “hot” subduction, ~30 % of the total sulfur loss occurs as H_2S and HS^- at shallow depths prior to the sulfide-sulfate transition, followed by a loss of oxidised sulfur at greater depths. Little sulfur is lost prior to the sulfide-sulfate transition in “cold” subduction zones. Therefore, the shallow mantle wedge and forearc magmas may be less oxidised than their arc equivalents. This mechanism is consistent with low $\text{Fe}^{3+}/\Sigma\text{Fe}$ and sulfur concentrations in Mariana forearc magmas relative to those in the main Mariana arc (Kelley and Cottrell, 2012; Brounce *et al.*, 2014, 2016). The predicted SO_x fluxes are also consistent with the oxidised nature of trench proximal Cu porphyry deposits in the Andes and elsewhere (*e.g.*, Tomkins and Evans, 2015). As a result, arc magmas and subarc mantle in cold subduction zones may be more oxidised relative to hot subduction zones.

Summary

We have demonstrated that sulfur–iron redox reactions in subducting AOC can produce oxidised fluids. Our model predictions are consistent with the petrographic, isotopic, and geochemical record of exhumed high pressure rocks, mantle xenoliths, and arc magmas. Sulfur release is a function of the redox budget of the slab and subduction zone thermal structure, with cold subduction of oxidised crust most efficiently

releasing SO_x species. We conclude that sulfur-bearing fluids from AOC may oxidise the arc-mantle system. However, the thermodynamics of sulfur-bearing silicate systems, Fe^{3+} incorporation in silicate minerals, and aqueous sulfur speciation at high pressures remain poorly constrained. It should be a priority for future studies to constrain further our model through the study of natural samples and high pressure experiments.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article2011>.





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