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Abstract

Oxidation of the sub-arc mantle driven by slab-derived fluids has been hypothesized to contribute to the formation of gold deposits in magmatic arc environments that host the majority of metal resources on Earth. However, the mechanism by which the infiltration of slab-derived fluids into the mantle wedge changes its oxidation state and affects Au enrichment remain poorly understood. Here we present the results of a numerical model that demonstrates that slab-derived fluids introduce large amounts of sulfate (S^{6+}) into the overlying mantle wedge that increase its oxygen fugacity by up to 3 to 4 log units relative to the pristine mantle. Our model predicts that as much as 1 wt.% of the total dissolved sulfur in slab-derived fluids reacting with mantle rocks is present as the trisulfur radical ion, S_3^-. This sulfur ligand stabilizes the aqueous $Au(HS)S_3^-$ complex, which can transport Au concentrations of several grams per cubic meter of fluid. Such concentrations are more than three orders of magnitude higher than the average abundance of Au in the mantle. Our data thus demonstrate that an aqueous fluid phase can extract 10–100 times more Au than in a fluid-absent rock-melt system during mantle partial melting at redox conditions close to the sulfide-sulfate boundary. We conclude that oxidation by slab-derived fluids is the primary cause of Au mobility and enrichment in the mantle wedge and that aqueous fluid-assisted mantle melting is a prerequisite for formation of Au-rich magmatic-hydrothermal and orogenic gold systems in subduction zone settings.

Significance Statement

Upon subduction, the oceanic crust releases aqueous fluids that infiltrate the overlying mantle. Compared to primitive mantle, this metasomatized mantle is enriched in gold and other economic metals to provide a source for mineral deposits. However, the fundamental causes of metal enrichment remain enigmatic. We demonstrate that sulfur is the key agent causing Au enrichment in the fluid upon its reaction with the mantle, by forming the soluble $Au(HS)S_3^-$ complex. This species concentrates in fluid up to 1000 times more Au than its average mantle abundance. This gold enrichment in fluid is a key condition for forming Au-rich melts by fluid-present mantle melting. Our work provides the first quantitative assessment of the behaviors of sulfur and gold during subduction-related processes.

Main Text

Introduction

Subduction zones are the main regions of mass exchange between the mantle and crust on Earth. In particular, metals, water and other volatiles are transferred from the subducting slab to overlying mantle wedge by fluids (1-3) and melts (4, 5). These fluids and melts are considered to be oxidized relative to those from the pristine mantle beneath the mid-ocean ridges (6). Different arc magma geochemical signatures, such as elevated total boron concentrations and $\delta^{11}B$ values (7) along with enrichment in large-ion lithophile elements (8) mirror those of the subducted oceanic slab, suggesting a connection between mantle wedge oxidation and the input of slab-related components (6). Thus, metasomatized peridotite xenoliths from the sub-arc mantle record oxygen fugacity values up to 2 log units higher than those of the conventional fayalite-magnetite-quartz buffer ($\log(fO_2)$ from ΔFMQ–1 to ΔFMQ+2) (9-11). Such redox conditions support the hypothesis that slab-derived fluids oxidize the mantle wedge.

Because oxidized sulfur (S^{4+} and S^{6+}), present as sulfate and sulfite species (HSO_4^-, SO_4^{2-},

HSO_3^-, SO_2) and their ion pairs with major cations (Na, K, Ca, Mg), is believed to be soluble in high-pressure aqueous fluids, infiltration of such fluids may explain why the sub-arc mantle wedge would be oxidized relative to depleted mantle (12-15). The input of sulfate-bearing slab-derived fluids is also supported by elevated $\delta^{34}S$ values in arc lavas (16, 17). Oxidizing agents such as sulfate and ferric iron are thought to be required for resorption of Au-bearing sulfides during partial melting of the mantle wedge (11, 18, 19), making such oxidation phenomena essential for the formation of porphyry and orogenic gold deposits. However, compared to more reduced sulfur species such as HS^-, H_2S, and S_3^-, which are major sulfur ligands for transporting Au in aqueous fluids (20, 21), sulfate has little capacity to form Au complexes. Because of a lack of quantitative assessment of the impact of such sulfur-mediated redox reactions both on the oxidation state of the mantle wedge and gold solubility in aqueous fluids and silicate melts originating from the metasomatized mantle, it is unclear how these opposing factors can be reconciled to explain gold transport within the mantle wedge.

Here we report the results of thermodynamic simulations that quantitatively predict the chemistry of fluids generated by prograde devolatilization of subducted oceanic crust. We show that the resulting sulfate-bearing fluids oxidize ferrous iron in the silicate minerals within the mantle wedge. As a consequence of this oxidation, the fluid becomes reduced and enriched in trisulfur radical ion, S_3^-, which forms soluble complexes such as $Au(HS)S_3^-$ with Au. We propose that this sulfur-driven redox phenomenon is the fundamental mechanism of Au enrichment in magmatic arcs that host a major proportion of global economic resources of gold. These findings highlight that mantle oxidation improves the recycling efficiency of volatiles and metals in subduction zones.

Results

Devolatilization of altered oceanic crust and sulfur mobility

Results from the devolatilization models (see Materials and Methods below) of altered oceanic crust (AOC) reveal two dominant dehydration stages along hot (1000 °C, 2.4 GPa) and cold (1000 °C, 3.3 GPa) subduction geothermal gradients (Fig. 1). The dehydration of chlorite and talc occurs at temperatures (T) T < 575 °C with removal of ~20% of the total water contained in the hydrated AOC (Figs. 1A, B and S1). The second stage occurs at fore-arc to sub-arc depths of 60–80 km for warm subduction, and of 80–120 km for cold subduction. During this stage, ~75% of the initial water contained in the AOC is released through dehydration of epidote, lawsonite, pumpellyite, and stilpnomelane. Lawsonite and muscovite are predicted to carry the remaining ~5% of water in the AOC to the deep mantle (> 120 km) in the cold subduction regime (Fig. 1B).

Our model predicts that about 60% and 90% of the initial sulfur in AOC is released from hot and cold subducting slabs, respectively, during the second stage of dehydration (Figs. S1A and B). Aqueous sulfur speciation evolves along the hot geotherm, transforming from dominantly reduced (HS^- and H_2S) in the first dehydration stage to dominantly oxidized (HSO_4^-, SO_4^{2-}, KSO_4^-, HSO_3^- and SO_2) during the second dehydration stage (Fig. 1C). In contrast, fluid speciation along the cold geotherm is always dominated by sulfate with only minor H_2S, HS^- and SO_2 (Fig. 1D). For both hot and cold subduction geotherms, the majority of the S is released to the aqueous fluid when pyrite (S^-) is oxidized to anhydrite (S^{6+}) in the 475–600 °C range (Figs. 1 and S2). Our model predicts an increase in the $Fe^{3+}/\Sigma Fe$ ratio of garnet and decrease in clinopyroxene and the bulk rock system, over the interval of pyrite oxidation to anhydrite, both for cold and hot subduction scenarios (Figs. S1 and S2).

Oxidative capacity of slab-derived fluid

To evaluate the metasomatic effects induced by slab-derived fluids in hot and cold subduction zones, we calculated the change in oxygen fugacity (fO_2) caused by the infiltration of fluids containing different S^{6+} concentrations (Fig. 2) into depleted mantle peridotite. For both hot and cold subduction geotherms, the interaction of mantle rocks with a fluid typically containing 1 to 2 wt.% S^{6+} increases the mantle fO_2 by at least two log units at plausible fluid/rock mass ratios (R) of 0.02 to 0.05 (Figs. 2A and B top curves). In contrast, in both regimes, only a weak increase in fO_2 (0.2-

0.5 log units) can be achieved by sulfur-poor (0.01-0.02 wt.% S) fluids and only at higher fluid/rock ratios (R > 0.2) (Figs. 2A and B, bottom curves). This difference demonstrates the importance of sulfur in the mantle oxidation process. Our model predicts that the mantle oxygen fugacity steeply increases during the initial infiltration of the S^{6+}-bearing fluid. With further fluid infiltration, the increase in fO_2 decreases (Figs. 2A and B). A similar pattern is displayed in the $Fe^{3+}/\Sigma Fe$ ratio of garnet and pyroxene and X_{Mg} (Mg/(Mg+Fe)) values of olivine (Fig. S3). These results demonstrate that the concentration of sulfate of the fluid plays a major role in the oxidation of the mantle wedge. In addition, the fluid infiltration model (see Materials and Methods below) predicts that pyrrhotite and pyrite are the dominant sulfide minerals for low to moderate degrees of metasomatism (i.e. low fluid/rock ratios, R < 0.01). With increasing fluid/rock ratio, Py + Anh and Pyh + Anh become the stable S-bearing mineral assemblages. The transition from Py + Anh to Pyh + Anh occurs at ~930 °C and ~1050 °C for hot and cold subduction models, respectively (Figs. 3C and D).

Sulfur and gold abundances and chemical speciation in fluid reacted with mantle wedge

The concentrations of sulfur species in slab-derived fluids after reaction with depleted mantle peridotite were computed for temperature of 1000 °C and pressures of 2.4 and 3.3 GPa (Figs. 3, S4 and S5). At 2.4 GPa, in the presence of Py, Pyh and Anh, elevated concentrations of sulfate and sulfite (HSO_4^-, SO_4^{2-}, HSO_3^-, SO_2) persist over a wide range of temperature (Figs. S4C–F). At low fluid/rock mass ratios (R < 0.01), H_2S is the dominant aqueous sulfur species but the high concentrations of HS^- in the reacted aqueous fluid occur only at 800–900 °C, as pH changes toward more alkaline values (Figs. S4A and B). The highest concentrations of trisulfur radical ion S_3^- in the reacted fluid occur at 700–1100 °C (Fig. 3A). Compared to H_2S and HS^-, S_3^- is more abundant at higher fO_2 conditions, and accounts for ≥ 50% of the total sulfur at fO_2 between ΔFMQ+0.5 and ΔFMQ+1.5 (Figs. 2C and 3A). At 3.3 GPa, higher concentrations of HSO_4^-, HSO_3^- and SO_2 are predicted over a wide range of temperatures and fluid/rock ratios (Figs. S5C-F). Significant concentrations of H_2S and HS^- are restricted to areas of low fluid-rock ratios and to low temperatures (< 900 °C) for HS^- (Figs. S5A and B). At R values between 0.002 and 0.02 (corresponding to fO_2 from ΔFMQ–0.5 to ΔFMQ+1.5), S_3^- is the dominant aqueous sulfur species accounting for 50–90% of the total sulfur in the fluid (Fig. 3B). In both models, the abundance of S_3^- is a strong function of fO_2 and the concentrations of S_3^- are one to three orders of magnitude higher than those of HS^- at redox conditions, thus permitting sulfide-sulfate coexistence. Such concentrations are expected to favor the formation of gold complexes with the S_3^- ligand.

To support this conclusion, we calculated the speciation and solubility of gold in a metamorphic fluid (containing 3 wt.% S and 5 wt.% NaCl) typical of subduction zones at 600 °C and 1.5 GPa (Figs. 3C and D). These calculations show that while $Au(HS)_2^-$ is the dominant gold complex below FMQ redox conditions, $Au(HS)S_3^-$ becomes the dominant gold carrier at higher oxygen fugacity, followed by $AuCl_2^-$ at highly oxidizing conditions (> ΔFMQ+3) (Fig. 3C). The highest abundance of $Au(HS)S_3^-$ occurs at redox conditions of the pyrite-pyrrhotite-magnetite buffer (~ΔFMQ+1), when the gold solubility is 2 ppm (Fig. 3C). In addition to redox conditions, the sulfur-content of the fluid is an important parameter affecting Au solubility. At 600 °C, 1.5 GPa and redox conditions of H_2S:SO_2=1:1, the concentration of $Au(HS)S_3^-$ complex is strongly enhanced in sulfur-rich (> 1 wt.% S) fluids (Fig. 3D). Our calculations show that $Au(HS)S_3^-$ remains the major gold complex in sulfur-rich solutions at 700 °C and 800 °C, in which Au solubility attains 100–300 ppb (Fig. S6). Gold solubility and aqueous speciation are also functions of the fluid alkalinity (here defined as ΔpH = pH–pH_n, where pH_n is the pH value of the water neutrality point). At more acidic pH (ΔpH < –1), $AuCl_2^-$ becomes more important, but its abundance largely decreases with increasing pH (Fig. S7). In contrast, $Au(HS)S_3^-$ and $Au(HS)_2^-$ complexes may transport ~2 ppm Au in the aqueous fluid at neutral to alkaline conditions of ΔpH 0.0 to 2.5, which are typical of slab-derived fluids in equilibrium with mantle peridotite (Fig. S7 and Supplementary Text). In summary, these mantle-wedge fluids are expected to mobilize and concentrate large amounts of Au by forming abundant $Au(HS)S_3^-$ during mantle metasomatism.

Efficiency of gold extraction from oxidized hydrous mantle by partial melting

We estimated the gold extraction efficiency from a fertile mantle (containing 3.5 ppb Au and 600 ppm S) by modeling fluid-present batch melting at oxygen fugacities of ΔFMQ–1.0 (reducing) and ΔFMQ+1.5 (moderately oxidizing), respectively (Figs. 4, S8 and S9). Two scenarios were simulated: i) low-temperature melting (1100 °C, 1.5 GPa) with large fractions of monosulfide solid solution (MSS) and ii) high-temperature melting (1300 °C, 1.5 GPa) in the presence of sulfide liquid (SL). Both scenarios indicate that the consumption of mantle sulfide is favored by moderately oxidizing conditions. At fO_2 of ΔFMQ+1.5, the silicate melt contains all Au and S for a melt degree (F) of < 7.5%, due to the exhaustion of sulfide (Figs. 4B and D). At fO_2 of ΔFMQ–1.0, only a small fraction of mantle Au is released into the silicate melt at a high degree of partial melting (up to 15%, Figs. 4A and C). Results for fluid-present melting models demonstrate that the coexistence of aqueous fluid and silicate melt is far more favorable for extraction of Au and S from mantle than in the absence of a fluid phase (Fig. 4). As shown in Figs. 4A and B, with only 1% partial melting, ~70% of Au in the mantle can be extracted in the presence of 0.3 wt.% fluid, with concentrations of 8 ppb Au in the water-saturated melt and 800 ppb Au in the coexisting fluid. With only 5.5% melting at fO_2 of ΔFMQ+1.5 and in the presence of 0.2 wt.% fluid, mantle sulfide becomes exhausted (Figs. 4B and D). Thus, our models reveal that the stability of sulfide liquid is greatly diminished when the fluid phase appears. This fluid phase has the ability to transport ~60 times more Au than a silicate melt at mantle-wedge conditions of ΔFMQ+1.5, 5 % melting fraction and only 0.2 wt.% aqueous fluid in the system.

Discussion

Controls on sulfur mass transfer at the slab-mantle interface

Previous thermodynamic modelling (14, 22, 23) has shown that slab devolatilization releases fluids in which sulfur could be present as $CaSO_4^0$(aq), SO_4^{2-}, HSO_4^- HSO_3^-, SO_2, H_2S, and HS^-. However, these ignored the trisulfur radical ion, S_3^-, that becomes increasingly abundant at elevated temperatures and pressures. Our study reveals that S_3^- is the dominant reduced species in fluids across a wide range of redox conditions after reaction with overlying mantle (Fig. 3). Figure 1 shows that the concentrations of sulfate and sulfite (e.g., SO_4^{2-}, HSO_4^-, HSO_3^-) in the fluid sharply increase, by one to three orders of magnitude, before reaching a plateau when pyrite is oxidized to anhydrite along both hot and cold subduction geotherms. The results presented here show that a maximum flux of oxidized fluid will be generated from AOC at 60–80 km and 80–120 km for hot and cold subduction zones, respectively. These predictions are similar to conditions at the depth of arc-magma formation. Results from the mantle infiltration model indicate that fluids released at sub-arc depth are capable of oxidizing the overlying mantle to ΔFMQ+2 to 3, whereas fluids from fore-arc depths cannot increase mantle fO_2 values to more than ΔFMQ+1 (Fig. 2). The higher oxidation state of sub-arc mantle is also consistent with the higher bulk-rock $Fe^{3+}/\Sigma Fe$ ratios of magmatic rocks (0.18–0.32) at volcanic arcs relative to those in back-arc, mid-ocean ridge, and fore-arc settings (6). Our predictions also fall in the fO_2 range of metasomatized mantle inferred from mantle xenoliths and arc magmas (9, 11).

As shown in Figs. 1 and S2, increasing temperature during prograde metamorphism of the subducting slab results in the oxidation of pyrite to anhydrite and the breakdown of hydrous minerals including epidote, chlorite and lawsonite. This process results in the growth of garnet at ~550 °C, a decrease of the $Fe^{3+}/\Sigma Fe$ ratio of clinopyroxene, and an increase in garnet with increasing temperature (Figs. S2C–H). The total Fe^{3+} content of the residual solid decreases by ~0.2 mol/kg rock over the temperature range within which pyrite is oxidized to anhydrite (Figs. S1C and D). From the sulfur loss curves and mineral modal abundances, ~0.03 mol/kg rock S^- (i.e. total initial sulfur content in model) is oxidized to S^{6+} when pyrite transforms to anhydrite (Figs. 1 and S1). Consequently, mass balance calculations indicate that this redox process is consistent with the general reaction:

$$FeS_{2(solid)} + 7Fe_2O_{3(in\ silicates)} + 2CaO_{(in\ silicates\ or\ fluid)} = 2CaSO_{4(solid\ or\ in\ fluid)} + 15FeO_{(in\ silicates)} \quad (1)$$

Our model suggests that the oxidation of S during the thermally-inducted breakdown of pyrite is

balanced by reduction of Fe^{3+} in bulk rock rather than reduction of CO_2 as previously proposed (14). Indeed, the bulk rock is the greatest reservoir of iron, including Fe^{3+}, which is much greater than possible CO_2 input. The results indicate that the production of sulfate in the slab is a function of the Fe^{3+} content of the protolith. It follows that the transfer of sulfate to the slab-derived fluid will leave a reduced residual mineral assemblage in the subducting oceanic crust. This conclusion is consistent with natural observations, such that the increase of core to rim $\delta^{56}Fe$ values of garnet in garnet-epidote blueschist from the Sifnos subduction zone, Greece, which was attributed to the loss of oxidizing fluids during devolatilization of the subducting slab (10). Previous thermodynamic studies concluded that the transformation of pyrite to pyrrhotite dominates the release of sulfur from the subducted slab (23). Instead, our results suggest that the oxidation of pyrite to soluble sulfate during the blueschist to eclogite transition is responsible for introducing the major fraction of oxidized sulfur from the subducted slab into the sub-arc mantle.

The mantle oxidation model presented here predicts a positive correlation between the fO_2 of mantle and the increase of $Fe^{3+}/\Sigma Fe$ ratios in pyroxene and garnet with the continuous infiltration of a S^{6+}-bearing slab-derived fluid (Figs. 2 and S3). The consumption of Fe^{2+} is manifested by an increase in the modal abundances of orthopyroxene at the expense of olivine and clinopyroxene and an increase in the X_{Mg} value of olivine (Figs. S3A and B). Additionally, oxidized sulfur species (HSO_4^-, SO_4^{2-}, HSO_3^-) in the infiltrating slab-derived fluid are reduced to HS^-, H_2S, and S_3^- as the fluid is reacting with the mantle rock (Figs. 3, S4 and S5). These sulfate reduction reactions are consistent with a decrease in fO_2 values of slab-derived fluids after interaction with depleted mantle, for instance decreasing from ΔFMQ+5 to ΔFMQ+3 at sub-arc depths (Fig. 5A). We therefore propose that the following schematic reactions illustrating the control of sulfur and iron redox state in the mantle wedge:

$$SO_4^{2-} + 2H^+ = H_2S + 2O_2 \quad (2)$$

$$SO_4^{2-} + 2H_2S + H^+ = S_3^- + 0.75O_2 + 2.5\,H_2O \quad (3)$$

$$2FeO_{\text{(in silicates)}} + 0.5O_{2\text{ (in fluid)}} = Fe_2O_{3\text{ (in silicates)}} \quad (4)$$

Our model predicts that fluid-altered clinopyroxene and orthopyroxene in the mantle wedge will have $Fe^{3+}/\Sigma Fe$ ratios of 0.30–0.45 and 0.10–0.20, respectively (Figs. S3C and D). These ratios broadly agree with analyzed values of 0.48–0.51 and 0.10–0.15 in fluid-altered metasomatic mantle peridotite from the Sulu orogeny in China (24), for clinopyroxene and orthopyroxene, respectively. Furthermore, increase of $Fe^{3+}/\Sigma Fe$ values in metasomatized garnet is consistent with values for peridotite samples of the sub-arc mantle from Bardane in Norway (13). These observations collectively indicate that the oxidized state of the mantle wedge is caused by S^{6+}-bearing slab-derived fluid metasomatism that results in the oxidation of Fe^{2+} in the silicate minerals, dissolution of sulfide minerals, and generation of reduced sulfur Au-complexing ligands such as H_2S (HS^-) and S_3^- (Fig. 5).

Enhanced mobility and enrichment of gold in mantle wedge

Mantle wedge metasomatized by slab-derived fluid and melts generally results in enrichment in metals (e.g., up to hundreds ppb Au and thousands ppm Te) and elevated oxygen fugacity (>ΔFMQ+1) (25, 26). However, the causes of metal enrichment during mantle oxidation process were poorly understood. Recent experimental studies imply that slab melts carry no more than ¼ of the Au from the downgoing lithosphere to the overlying mantle wedge. These data are corroborated by the low gold abundances (< 1ppb) in primitive melts from subduction-related eclogite (27, 28). Although some studies have inferred Au loss into devolatilization-induced fluids by prograde sulfide breakdown during slab subduction (29, 30), this gold input cannot explain the elevated Au abundance of the overall metasomatic mantle (31). We posit an alternative model in which the mobilization and redistribution of mantle Au plays a first-order control on the formation of auriferous metasomatized mantle by locally enhancing gold fertility of mantle lithosphere. Naturalistic support for this model comes from numerous reports of gold-rich lithospheric mantle in the Ivrea Zone, Italy (25), the Deseado Massif, Argentina (32), and at Tallante, southern Spain (33). In these settings, melt- or fluid- metasomatized mantle peridotite and pyroxenite have 10–100 times more Au than pristine mantle and some samples even contain visible native gold particles.

A statistical analysis of mantle peridotites (34) concluded that the Au concentrations gradually

increase with the evolution from deep garnet-bearing peridotite (0.5–1.5 ppb, max 3 ppb) to shallow plagioclase-bearing peridotite (2–4 ppb, max 15 ppb). The Au abundances exhibit positive correlations with the concentrations of incompatible elements in some mantle xenoliths (35). These data collectively indicate upward mobilization of Au by aqueous fluids or hydrous melts, but the abilities of fluid and melt to carry Au have not been quantified. Our numerical results show that the S-bearing fluids can carry hundreds to thousands ppb of gold as the $Au(HS)S_3^-$ complex across a wide fO_2 (FMQ to ΔFMQ+2) and pH (ΔpH = 0.0–2.5) due to generation of abundant S_3^- in slab-derived fluids upon reaction with depleted mantle (Figs. 3, S6 and S7). This enhanced transport capacity provides an explanation for the Au enrichment in oxidized metasomatized mantle (Fig. 5B). The consumption of these auriferous fluids during ascent through the mantle by hydration reactions would form a mantle source locally enriched in Au and volatile elements (C-O-H-S) (Fig. 5A). This scenario explains why sulfides hosted in weakly metasomatized mantle xenoliths (free of secondary alteration minerals) have higher gold abundances (2 ppm) in comparison to those (<0.5 ppm) hosted in strongly metasomatized rocks with secondary amphibole and apatite, such as in Spitsbergen island, Norway (36). Alternatively, the Au-rich fluids produced by subduction-modified mantle may directly contribute to the formation of gold deposits hosted in island arc zones, such as Ladolam Au deposit, Papua New Guinea (37), and volcanogenic massive sulfide gold deposit in Kermadec Arc (38). Due to a thinner lithosphere in such zones, auriferous fluid would transport abundant Au and volatiles away from residual mantle sources to domains of arc-melt generated. In summary, oxidation controls the metal enrichment in the metasomatized mantle via enhanced mobilization of Au in complex with the trisulfur radical ion in aqueous fluid under more oxidizing conditions than those of pristine mantle (Fig. 5).

Facilitated metal extraction and formation of gold deposits

Partial melting of metasomatized mantle is regarded as a key process for the formation of porphyry Cu-Au-Mo and epithermal Au-Ag deposits (32, 39). Gold concentrations of primary mantle melts depend on the oxidation state of their source, degree of partial melting, and gold partitioning between the sulfide phases and silicate melts (18, 40, 41). Low-degree melting of oxidized mantle has been invoked to explain the formation of Au-rich parental arc magmas. For instance, ~2.4% partial melting can yield Siberian picrite that contains abnormally high concentrations of Au and platinum-group elements at redox conditions of ΔFMQ+2 (42). Furthermore, oxidized mantle xenoliths (with ΔFMQ+1 to ΔFMQ+2) from Lake Bullen Merri in Australia record extensive sulfide dissolution at very low degrees of partial melting, of ~2% (11). These data are consistent with our modeling that suggests gold is preferentially enriched in moderately oxidized (~ΔFMQ+1.5) and hydrous melts (Figs. 4, S8 and S9). Gold partitioning between silicate melt and sulfide is another factor influencing the Au concentration of magma. Previous experimental investigations demonstrate that iron sulfide occurs as both MSS and SL in upper mantle at redox conditions close to the sulfide-sulfate boundary (SSO, ~ΔFMQ+1.5), which is regarded as typical fO_2 conditions of metasomatized mantle (9, 43). The high Au partition coefficients (> 1000) between SL and mantle melts result in most gold being retained in the residual SL until its complete resorption at higher fO_2 (44, 45). Consequently, increasing fO_2 to higher than SSO levels by the addition of slab-derived Fe^{3+} was thought to account for the formation of Au-rich melts at high-temperature melting in the presence of sulfide liquid (18). However, our modeling quantitatively shows that the aqueous fluid only carries a few hundred ppm Fe^{3+} at sub-arc depths (Fig. S10). Whereas slab-derived hydrous melts may carry 1–2 orders of magnitude more ferric iron than aqueous fluid, they are generally expected to occur at slab depths greater than 100 km (4, 18, 46). Therefore, elevating fO_2 by adding slab-derived Fe^{3+} is unlikely to be a prevalent process that promotes the release of Au from sulfide liquid. Rather, fluid-present mantle melting can scavenge gold more efficiently from mantle sulfide liquid under moderately oxidizing conditions resulting in readily exhaustion of mantle sulfides even at small degrees of partial melting (Figs. 4 and S9). Note that the coexistence of aqueous fluid and peridotite melt at our T-P conditions is consistent with experimentally established phase diagrams (47), showing fluid-melt immiscibility up to at least 3.8 GPa and 1000-1100 °C. The fluid-present partial melting of mantle wedge is also documented by the coexisting fluid and silicate melt inclusions trapped in mantle peridotite xenoliths from western Hungary (48). These findings provide

a novel mechanism for generating Au-rich melts under redox conditions close to the coexistence of sulfide and sulfate. Our predictions are supported by natural examples such as basanitic magmas from Hawaii (formed at fO_2 of ΔFMQ+0.8) with Au concentrations up to 36 ppb (49), volatile-rich lamprophyres from Scotland, southern Africa, and the Yilgarn, Australia as the products of low-degree mantle melting having 100–1000 times higher Au abundances than other 'common' igneous rocks (50).

Gold grades of porphyry copper(-gold) deposits vary over three orders of magnitude, from ~0.001 to 1 ppm Au. High Au-tonnage deposits show 10–100 times higher average gold grades than those with high Cu tonnage (Fig. S11). Melt inclusion data from igneous rocks that were the source of ore fluids for porphyry Cu(-Au) deposits in the Maricunga Belt, Chile, indicate that the Au concentrations of magmas were as much as three orders of magnitude higher than those reported for magmas of Cu-rich porphyry deposits (51). These differences in Au grades are likely due to the sulfur control on the deep source of metals and variation of partial melting mechanism. Our calculations suggest that the aqueous fluid acts as an extremely effective agent to transport and concentrate Au within the metasomatic mantle wedge. Mass balance calculations further indicate that 20–80% of the original mantle Au are released at < 2% hydrous low-temperature (1100 °C) partial melting in the stability field of MSS (Figs. 4A and B). Therefore, the high fluid flux favors the gold enrichment into shallow mantle lithosphere by upward mobilization at active continental margins characterized by a thick lithosphere and cold mantle wedge, which, in turn leads to arc magmas derived from deep mantle becoming Au depleted. Furthermore, this enriched mantle can be stored hundreds of million years before a later tectonic melting event, as likely in the case of Lake Bullen Merri in Australia (11), and is therefore an important metal source for Au deposits formed in post-subduction settings (52). In contrast, in island arc subduction zone, high mantle temperature of > 1300 °C stabilizes the sulfide liquid, thereby resulting in > 80% of the initial Au retained in mantle source rather than extracted by silicate melt until exhaustion of sulfide (Figs. 4C and D). In these settings, according to our modeling fluid-assisted high-temperature melting of metasomatic mantle favors the generation of Au-enriched primary melts (Figs. 4 and S9), as suggested for the high-Au arc magmas (> 8 ppb) from Kermadec arc (53). Our findings thus offer another new perspective for understanding the variation of Au-grade in porphyry deposits located in thick or thin lithosphere zones (54).

Previous metamorphic devolatilization scenarios explain the formation of Phanerozoic orogenic gold from a metasomatized mantle source (e.g., in Jiaodong Peninsula in China (55, 56) and in northwestern Mexico (57)). These scenarios postulate that gold and sulfur are released into the fluids through breakdown of pyrite to pyrrhotite, conditions at which H_2S and HS^- are postulated to be the ligands transporting gold (58). In contrast, our numerical modeling reveals that the sulfide-sulfate transition provides the most favorable window for sulfur release under conditions typical of the metasomatized mantle. At such conditions, the high abundance of S_3^- enables at least 10 to 100 times more efficient mobilization of gold by S-rich fluids than any common ligand such as H_2S, HS^- or Cl^- (Figs. 3C and D). The breakdown of S_3^- at lower temperatures and pressures would trigger efficient and focused Au precipitation in upper levels of the crust where most deposits form (20, 59). Consequently, S_3^- may be a key factor ensuring the generation of an auriferous fluid in metasomatized mantle lithosphere (Fig. 5). In conclusion, our results demonstrate that mantle oxidation by S-bearing aqueous fluids is the key trigger mechanism for Au enrichment and release within mantle wedge, providing both the necessary source and transport conditions for the formation of gold-rich porphyry-epithermal and orogenic gold systems. Additional work on both chemical and physical reactive transport models will be a priority to advance our understanding of metal enrichment and the transfer of the fluid-saturated silicate melt through the mantle wedge and its ascent to shallower crust levels in subduction zones.

Materials and Methods

System compositions and redox budgets

Bulk rock compositions chosen to model the altered oceanic crust and depleted mantle peridotite systems were modified from refs. (60) and (61) (Table S1 and S2). Different water

contents were chosen for the hot and cold subduction zone regimes to enable H_2O saturation at the first P-T point, with contents of 4.7 and 7.6 wt.%, respectively. The redox budget (RB) is a critical variable for quantifying the potential redox capacity of a rock-fluid system, which is defined as:

$$RB = \sum n_j v_j$$

where v_j represents the number of electrons per mole required to convert a redox-sensitive element from a reduced state to the reference oxidation state, and n_j is the number of moles of the element per 1 kg of fluid-rock system. Here we only define the redox budget of initial solid rock, as the remaindert can be calculated using the thermodynamic modeling software. Iron, carbon and sulfur were considered to be the major redox-sensitive elements in our model. For depleted mantle peridotite, the initial oxidation states of iron, carbon and sulfur were set as Fe^{2+}, C^0, and S^{2-}, with minor Fe^{3+} corresponding to an $Fe^{3+}/\Sigma Fe$ ratio of 0.031 (15). In view of the limited contents of CO_2 (50 ppm) in the depleted mantle, their influence on the model results is negligible. Compared with the juvenile oceanic crust, the altered oceanic crust is characterized by higher $Fe^{3+}/\Sigma Fe$ values, which were adopted as 0.51. The redox states of sulfur were adopted to be S^- in pyrite and S^{6+} in anhydrite with concentrations of 700 ppm and 364 ppm S, respectively. The composition of the modeled rocks is listed in Table S1.

Phase equilibrium modeling

Our modeling includes a devolatilization model of AOC along hot and cold subduction paths, and a mantle infiltration model. The geothermal models of Central Honshu and Central Cascadia subduction zones were chosen to represent, respectively, the cold and hot thermal regime of the subducting slab (62). The devolatilization model was calculated along the top-of-slab P-T paths in both geothermal regimes, and each geotherm was discretized into 671 P-T points from 0.50 GPa to 7.20 GPa with a step of 0.01 GPa. When simulating the devolatilization processes of the subducting slab, the fluid produced at a given P-T point was separated from the bulk rock. To quantify the relative oxidation capacity of the slab-derived fluid, two methods were employed in simulating mantle infiltration processes: a titration scenario and a mixing scenario. In the former, fluid compositions were extracted from three different slab depths (see Fig. 1), then equilibrated with model mantle peridotite at 3.3 GPa, 1000 °C and 2.4 GPa, 1000 °C for cold and hot subduction models, respectively. The extracted fluid composition was normalized to 2 moles of hydrogen (H), which is roughly equivalent to 1 mole of H_2O-dominated fluid, corresponding to 18 g (Table S3). We divided 12 moles of such a fluid into 120 equal portions of 0.1 mole, and added one portion into 1 kg of model peridotite at each subsequent step. In the mixing scenario, 1 mole of fluid (normalized to 2 moles of H) released at sub-arc depth as an endmember was reacted with 1 kg of mantle peridotite as the other endmember at different fluid/rock mass ratios, from 700 °C to 1100 °C. The compositions of 1 mol fluid and 1 kg rock are expressed here as elemental concentrations in numbers of moles (Table S2 and S3). The fluid-rock ratio increases nonlinearly due to the following dependence between the masses of reacting fluid and rock in a mixing model:

$$R = \frac{m_{fluid} \times X_{fluid}}{m_{rock} \times (1 - X_{fluid})}$$

where R is fluid-rock mass ratio of the system at a specific X_{fluid} value, and m_{fluid} and m_{rock} represent initial masses of fluid (18 g) and mantle peridotite (1000 g), respectively. The X_{fluid} is an independent variable with values between 0 and 1. For example, an X_{fluid} value of 0.9 on this scale corresponds to a mass fluid/rock ratio of 0.16. All calculations were executed by Gibbs energy minimization in Perple_X 7.0.11 (14, 63), using so called "lagged speciation" method of Perple_X to compute the concentrations of aqueous species (14). Both for the devolatilization and mantle oxidation models, the fluid was considered as a H_2O-CO_2 binary solution (14). Thermodynamic data for aqueous species (except S_3^-) are taken from the SUCRT92 database (64) complemented by the Deep Earth Water model for Ca, Mg, Fe, Al and Si species (65) and those for minerals from the revised Holland and Powell mineral database (66). The thermodynamic parameters of S_3^- are taken from ref. (59) based on direct experimental measurements and revised Helgeson-Kirkham-Flowers (HKF) equation of state compatible with the DEW model. Organic species were excluded from the calculations. Amphibole, biotite, chlorite, clinopyroxene, dolomite, epidote, feldspar, garnet,

magnesite, muscovite, pumpellyite, pyrrhotite, olivine, orthopyroxene, stilpnomelane, and talc were treated as solid solutions. All other minerals were treated as pure phase compounds, including albite, anhydrite, coesite, kyanite, lawsonite, pyrite, quartz, and stilbite. For more details on solid solution models and fluid equations of state see Tables S4 and S5.

Modeling of Au speciation and solubility in the fluid phase

Gold speciation and solubility in H_2O-NaCl-S aqueous fluids at 1.5 GPa, 600 °C, which are typical dehydration conditions of AOC and serpentinized oceanic mantle, were modeled to explore the geochemical behavior of Au during mantle metasomatism. The main fluid constituents include 6 wt.% NaCl (67), 3 wt.% S (68) and an excess of native gold. The fluid pH was buffered at a value of about 5 by using the olivine-pyroxene-garnet mantle mineral assemblage, which corresponds to slightly alkaline conditions relative to the neutrality point of pure water (ΔpH=1.5 to 2.5, see Supplementary Materials). The thermodynamic properties of minerals and major fluid constituents, including most sulfur species, are from the updated Holland and Powell (69) and SUPCRT databases (64), respectively. The HKF equation of state parameters for the S_3^- ion were adopted from ref. (59). The complexes $Au(HS)_2^-$, $AuCl_2^-$, and $Au(HS)S_3^-$, for which robust thermodynamic data were constrained over a wide P-T range (20, 70, 71), were considered in the modeling. Species such as $AuHS^0$, $AuHS(H_2S)_3^0$, $AuOH^0$, $AuCl^0$, and $Au(OH)_2^-$ were ignored because of the large uncertainties associated with their identity and stability at elevated temperatures and inconsistencies in their published thermodynamic parameters. Sources of the thermodynamic properties of Au-HS-Cl-S_3^- species are reported in Table S5. These datasets arise from the large amount of experimental work described by the HKF equation of state, which enables plausible extrapolations to the high temperatures and pressures of our system. Calculations were conducted using the HCh package and modified and updated Unitherm database (72).

Estimation of gold extraction during hydrous mantle melting

The available partial melting models disregard the effects of an aqueous fluid phase on the element distribution. In this study, we applied mass balance relationships to quantify, for the first time, the Au contents released into the fluid and silicate melt during partial melting of mantle. We calculated a batch melting process at a given free aqueous fluid phase fraction varying from 0.1 to 0.3 wt.% of the melt-fluid-rock system. Mantle Au is stored almost exclusively by iron sulfide solid or liquid with negligible Au fractions in other silicate minerals or as a metallic gold particle. Therefore, the total Au content in a closed system at equilibrium is given by the following equation:

$$M_{Au} = C_{Au}^{sul} \times m_{sulfide} + C_{Au}^{fluid} \times m_{fluid} + C_{Au}^{melt} \times m_{melt}$$

where M_{Au} is the total Au content per unit mass of mantle rock, $m_{(j)}$ and $C_{Au}{}^{(j)}$ are the mass fraction and Au concentration of the iron sulfide phase, aqueous fluid phase and silicate melt phase, respectively. According to the gold partition coefficients of sulfide/melt ($D_{Au}^{sulide/melt}$) and fluid/melt ($D_{Au}^{fluid/melt}$), the above equation can be re-arranged to express the Au concentration in silicate melt:

$$C_{Au}^{melt} = \frac{M_{Au}}{D_{Au}^{sulfide/melt} \times m_{sulfide} + D_{Au}^{fluid/melt} \times m_{fluid} + m_{melt}}$$

The Au concentrations in aqueous fluid and sulfide can thus be estimated by mass balance in close-system batch melting, which is given by:

$$C_{Au}^{fluid} = C_{Au}^{melt} \times D_{Au}^{fluid/melt}; \quad C_{Au}^{sulfide} = C_{Au}^{melt} \times D_{Au}^{sulide/melt}$$

The mass fraction of melt, m_{melt} , depends on the melting degree, F, the mass fraction of residual sulfur in mantle rock at any given F value, and the fluid content:

$$M_S^{rock} = M_{S_t}^{i} - C_S^{fluid} \times m_{fluid} - C_S^{melt} \times F$$

where M_S^{rock} and $M_{S_t}^{i}$ represent the residual and initial sulfur content in mantle rock, C_S^{fluid} and C_S^{melt} are sulfur concentrations that solubilities in aqueous fluid and mantle melts, which were determined by regression of the available experimental data (Fig. S12). Sulfide has long been known to occur as both monosulfide solid solution (MSS) and liquid (SL) phases at upper mantle temperature and pressure, and its phase state (solid or liquid) exerts a first-order control on Au partitioning during

mantle melting (42, 45). Available experimental data indicate that MSS and SL are stable, respectively, at < 1200 °C and ≥ 1300 °C, at pressures of 1.5 GPa, corresponding to mantle partial melting depths (43). Therefore, in our melting model, two scenarios, a high-temperature (1300 °C) and a low-temperature (1100 °C) one, for hydrous mantle melting were simulated at two different redox conditions, of ΔFMQ+1.5 and ΔFMQ–1.0. The initial Au concentration of metasomatized mantle was assumed to be 3.5 ppb (34), and the sulfur concentration was chosen to be 600 ppm, corresponding to 0.17 wt.% of monosulfide solid solution in the system (73). The partition coefficients of Au between MSS or SL, and aqueous fluid and silicate melts are from the available experimental data (44, 74) whose typical values for the conditions of our study were adopted as $D_{Au}^{MSS/melt}$ of 200, $D_{Au}^{SL/melt}$ of 2200, and $D_{Au}^{fluid/melt}$ of 100. These data, both on sulfur solubility and Au partitioning are from direct fluid-saturated melting experiments, thereby allowing gold extraction from metasomatic mantle via hydrous melting to be estimated (see Supplementary Materials for more details for model limitations and uncertainties).

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Figures and Tables

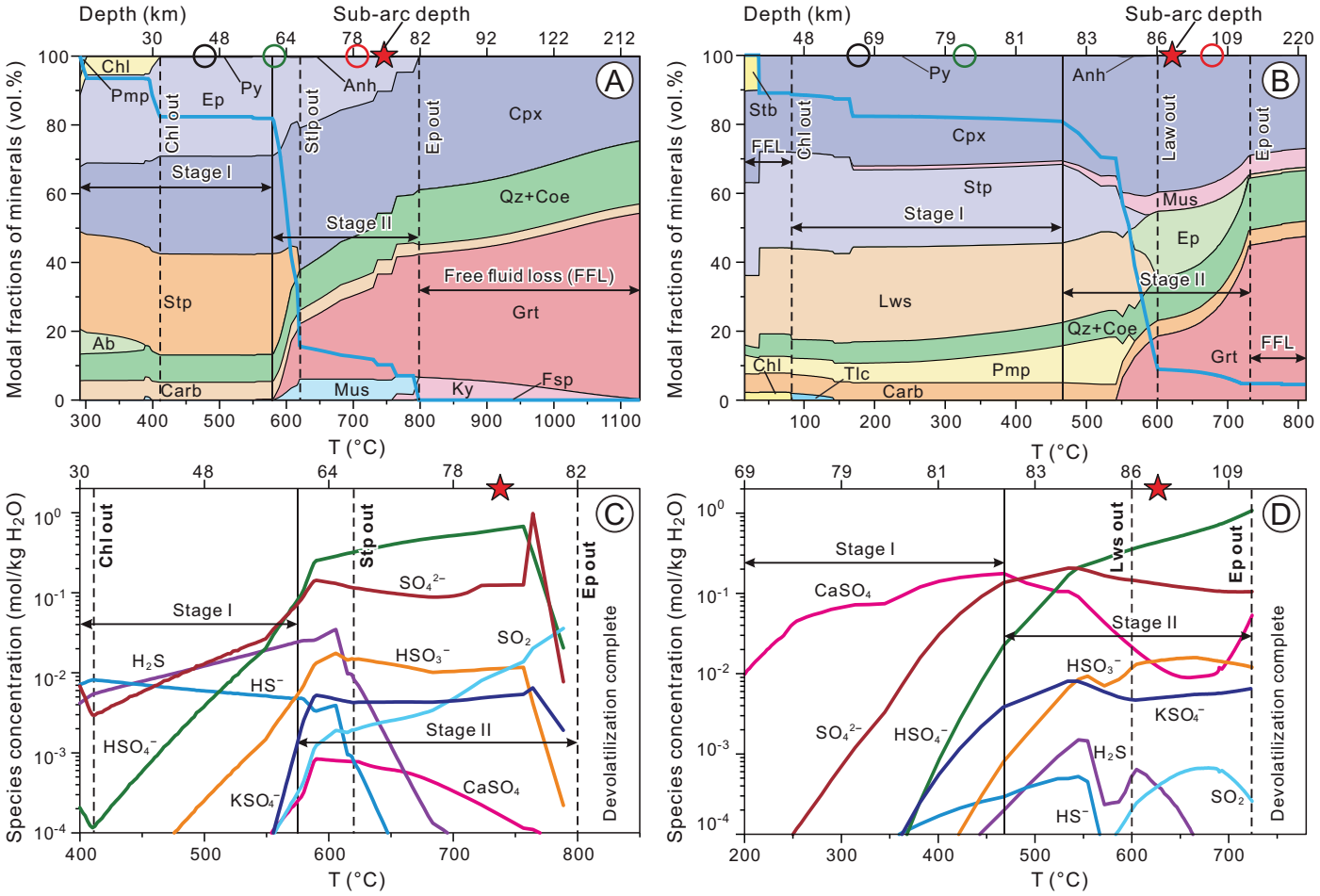
Figure 1. Mineral assemblages and dominant sulfur species in the devolatilization fluid for an average AOC along the hot (central Cascadia) and cold (central Honshu) subduction pressure-temperature (P-T) paths. (**A** and **B**) Proportions (vol.%) of main minerals along the hot (**A**) and cold (**B**) subduction geotherms. (**C** and **D**) Molality (mol/kg H_2O) of dominant sulfur aqueous species along the hot (**C**) and cold (**D**) P-T paths. Temperature and corresponding slab depth are both plotted along the x-axis. The vertical black dash lines mark the complete breakdown of the dominant hydrous phases. Blue curves in (**A**) and (**B**) show the percentage of H_2O in solid hydrous phases. Red stars show the boundary depth between lithosphere and asthenosphere beneath the volcanic arc of a hot and cold subduction zone. Slab subduction P-T paths are from ref. (62). The black, green and red open circles in (**A**) and (**B**) mark the extraction depths of fluids selected to compute the mantle infiltration model (see Materials and Methods). The S_3^- ion is not shown in panels **C** and **D** because of its concentrations < 10^{-4} mol/kg H_2O, due to too oxidizing conditions of the slab devolatilization fluid. Mineral abbreviations: Ab–albite, Anh–anhydrite, Carb–carbonate, Chl–chlorite, Coe–coesite, Cpx–clinopyroxene, Ep–epidote, Grt–garnet, Ky–kyanite, Lws–lawsonite, Mus–muscovite, Fsp–feldspar, Pmp–pumpellyite, Py–pyrite, Qz–quartz, Stb–stilbite, Stp–stilpnomelane, Tlc–talc.

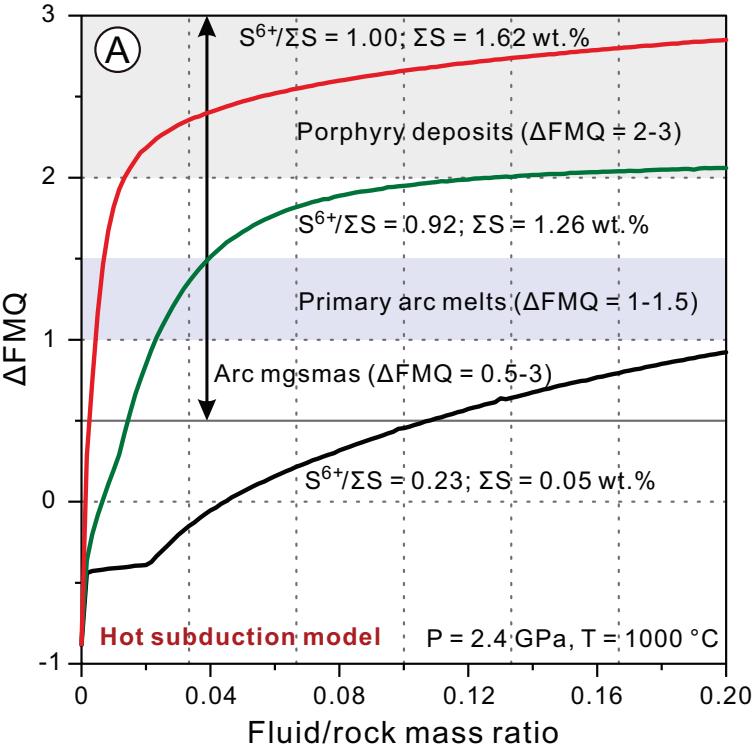
Figure 2. Mantle wedge oxidation models showing the oxidation capacity of slab devolatilization fluids. (**A** and **B**) The capacity of aqueous fluid containing different S^{6+} concentrations to oxidize the mantle wedge at near wet-solidus conditions is computed for a hot (1000 °C, 2.4 GPa) and a cold (1000 °C, 3.3 GPa) subduction geotherm. (**C** and **D**) Variation of oxygen fugacity (color coded) and stable mineral assemblages for T = 700–1100 °C and P = 2.4 and 3.3 GPa, computed by mixing depleted mantle peridotite and fluid released at sub-arc depth at different fluid/rock mass ratios (non-linear scale, see Materials and Methods). Horizontal blue-shaded region in (**A**) and (**B**) indicates the minimum range of oxygen fugacity of primitive arc melts (16, 75). The oxygen fugacity of typical porphyry deposits (76) is indicated by gray-shaded field in (**A**) and (**B**). Vertical lines with double-head arrows encompass the range of fO_2 values recorded in arc magmas (76). Mineral abbreviations: Amp–amphibole, Anh–anhydrite, Bt–biotite, Chl–Chlorite, Cpx–clinopyroxene, Dol–dolomite, F–fluid, Grt–garnet, Mgs–magnesite, Ol–olivine, Opx–orthopyroxene, Pyh–pyrrhotite, Py–pyrite.

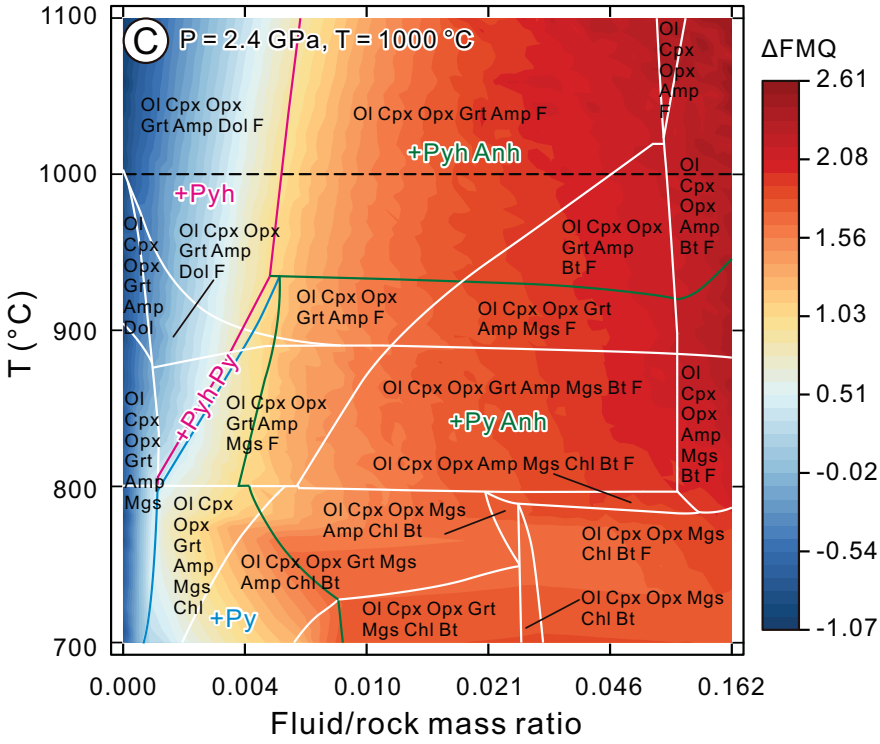
Figure 3. Distribution of S_3^- ion and indicated gold aqueous species in slab-derived fluid upon reaction with mantle peridotite. (**A** and **B**) Orange and blue contour maps show molality of S_3^- computed for the hot and cold subduction model, respectively. Color curves outline the phase boundaries of S-bearing minerals as a function of fluid/rock ratio (non-linear scale, see Materials and Methods). Gray contours state for the weight percent (wt.%) of fluid in the fluid-rock system. The color bar on the right of each panel shows the concentrations of S_3^-. (**C**) Variations of gold aqueous species concentrations as a function of oxygen fugacity at pH ~5 as buffered by the olivine-pyroxene-garnet mantle rock assemblage at a fluid/rock mass ratio of 0.1. The vertical dashed lines show the $\log_{10}(fO_2)$ values of the fayalite-magnetite-quartz (FMQ), pyrite-pyrrhotite-magnetite (PPM) and hematite-magnetite (HM) conventional redox buffers. The oxygen fugacity of metasomatized mantle (from FMQ to ΔFMQ+2) is marked by vertical blue-shaded region (11). (**D**) The effects of total dissolved sulfur concentration on the equilibrium distribution of gold aqueous species calculated for subducted slab-derived metamorphic fluid at pH of 5 and fO_2 of the H_2S-SO_2 equilibrium (corresponding to ΔFMQ+1.5). The horizontal lines with double-head arrows and vertical blue-shaded region display the sulfur contents of aqueous fluid as constrained by experiments from ref. (68).

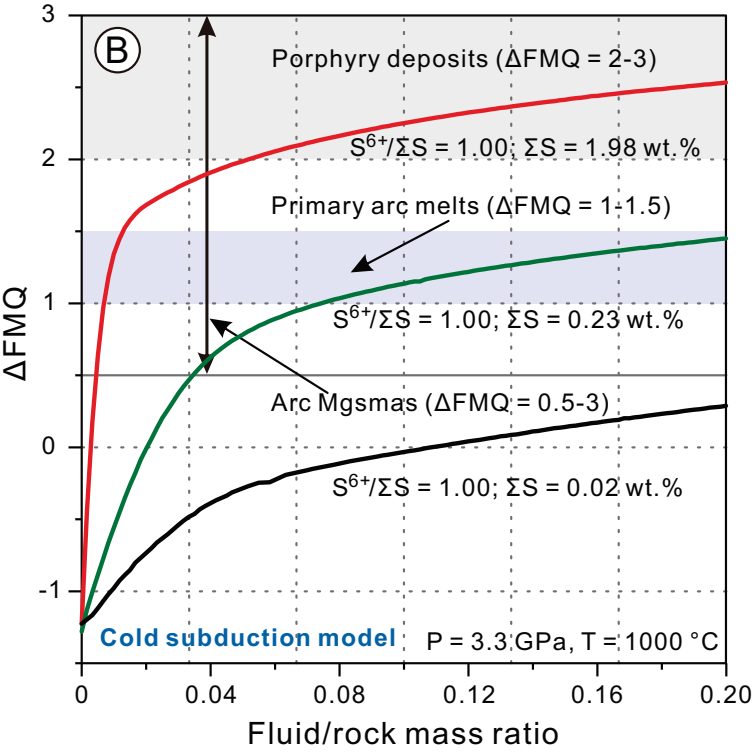
Figure 4. Estimated total Au contents in fluid and silicate melt during hydrous mantle melting at different redox conditions. (**A** and **B**) Fractions of total Au in the fluid and melt as a function of degree of melting (F) and at different aqueous fluid contents at low-temperature melting in the stability field of MSS at redox conditions of ΔFMQ-1.0 and ΔFMQ+1.5. (**C** and **D**) Total gold fractions released into both the fluid and silicate melt (C) as a function of F value and for high-temperature partial melting in the presence of sulfide liquid at ΔFMQ-1.0 (C) and ΔFMQ+1.5 (D). The vertical, blue-shaded region defines a low-degree melting range, typically of 5% for lamprophyre. Fluid proportions indicated in all panels represent the assumed fraction of the free aqueous fluid of the system. The Au content released into the fluid and melt is simulated by mass balance and using experimentally available Au partition coefficients (see Materials and Methods).

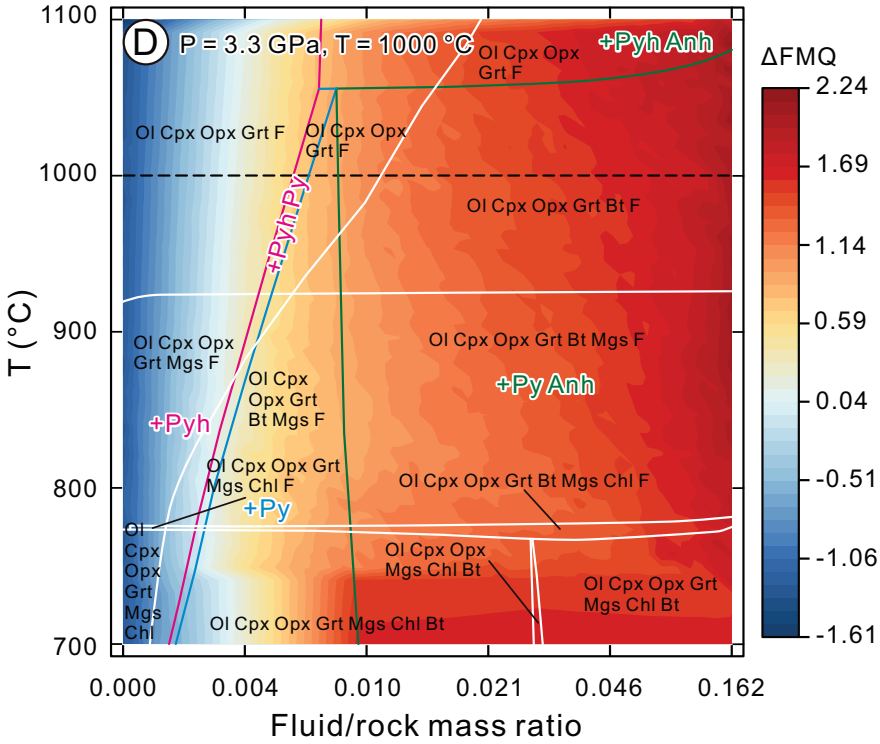
Figure 5. Proposed scenarios for progressive devolatilization and redox processes at slab-mantle interface. (**A**) Schematic profile of a subduction zone with associated metamorphic devolatilization and magmatism (modified from (77) and (78)) showing the redox conditions and mobilization and concentration of sulfur and gold during mantle metasomatism as derived in this study. The white stars mark the slab depths of fore-arc and sub-arc settings. (**B**) Schematic representation of a slab-derived fluid oxidizing overlying mantle wedge and concentrating sulfur and gold. The fluid liberated from AOC carries abundant S^{6+} into the mantle wedge to oxidize Fe^{2+} in silicate minerals, thereby modifying the mantle oxidation state and leading to gold enrichment in the fluid due to reduction of S^{6+} to S_3^- and H_2S/HS^- ligands that strongly complex gold. Mineral abbreviations: Px–pyroxene; Grt–garnet; Ol–olivine.

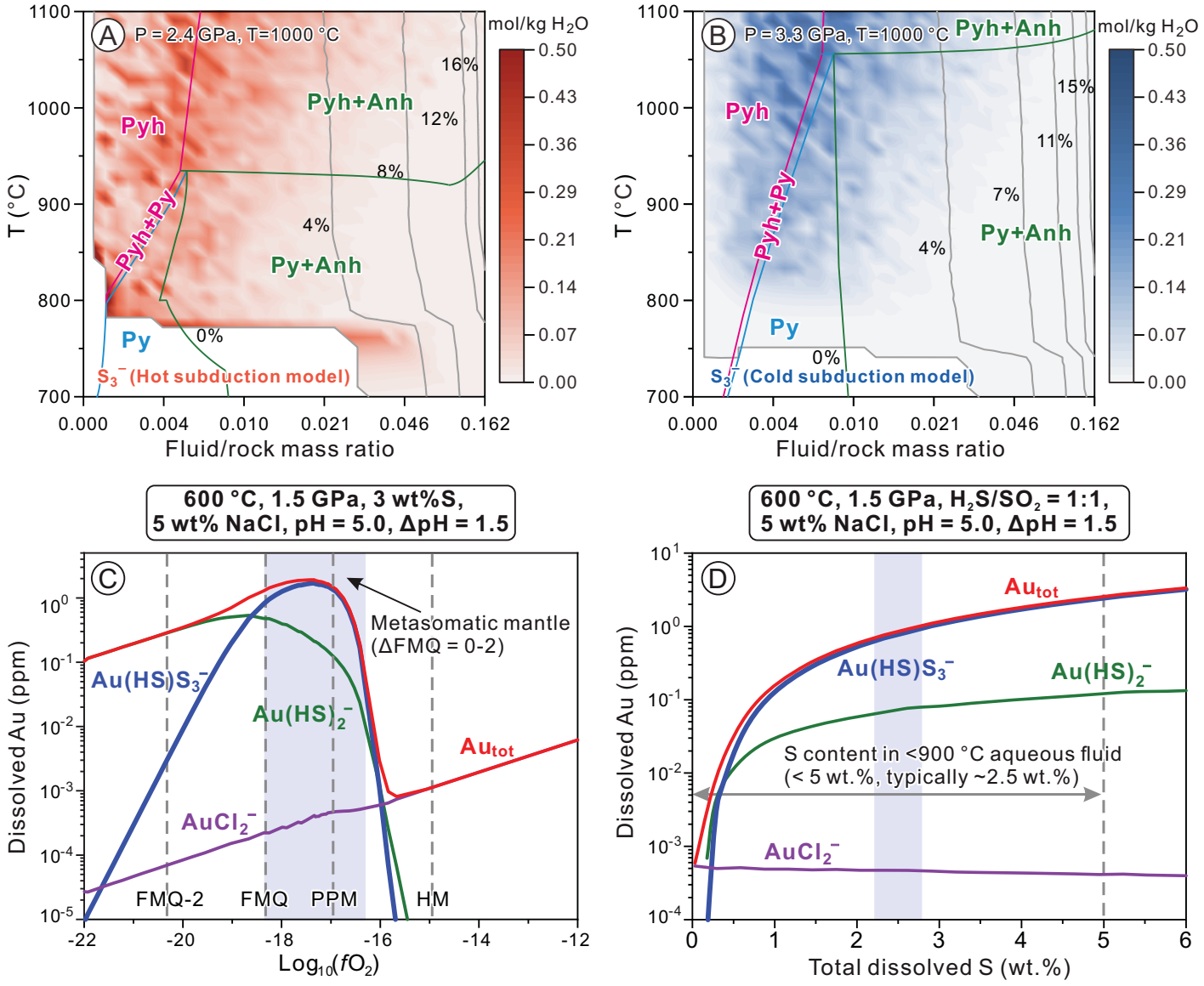

Depth (km)
Sub-arc depth
Modal fractions of minerals (vol.%)
T (°C)
A
Chl
Pmp
Py
Ep
Anh
Cpx
Chl out
Stp out
Ep out
Stage I
Stage II
Qz+Coe
Free fluid loss (FFL)
Grt
Stp
Ab
Carb
Mus
Ky
Fsp
B
Stb
FFL
Lws out
Lws
Tlc
Species concentration (mol/kg H2O)
C
D
Devolatilization complete
SO4 2−
HSO4−
H2S
HS−
SO2
HSO3−
KSO4−
CaSO4

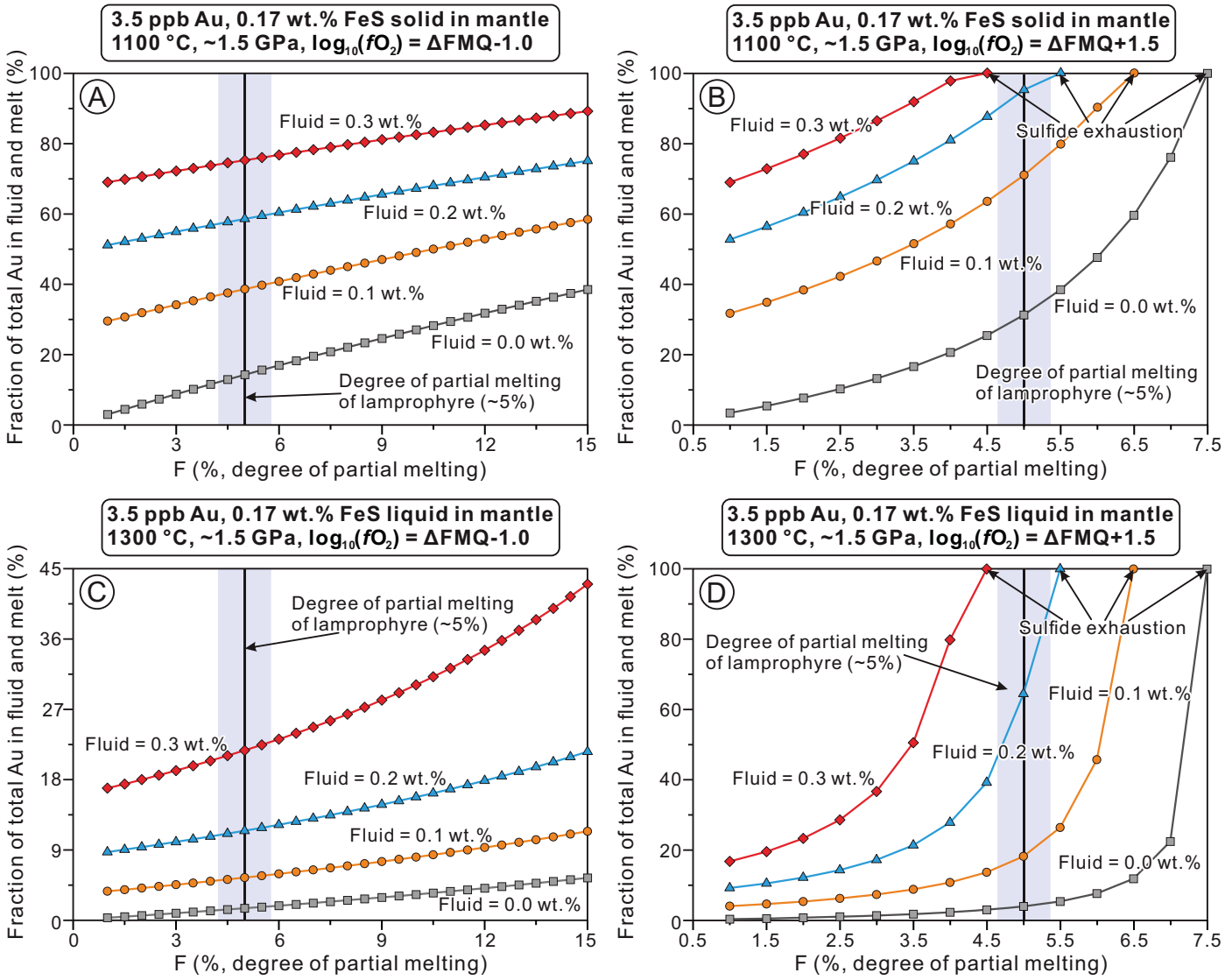

A
S6+/ΣS = 1.00; ΣS = 1.62 wt.%
Porphyry deposits (ΔFMQ = 2-3)
S6+/ΣS = 0.92; ΣS = 1.26 wt.%
Primary arc melts (ΔFMQ = 1-1.5)
Arc mgsmas (ΔFMQ = 0.5-3)
S6+/ΣS = 0.23; ΣS = 0.05 wt.%
Hot subduction model
P = 2.4 GPa, T = 1000 °C
ΔFMQ
Fluid/rock mass ratio

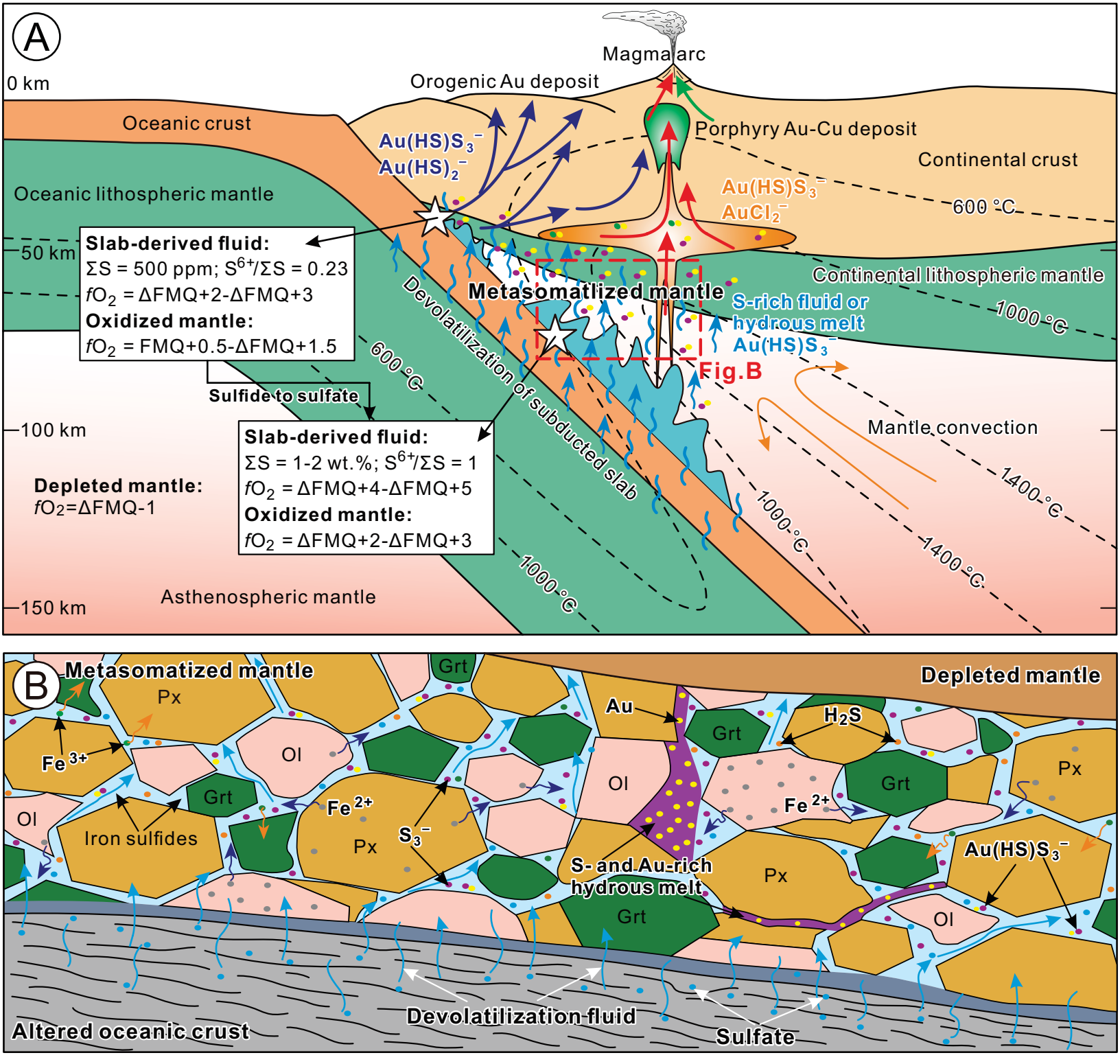

C
P = 2.4 GPa, T = 1000 °C
Ol Cpx Opx Grt Amp Dol F
Ol Cpx Opx Grt Amp F
Ol Cpx Opx Amp F
+Pyh Anh
+Pyh
Ol Cpx Opx Grt Amp Dol F
Ol Cpx Opx Grt Amp Bt F
Ol Cpx Opx Grt Amp Dol
Ol Cpx Opx Grt Amp F
Ol Cpx Opx Grt Amp Mgs F
Ol Cpx Opx Amp Bt F
+Pyh-Py
Ol Cpx Opx Grt Amp Mgs Bt F
Ol Cpx Opx Grt Amp Mgs F
+Py Anh
Ol Cpx Opx Amp Mgs Chl Bt F
Ol Cpx Opx Amp Mgs Bt F
Ol Cpx Opx Grt Amp Mgs Chl
Ol Cpx Opx Mgs Amp Chl Bt
Ol Cpx Opx Mgs Chl Bt F
Ol Cpx Opx Grt Mgs Amp Chl Bt
+Py
Ol Cpx Opx Grt Mgs Chl Bt
Ol Cpx Opx Mgs Chl Bt
ΔFMQ
T (°C)
Fluid/rock mass ratio


B
Porphyry deposits (ΔFMQ = 2-3)
S6+/ΣS = 1.00; ΣS = 1.98 wt.%
Primary arc melts (ΔFMQ = 1-1.5)
S6+/ΣS = 1.00; ΣS = 0.23 wt.%
Arc Mgsmas (ΔFMQ = 0.5-3)
S6+/ΣS = 1.00; ΣS = 0.02 wt.%
Cold subduction model
P = 3.3 GPa, T = 1000 °C
ΔFMQ
Fluid/rock mass ratio


D
P = 3.3 GPa, T = 1000 °C
Ol Cpx Opx Grt F
+Pyh Anh
Ol Cpx Opx Grt F
Ol Cpx Opx Grt F
+Pyh-Py
Ol Cpx Opx Grt Bt F
Ol Cpx Opx Grt Mgs F
Ol Cpx Opx Grt Bt Mgs F
+Py Anh
Ol Cpx Opx Grt Bt Mgs
+Pyh
Ol Cpx Opx Grt Mgs Chl F
Ol Cpx Opx Grt Bt Mgs Chl F
+Py
Ol Cpx Opx Grt Mgs Chl
Ol Cpx Opx Mgs Chl Bt
Ol Cpx Opx Grt Mgs Chl Bt
Ol Cpx Opx Grt Mgs Chl Bt
ΔFMQ
T (°C)
Fluid/rock mass ratio


A
P = 2.4 GPa, T=1000 °C
Pyh
Pyh+Anh
Pyh+Py
Py+Anh
Py
16%
12%
8%
4%
0%
S3− (Hot subduction model)
mol/kg H2O
0.50
0.43
0.36
0.29
0.21
0.14
0.07
0.00
T (°C)
1100
1000
900
800
700
0.000
0.004
0.010
0.021
0.046
0.162
Fluid/rock mass ratio
B
P = 3.3 GPa, T=1000 °C
Pyh+Anh
Pyh
Pyh+Py
Py+Anh
Py
15%
11%
7%
4%
0%
S3− (Cold subduction model)
600 °C, 1.5 GPa, 3 wt%S,
5 wt% NaCl, pH = 5.0, ΔpH = 1.5
C
Metasomatic mantle
(ΔFMQ = 0-2)
Au(HS)S3−
Au(HS)2−
Autot
AuCl2−
FMQ-2
FMQ
PPM
HM
Dissolved Au (ppm)
Log10(fO2)
600 °C, 1.5 GPa, H2S/SO2 = 1:1,
5 wt% NaCl, pH = 5.0, ΔpH = 1.5
D
Autot
Au(HS)S3−
Au(HS)2−
S content in <900 °C aqueous fluid
(< 5 wt.%, typically ~2.5 wt.%)
AuCl2−
Total dissolved S (wt.%)


3.5 ppb Au, 0.17 wt.% FeS solid in mantle
1100 °C, ~1.5 GPa, log10(fO2) = ΔFMQ-1.0
A
Fluid = 0.3 wt.%
Fluid = 0.2 wt.%
Fluid = 0.1 wt.%
Fluid = 0.0 wt.%
Degree of partial melting of lamprophyre (~5%)
Fraction of total Au in fluid and melt (%)
F (%, degree of partial melting)
3.5 ppb Au, 0.17 wt.% FeS solid in mantle
1100 °C, ~1.5 GPa, log10(fO2) = ΔFMQ+1.5
B
Fluid = 0.3 wt.%
Sulfide exhaustion
Fluid = 0.2 wt.%
Fluid = 0.1 wt.%
Fluid = 0.0 wt.%
Degree of partial melting of lamprophyre (~5%)
Fraction of total Au in fluid and melt (%)
F (%, degree of partial melting)
3.5 ppb Au, 0.17 wt.% FeS liquid in mantle
1300 °C, ~1.5 GPa, log10(fO2) = ΔFMQ-1.0
C
Degree of partial melting of lamprophyre (~5%)
Fluid = 0.3 wt.%
Fluid = 0.2 wt.%
Fluid = 0.1 wt.%
Fluid = 0.0 wt.%
Fraction of total Au in fluid and melt (%)
F (%, degree of partial melting)
3.5 ppb Au, 0.17 wt.% FeS liquid in mantle
1300 °C, ~1.5 GPa, log10(fO2) = ΔFMQ+1.5
D
Sulfide exhaustion
Degree of partial melting of lamprophyre (~5%)
Fluid = 0.1 wt.%
Fluid = 0.2 wt.%
Fluid = 0.3 wt.%
Fluid = 0.0 wt.%
Fraction of total Au in fluid and melt (%)
F (%, degree of partial melting)


A
0 km
Magma arc
Orogenic Au deposit
Oceanic crust
Porphyry Au-Cu deposit
Continental crust
Au(HS)S3−
Au(HS)2−
Oceanic lithospheric mantle
Au(HS)S3−
AuCl2−
600 °C
50 km
Slab-derived fluid:
ΣS = 500 ppm; S6+/ΣS = 0.23
fO2 = ΔFMQ+2-ΔFMQ+3
Oxidized mantle:
fO2 = FMQ+0.5-ΔFMQ+1.5
Metasomatlized mantle
Continental lithospheric mantle
S-rich fluid or
hydrous melt
Au(HS)S3−
1000 °C
Devolatilization of subducted slab
600 °C
Fig.B
Sulfide to sulfate
Mantle convection
100 km
Slab-derived fluid:
ΣS = 1-2 wt.%; S6+/ΣS = 1
fO2 = ΔFMQ+4-ΔFMQ+5
Oxidized mantle:
fO2 = ΔFMQ+2-ΔFMQ+3
1400 °C
Depleted mantle:
fO2=ΔFMQ-1
1000 °C
1400 °C
1000 °C
Asthenospheric mantle
150 km
B
Metasomatized mantle
Px
Grt
Depleted mantle
Au
H2S
Fe3+
Ol
Grt
Ol
Fe2+
Grt
Px
Ol
Iron sulfides
Grt
Fe2+
S3−
Px
Au(HS)S3−
S- and Au-rich
hydrous melt
Px
Grt
Ol
Devolatilization fluid
Sulfate
Altered oceanic crust