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# An essential role for sulfur in sulfide-silicate melt partitioning of gold and magmatic gold transport at subduction settings

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ABSTRACT

Sulfide-silicate melt partitioning controls the behavior of gold in magmas, which is critical for understanding the Earth's deep gold cycle and formation of gold deposits. However, the mechanisms that control the sulfide-silicate melt partitioning of gold remain largely unknown. Here we present constraints from laboratory experiments on the partition coefficient of gold between monosulfide-solid-solution (MSS) and silicate melt ($D_{Au}^{MSS/SM}$) under conditions relevant for magmatism at subduction settings. Thirty-five experiments were performed in Au capsules to determine $D_{Au}^{MSS/SM}$ at 950-1050 °C, 0.5-3 GPa, oxygen fugacity ($fO_2$) of ~FMQ-1.7 to FMQ+2.7 (FMQ refers to the fayalite-magnetite-quartz buffer), and sulfur fugacity ($fS_2$) of −2.2 to 2.1, using a piston cylinder apparatus. The silicate melt composition changes from dry to hydrous andesite to rhyolite. The results obtained from electron microprobe and laser-ablation ICP-MS analyses show that the gold solubility in silicate melts ranges from 0.01 to 55.3 ppm and is strongly correlated with the melt sulfur content $[S]_{melt}$ at $fO_2$ of ~FMQ-1.7 to FMQ+1.6, which can be explained by the formation of complex Au-S species in the silicate melts. The gold solubility in MSS ranges from 130 to 2800 ppm, which is mainly controlled by $fS_2$. $D_{Au}^{MSS/SM}$ ranges from 10 to 14000 at $fO_2$ of ~FMQ-1.7 to FMQ+1.6, the large variation of which can be fully explained by combined $[S]_{melt}$ and $fS_2$. Therefore, all of the parameters that can directly affect $[S]_{melt}$ and $fS_2$, such as alkali metals, water, FeO, and $fO_2$, can indirectly affect $D_{Au}^{MSS/SM}$. The mechanisms that control the sulfide-silicate melt partitioning of gold and the other chalcophile elements, such as Ni, Re, and Mo, differ significantly. This is because gold is dissolved mainly as Au-S species in the silicate melts, while the other chalcophile elements are dissolved mainly as metal oxides in the silicate melts. Applying the correlation between $D_{Au}^{MSS/SM}$ and $[S]_{melt}$ to slab melting and arc magmatic differentiation under different redox conditions, we find that ancient to modern slab melts carry negligible to less than 25% of the slab gold to the subarc mantle; however, gold-enrichment can occur in MSS-saturated arc magmas that have differentiated under moderately oxidized conditions with $fO_2$ between FMQ and FMQ+1.6, in particular if the magmatic crystallization follows a fractional crystallization model. We conclude that moderately oxidized magmas with high contents of alkali metals, sulfur, and water, owing to their low $D_{Au}^{MSS/SM}$ and efficient magma-to-fluid transfer of gold and sulfur, have a high potential to form gold deposits.

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## 1. Introduction

Understanding the factors that control the behavior of gold (Au) in magmas is of fundamental importance in understanding magmatic Au transport, Au mineralization, and the exploration of Au deposits in Earth's crust (Botcharnikov et al., 2011; Jégo et al., 2010; Muntean et al., 2011; Tassara et al., 2017; Zajacz et al., 2013; Zajacz et al., 2010). The behavior of Au as a chalcophile element is controlled by sulfides, and Au-rich magmas form readily when sulfides are absent during magmatic genesis and/or differentiation (Mungall, 2002; Sillitoe, 1997). However, sulfides are

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ubiquitous in mantle rocks (Alard et al., 2011), subduction zone rocks (Aulbach et al., 2012; Evans et al., 2014), and arc magmatic rocks (Lee et al., 2012; Parat et al., 2011; Wallace and Edmonds, 2011). Depending on the temperature, pressure, and composition, these sulfides can be crystalline monosulfide-solid-solution (MSS) and/or sulfide liquid (Bockrath et al., 2004; Jenner, 2017; Li and Audétat, 2012). Recent studies have demonstrated that the main sulfide phase fractionated during arc magmatic differentiation is MSS, which causes the depletion of Cu in variously evolved arc magmas and the continental crust (Jenner, 2017; Lee et al., 2012; Li and Audétat, 2013; Wang et al., 2018). The enrichment of Au in magmas is a key ingredient in the production of giant Au deposits and districts (Mungall, 2002; Muntean et al., 2011; Sillitoe, 1997; Tassara et al., 2017), so it is of great interest to investigate whether Au-enrichment can form in the differentiating arc magmas that are saturated with MSS. On the other hand, geochemical studies and experimental simulations suggest that the subducting slab contributes sulfur via slab melts or fluids to the subarc mantle (Jégo and Dasgupta, 2013, 2014; Wallace, 2005), although most of the sulfur in the subducting slab enters the deep mantle (Evans, 2012; Jégo and Dasgupta, 2013). However, the capability of such S-bearing slab melts or fluids in transporting slab chalcophile elements, in general, and Au, in particular, to the subarc mantle has received little attention (Canil and Fellows, 2017). The fate of Au during slab melting is essentially linked to the long-term deep Au cycle, as extensive melting of altered oceanic crust and/or sediments occurs in both ancient and modern subduction zones (Martin and Moyen, 2002; Spencer et al., 2017).

Investigating the behavior of Au in sulfide-saturated magmas requires knowledge of the sulfide-silicate melt partitioning for Au. Most recent studies show that the sulfide liquid-silicate melt partition coefficient of Au ($D_{Au}^{SL/SM}$) varies from ~1000 to 30000 under conditions of 1000-1250 °C, 1 bar to 2.5 GPa, and $fO_2$ of FMQ-3 to FMQ+1 (Botcharnikov et al., 2013; Li and Audétat, 2013). Whereas, the MSS-silicate melt partition coefficient of Au ($D_{Au}^{MSS/SM}$) is lower, varying from ~40 to 3000 under conditions of 800-1250 °C, 1 bar to 2.5 GPa, and $fO_2$ of FMQ-3 to FMQ+1 (Botcharnikov et al., 2011; Li and Audétat, 2013, 2015; Zajacz et al., 2013). Assuming a typical chalcophile element M dissolves in the silicate melt as metal oxides (Kiseeva and Wood, 2013, 2015), the sulfide-silicate melt partitioning of the element M can be described as:

$$\log D_M^{Sulf/SM} = A + \frac{x}{2}\log[FeO] \quad (1)$$

in which A is a constant; $x$ is a constant related to valence state of the element M; and [FeO] is the FeO content in the silicate melt in wt.%. In case the valence state of the element M varies with $fO_2$, $\log D_M^{Sulf/SM}$ can be described by including an $fO_2$-term in Eq. (1) (Feng and Li, 2019; Li and Audétat, 2015):

$$\log D_M^{Sulf/SM} = A + B\Delta FMQ + \frac{x}{2}\log[FeO] \quad (2)$$

in which B is a coefficient for ΔFMQ, and ΔFMQ refers to $fO_2$ relative to the FMQ (fayalite-magnetite-quartz) buffer. The relationships between $D_M^{Sulf/SM}$, the melt FeO content, and $fO_2$, as summarized by Eqs. (1) and (2), have been successfully tested on a large number (>15) of chalcophile elements and have proved to be valid for a broad range of temperatures and sulfide and silicate melt compositions (Feng and Li, 2019; Kiseeva and Wood, 2013, 2015; Li and Audétat, 2015). However, as shown in Fig. S1, the models of Eqs. (1) and (2) are not followed by Au, although Li and Audétat (2015) and Zajacz et al. (2013) observed an increase from 6000 to 30000 for $D_{Au}^{SL/SM}$ and 180 to 2900 for $D_{Au}^{MSS/SM}$, respectively, when the silicate melt varies from basalt to rhyolite at fixed $fO_2$. Fitting all of the $D_{Au}^{MSS/SM}$ data compiled in Fig. S1 into Eqs. (1) and (2) yielded $R^2$ of 0.16 and 0.11, respectively, which suggests that neither the model of Eq. (1) nor (2) can interpret the MSS-silicate melt partitioning of Au. Therefore, the mechanism that controls the sulfide-silicate melt partitioning of Au and the other chalcophile elements could differ significantly.

The solubility of Au in S-free silicate melts, dissolved mainly as $Au^+$ oxide, is rather low (<1 ppm) under mantle-crust conditions (Botcharnikov et al., 2011; Jégo and Pichavant, 2012; Jégo et al., 2010; Li and Audétat, 2013; Zajacz et al., 2013). Several recent studies, however, show the enhancement of Au solubility by sulfide ($S^{2-}$) via the formation of Au-sulfide species in the silicate melts at 800-1200 °C and 0.2-1.5 GPa (Botcharnikov et al., 2011; Jégo et al., 2016; Jégo and Pichavant, 2012; Jégo et al., 2010; Li and Audétat, 2013; Zajacz et al., 2013; Zajacz et al., 2012). The sulfur in the silicate melts may thus play an important role in controlling the sulfide-silicate melt partitioning of Au. However, the actual role played by sulfur and the role played by other parameters that potentially affect $D_{Au}^{SL/SM}$ or $D_{Au}^{MSS/SM}$ have never been investigated. In this study, we investigate systematically the MSS-silicate melt partitioning of Au by measuring the solubility of Au in coexisting MSS and silicate melt under conditions relevant for slab melting and arc magmatic differentiation. We find that $D_{Au}^{MSS/SM}$ varies by more than three orders of magnitudes and the variation is strongly controlled by sulfur fugacity ($fS_2$) and the melt sulfur content over an $fO_2$ range of ~FMQ-1.7 to FMQ+1.6. These new findings place tight constraints on the deep Au cycle and the potential of arc magmas in forming Au deposits at subduction settings.

## 2. Experimental methods

### 2.1. Starting materials

The starting materials included synthetic and natural silicate glasses and rocks, synthetic Ni-Cu-bearing sulfide, natural magnetite, distilled water, reagent-grade $CaSO_4$ (anhydrite), FeS (pyrrhotite) and graphite powder. The dacitic glass was synthesized from analytical grade oxides (MgO, FeO, MnO, NiO, $SiO_2$, $TiO_2$, $Al_2O_3$, $Cr_2O_3$, and $P_2O_5$) and carbonates ($Na_2CO_3$, $K_2CO_3$, and $CaCO_3$). The natural silicate rocks included partly glassy andesite and glassy rhyolite. The major element compositions of all of the used silicate glasses/rocks are given in Table S1. The Ni-Cu-bearing sulfide was synthesized at 1200 °C in an evacuated $SiO_2$ glass ampoule using the method described in Li and Audétat (2012); its major element composition is given in Table S1. All of the starting silicates and sulfides were powdered to ensure homogeneity before loading into sample capsules.

### 2.2. Sample capsules and high-pressure experiments

Thirty-five experiments were performed to study the partitioning of Au in sulfide ± sulfate and silicate melt systems under conditions relevant for slab melting and arc magmatic differentiation (Table 1). A first set of four experiments was performed at 950-1040 °C and 1-3 GPa, with andesitic silicate and ~15 wt.% Cu-Ni-bearing sulfide contained in Au capsules. In each Au capsule, ~5 wt.% distilled water was added to generate hydrous silicate melt. For this set of experiments, the $fO_2$ was not buffered by any $fO_2$ buffer, and the run duration ranged from 48 to 312 hours.

A second set of thirteen experiments was performed at 1040 °C and 0.5-3 GPa, with dacitic silicate and ~15 wt.% Cu-Ni-bearing sulfide or FeS (pyrrhotite) contained in Au capsules. In each Au capsule, ~0-10 wt.% distilled water was added. In addition, ~2-15 wt.% anhydrite was added in the Au capsules of runs Sulf-3, Sulf-5, Da-2A, and Da-1B to obtain a high $fO_2$. Available studies show that the $fO_2$ for the coexistence of sulfide and anhydrite in natural

**Table 1**
Overview of experimental conditions and run products.

| Run No. | T (°C) | P (GPa) | Duration (h) | Capsule | Starting material | Main run products | $S^{6+}/S_{tot}$ | [a] $\log fO_2$ (ΔFMQ) | [b] $\log fS_2$ | S in SM (ppm) | Au in SM (ppm) | Au in MSS (ppm) | $D_{Au}^{MSS/SM}$ | Melt NBO/T |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Set-1 Experiments** | | | | | | | | | | | | | | |
| A-1 | 950 | 2 | 96 | Au | Ande+Sulf+$H_2O$ | MSS+SM+Cpx+Grt | −0.05 ± 0.00 | n.d. | −0.39 | 401 ± 167 | 0.4 ± 0.1 | 134 ± 8 | 386 ± 160 | 0.093 |
| A-2 | 950 | 1 | 192 | Au | Ande+Sulf+$H_2O$ | MSS+SM+Cpx+Mag | 0.60 ± 0.25 | 1.47 ± 0.47 | 1.11 | 976 ± 88 | 1.6 ± 0.6 | 697 ± 46 | 436 ± 166 | 0.088 |
| A-4 | 975 | 3 | 312 | Au | Ande+Sulf+$H_2O$ | MSS+SM+Cpx+Grt | n.d. | n.d. | 0.86 | 248 ± 45 | 0.3 ± 0.0 | 359 ± 68 | 1237 ± 300 | 0.044 |
| A-6 | 1040 | 2 | 48 | Au | Ande+Sulf+$H_2O$ | MSS+SM+Cpx+Grt+Mag | n.d. | n.d. | 1.18 | 1040 ± 267 | 1.5 ± 0.1 | 453 ± 30 | 309 ± 31 | 0.225 |
| **Set-2 Experiments** | | | | | | | | | | | | | | |
| Sulf-1 | 1040 | 0.6 | 144 | Au | Daci+Sulf+$H_2O$ | MSS+SM+Mag | 0.68 ± 0.22 | 1.63 ± 0.42 | 0.48 | 1182 ± 169 | 11.0 ± 0.4 | 888 ± 120 | 81 ± 11 | 0.196 |
| Sulf-2 | 1040 | 0.6 | 168 | Au | Daci+Sulf+$H_2O$ | MSS+SM | 0.53 ± 0.28 | 1.34 ± 0.56 | 0.92 | 659 ± 84 | 4.7 ± 0.5 | 750 ± 82 | 160 ± 24 | 0.175 |
| Sulf-3 | 1040 | 0.6 | 144 | Au | Daci+Sulf+$H_2O$ +Anhy | MSS+SM+Mag | 0.56 ± 0.21 | 1.39 ± 0.39 | 0.92 | 1121 ± 124 | 5.2 ± 1.0 | 801 ± 215 | 154 ± 51 | 0.111 |
| Sulf-4 | 1040 | 2.0 | 168 | Au | Daci+Sulf+$H_2O$ | MSS+SM+Cpx+Grt | n.d. | n.d. | 0.48 | 243 ± 21 | 0.2 ± 0.1 | 459 ± 42 | 2691 ± 885 | 0.087 |
| Sulf-6 | 1040 | 3.0 | 96 | Au | Daci+Sulf+$H_2O$ | MSS+SM+Cpx+Grt | 0.52 ± 0.27 | 1.32 ± 0.54 | 2.08 | 637 ± 21 | 1.0 ± 0.3 | 1083 ± 94 | 1081 ± 334 | 0.076 |
| Da-2B | 1040 | 2 | 48 | Au | Daci+FeS+$H_2O$ | MSS+SM+Cpx+Grt | 0.32 ± 0.06 | 0.94 ± 0.13 | 1.18 | 358 ± 45 | 0.63 ± 0.03 | 1599 ± 125 | 2531 ± 222 | 0.125 |
| Da-1C | 1040 | 0.5 | 48 | Au | Daci+FeS | MSS+SM+Cpx | n.d. | n.d. | 0.06 | 148 ± 40 | 0.19 ± 0.08 | 482 ± 114 | 2503 ± 1230 | 0.082 |
| Da-1A | 1040 | 0.5 | 48 | Au | Daci+FeS+Graph | MSS+SM+Graph+Cpx | n.d. | −1.67 | 0.12 | 165 ± 76 | 0.44 ± 0.25 | 911 ± 84 | 2069 ± 1207 | 0.075 |
| Da-3A | 1040 | 0.5 | 35 | Au | Daci+FeS+$H_2O$ | MSS+SM+Cpx | 0.56 ± 0.11 | 1.39 ± 0.39 | −1.07 | 550 ± 141 | cont. | 556 ± 19 | n.d. | 0.212 |
| Da-3B | 1040 | 0.5 | 35 | Au | Daci+FeS+Graph+$H_2O$ | MSS+SM+Graph+Cpx | n.d. | −1.67 | −0.87 | 196 ± 88 | cont. | 226 ± 47 | n.d. | 0.199 |
| Sulf-5 | 1040 | 2.0 | 120 | Au | Daci+Sulf+$H_2O$ +Anhy | MSS+SM+Cpx+Anhy | 0.75 ± 0.10 | 1.79 ± 0.22 | 1.82 | 1674 ± 76 | 2.0 ± 0.7 | 1422 ± 149 | 722 ± 252 | 0.165 |
| Da-2A | 1040 | 2 | 48 | Au | Daci+FeS+Anhy+$H_2O$ | MSS+SM+Cpx+Anhy | 0.96 ± 0.04 | 2.74 ± 0.34 | 1.48 | 5536 ± 376 | 2.73 ± 0.08 | 2181 ± 534 | 799 ± 197 | 0.273 |
| Da-1B | 1040 | 0.5 | 48 | Au | Daci+FeS+Anhy | MSS+SM+Anhy | 0.75 ± 0.00 | 1.79 ± 0.00 | 1.27 | 1824 ± 126 | 3.28 ± 0.40 | 528 ± 177 | 161 ± 58 | 0.221 |
| Da-1D | 1040 | 0.5 | 48 | Au | Daci+Anhy | SM+Anhy+Mag | 0.84 ± 0.21 | 2.04 ± 0.51 | n.d. | 1032 ± 55 | 0.34 ± 0.05 | n.d. | n.d. | 0.135 |
| **Set-3 Experiments** | | | | | | | | | | | | | | |
| Rh-3A | 1040 | 2 | 48 | Au | Rhyo+FeS+$H_2O$ | MSS+SM | 0.33 ± 0.13 | 0.96 ± 0.31 | 1.34 | 316 ± 57 | 0.49 ± 0.03 | 1886 ± 47 | 3820 ± 259 | 0.072 |
| Rh-1C | 1040 | 0.5 | 48 | Au | Rhyo+FeS | MSS+SM | n.d. | n.d. | 0.54 | 90 ± 30 | 0.055 | 378 ± 80 | 6873 ± 1455 | 0.064 |
| Rh-1D | 1040 | 0.5 | 48 | Au | Rhyo+FeS+Graph | MSS+SM+Graph | n.d. | −1.67 | −0.57 | 50 ± 10 | 0.012 ± 0.005 | 175 ± 20 | 14194 ± 1622 | 0.056 |
| Rh-2C | 1000 | 0.5 | 48 | Au | Rhyo+FeS+Graph | MSS+SM+Graph | n.d. | −1.67 | 0.18 | 144 ± 72 | 0.12 ± 0.08 | n.d. | n.d. | 0.054 |
| Rh-4B | 1040 | 0.5 | 35 | Au | Rhyo+FeS+$H_2O$ | MSS+SM | n.d. | n.d. | −0.87 | 63 ± 36 | 0.05 ± 0.02 | 393 ± 100 | 8363 ± 3412 | 0.012 |
| Rh-4A | 1040 | 0.5 | 35 | Au | Rhyo+FeS+Graph+$H_2O$ | MSS+SM+Graph | n.d. | −1.67 | −0.75 | 67 ± 46 | 0.05 ± 0.02 | 253 ± 22 | 5554 ± 3000 | 0.014 |
| Rh-1B | 1040 | 0.5 | 48 | Au | Rhyo+FeS+Anhy | MSS+SM+Anhy | 0.61 ± 0.23 | 1.49 ± 0.43 | 1.08 | 792 ± 130 | 2.86 ± 0.24 | 2090 ± 248 | 730 ± 106 | 0.129 |
| Rh-2A | 1000 | 0.5 | 48 | Au | Rhyo+FeS+Anhy | MSS+SM+Anhy | 0.63 ± 0.17 | 1.53 ± 0.32 | 1.19 | 280 ± 32 | 0.79 ± 0.04 | 1459 ± 271 | 1856 ± 355 | 0.039 |
| Rh-3B | 1040 | 2 | 48 | Au | Rhyo+FeS+Anhy+$H_2O$ | MSS+SM+Anhy | 0.80 ± 0.05 | 1.92 ± 0.13 | 1.61 | 5107 ± 506 | 2.74 ± 0.07 | 2777 ± 282 | 1015 ± 107 | 0.140 |
| Rh-1A | 1040 | 0.5 | 48 | Au | Rhyo+Anhy | SM+Anhy | n.d. | n.d. | n.d. | 63 ± 15 | 0.10 ± 0.03 | n.d. | n.d. | 0.015 |
| Rh-2B | 1000 | 0.5 | 48 | Au | Rhyo+Anhy | SM+Anhy | n.d. | n.d. | n.d. | 48 ± 29 | cont. | n.d. | n.d. | 0.012 |
| **Set-4 Experiments** | | | | | | | | | | | | | | |
| C-9a | 1000 | 0.5 | 45 | Au | Daci+Sulf+$H_2O$+Mag+$Au_{95}Cu_{05}$ | MSS+SM | 0.34 ± 0.29 | 0.98 ± 0.60 | −2.17 | 693 ± 52 | 3.1 ± 0.2 | 220 ± 24 | 70 ± 9 | 0.302 |
| C-9b | 1000 | 0.5 | 45 | Au | Rhyo+Sulf+$H_2O$+Mag+$Au_{95}Cu_{05}$ | MSS+SM | 0.47 ± 0.22 | 1.23 ± 0.45 | −1.28 | 827 ± 21 | 3.2 ± 0.3 | 280 ± 19 | 89 ± 11 | 0.294 |
| C-10a | 1000 | 0.5 | 43 | Au | Daci+Sulf+$H_2O$+Mag+Anhy+$Au_{95}Cu_{05}$ | MSS+SM | 0.50 ± 0.17 | 1.28 ± 0.32 | −1.05 | 1511 ± 113 | 13.4 ± 0.3 | 370 ± 30 | 28 ± 2 | 0.375 |
| C-10b | 1000 | 0.5 | 43 | Au | Rhyo+Sulf+$H_2O$+Mag+Anhy+$Au_{95}Cu_{05}$ | MSS+SM | 0.20 ± 0.04 | 0.65 ± 0.12 | −1.06 | 704 ± 65 | 3.5 ± 0.5 | 670 ± 61 | 180 ± 23 | 0.288 |
| C-13a | 1000 | 0.5 | 46 | Au | Daci+Sulf+$H_2O$+Anhy+$Au_{95}Cu_{05}$ | MSS+SM | 0.30 ± 0.21 | 0.90 ± 0.67 | n.d. | 3180 ± 677 | 55.3 ± 2.2 | 570 ± 190 | 10 ± 3 | 0.441 |
| C-13b | 1000 | 0.5 | 46 | Au | Rhyo+Sulf+$H_2O$+Anhy+$Au_{95}Cu_{05}$ | MSS+SM | 0.21 ± 0.05 | 0.68 ± 0.15 | n.d. | 1754 ± 114 | 8.1 ± 1.8 | 350 ± 50 | 43 ± 12 | 0.323 |

Ande=andesite; Daci=dacite; Rhyo=rhyolite; Mag=magnetite; Anhy=anhydrite; MSS=crystalline monosulfide solid solution; SM=quenched silicate melt.
a. See the Supplementary Materials for the estimation of oxygen fugacity. b. 1-$\sigma$ deviation for the estimated $\log fS_2$ is below 0.1 based on the replicate analyses of MSS.
n.d. not determined; cont. contaminated by Au nuggets so the data are discarded.
NBO/T=2 Total O/T-4 (T=Si+Ti+Al+Cr+P).

andesitic to rhyolitic arc magmas is usually higher than FMQ+1.5 (Chang and Audétat, 2018; Parat et al., 2011). Therefore, the addition of ~2-15 wt.% anhydrite in runs Sulf-3, Sulf-5, Da-2A, and Da-1B could enable us to obtain a relatively high $fO_2$ that is associated with oxidized arc magmas. Approximately 10 wt.% graphite powder was added at the bottom of each Au capsule of runs Da-1A and Da-3B. At graphite-saturation, the experimental $fO_2$ must be no larger than the C-$CO_2$ buffer (~1-2 log units below FMQ). Therefore, runs Da-1A and Da-3B should reach a rather low $fO_2$. In run Da-1D, only anhydrite but no sulfide was added in the Au capsule. For other runs (Sulf-1, Sulf-2, Sulf-4, Sulf-6, Da-2B, Da-1C, and Da-3A), the $fO_2$ was not constrained by any $fO_2$ buffer. The run duration of this set of fourteen experiments ranged from 96 to 168 hours.

A third set of eleven experiments was performed at 1000-1040 °C and 0.5-2 GPa, with rhyolitic silicate, ~0-10 wt.% distilled water, and ~20 wt.% FeS (pyrrhotite) and/or anhydrite contained in Au capsules. In runs Rh-1B, Rh-2A, and Rh-3B, both FeS and anhydrite were added to the Au capsules; whereas in runs Rh-1A and Rh-2B, only anhydrite but no sulfide was added to the Au capsules. In runs Rh-1D, Rh-2C, and Rh-4A, ~10 wt.% graphite powder was added at the bottom of each Au capsule, to obtain a low $fO_2$. The run duration of this set of experiments ranged from 35 to 48 hours.

A fourth set of six experiments was performed at 1000 °C and 0.5 GPa in Au capsules (runs C-9a, C-9b, C-10a, C-10b, C-13a, and C-13b). The major and trace element compositions of this set of experiments have been reported in our previous study (Li and Audétat, 2015), but $S^{6+}/S_{tot}$ in the silicate melts was not measured and the SCSS and $D_{Au}^{MSS/SM}$ data were not discussed. In the Set-4 experiments, the starting materials included ~84-87 wt.% dacitic or rhyolitic silicate, ~10 wt.% Cu-Ni-bearing sulfide, and ~0-6 wt.% distilled water. In addition, ~10 wt.% magnetite was added to each Au capsule of runs C-9a, C-9b, C-10a, and C-10b, and ~3 wt.% anhydrite was added to each Au capsule of runs C-10a, C-10b, C-13a, and C-13b (Table 1). The aim of adding magnetite was, on one hand, to obtain an intermediate $fO_2$ via magnetite dissolution in the silicate melts, and on the other hand, to saturate the silicate melts with magnetite. The aim of adding anhydrite was to impose a high $fO_2$. However, neither magnetite nor anhydrite was found after the experiments because of complete dissolution of magnetite and/or anhydrite in the silicate melts (see below). Furthermore, to reduce the loss of Cu from Cu-Ni-bearing sulfides into the Au capsule walls, a small piece of $Au_{95}Cu_{05}$ alloy was placed at the bottom of each Au capsule of all six experiments. For this set of experiments, the $fO_2$ was not buffered by any $fO_2$ buffer, and the run duration ranged from 43 to 46 hours.

The Set-1 to Set-4 experiments were not designed to be fluid-saturated, so the traditional external $fO_2$ buffers (Chou, 1987), such as used by Jégo and Dasgupta (2014), were not adopted to buffer the experimental $fO_2$. However, all experiments that were not buffered by any $fO_2$ buffer were essentially buffered by the combined starting materials and used solid pressure media, although the $fO_2$ could vary from run to run due to the difference in the starting materials (Prouteau and Scaillet, 2012).

All experiments were conducted in an end-loaded, solid-media piston cylinder apparatus, using 0.5-inch diameter MgO-NaCl assemblies with stepped graphite heaters. All experiments were quenched to below 100 °C within 10-20 s by switching off the electric power to the graphite heaters. The details of the high-pressure equipment and the demonstration of equilibrium partitioning of Au are provided in the Supplementary Materials.

### 2.3. Analytical methods

Major element compositions of the quenched silicate melts and sulfides (MSS) were measured with a JEOL JXA-8200 electron microprobe, using procedures as described in previous studies (Li and Audétat, 2012, 2013, 2015). The oxidation state of sulfur ($S^{6+}/S_{tot}$) was determined based on the shift of the $SK_\alpha$ lines with respect to the $BaSO_4$ and ZnS standards (Carroll and Rutherford, 1988), using the same microprobe. Trace element analyses of Au, Cu, Ni, Co, and Ag in the quenched silicate melts and MSS were conducted on an Agilent 7900 Quadrupole ICP-MS coupled to a Photon Machines Analyte HE 193-nm ArF Excimer Laser Ablation system. The detection limit for Au in the quenched silicate melts was ~0.01 ppm. Detailed descriptions of all of the analytical methods are provided in the Supplementary Materials.

## 3. Results

### 3.1. Sample petrography

All of the experimental conditions and obtained products are summarized in Table 1. Some representative textures are shown in Fig. 1. A large silicate melt pool was produced in all experiments, and sulfides are present in all experiments where sulfides were added as a starting material. The produced silicate melts and sulfides are the analytical targets of this study. In the Set-1 experiments, the samples contain ~20 to 40% crystals of clinopyroxene ± amphibole ± garnet, and the volume of crystals increases with increasing pressure. In the Set-2 experiments, only a few crystals of clinopyroxene and garnet are present in the hydrous runs at pressures of 2-3 GPa. Graphite is present in all experiments where graphite powder was added as a starting material, and anhydrite is present in all experiments where anhydrite was added, except for run Sulf-3, in which anhydrite was completely dissolved in the silicate melts. In the Set-3 experiments, no silicate crystals were found, and the silicate melts coexist with sulfide ± anhydrite or anhydrite alone. In the Set-4 experiments, only a few crystals of amphibole and/or clinopyroxene are embedded in the silicate melts, but crystals of magnetite and anhydrite were not found because of their complete dissolution in the silicate melts.

In all of the experiments, sulfides are present as Cu-Ni-bearing pyrrhotite (monosulfide solid solution=MSS) or FeS-pyrrhotite crystals (both referred to as MSS hereafter) and were quenched to a homogeneous solid, as indicated by their optical appearance and chemical homogeneity (Fig. 1; Table S3).

### 3.2. Major element compositions of the silicate melts

Major element contents of all of the quenched silicate melts are listed in Table S2. The produced silicate melts are andesitic to rhyolitic, with NBO/T (=2TotalO/T-4; T=Si+Ti+Al+Cr+P) ranging from 0.012 to 0.441. For the Set-1 and Set-2 experiments, the silicate melt composition deviates from the starting andesite or dacite by showing, in general, lower FeO and MgO contents, which result from partial crystallization. In the Set-3 experiments, the silicate melts that are saturated with MSS are now FeO-rich compared to the starting rhyolitic silicate. The silicate melts that are saturated with both sulfide and anhydrite are a few wt.% higher in FeO than the silicate melts that are saturated with only sulfide but were synthesized under the same *P-T* conditions. The FeO-enrichment in the silicate melts should be caused by oxidation of sulfides during the run. In the Set-4 experiments, the silicate melts of runs C-9a, C-9b, C-10a, and C-10b differ from their starting dacitic and rhyolitic compositions and are now andesitic to dacitic due to magnetite dissolution; while the silicate melts of runs C-10a, C-10b, C-13a, and C-13b became CaO-rich due to anhydrite dissolution. In

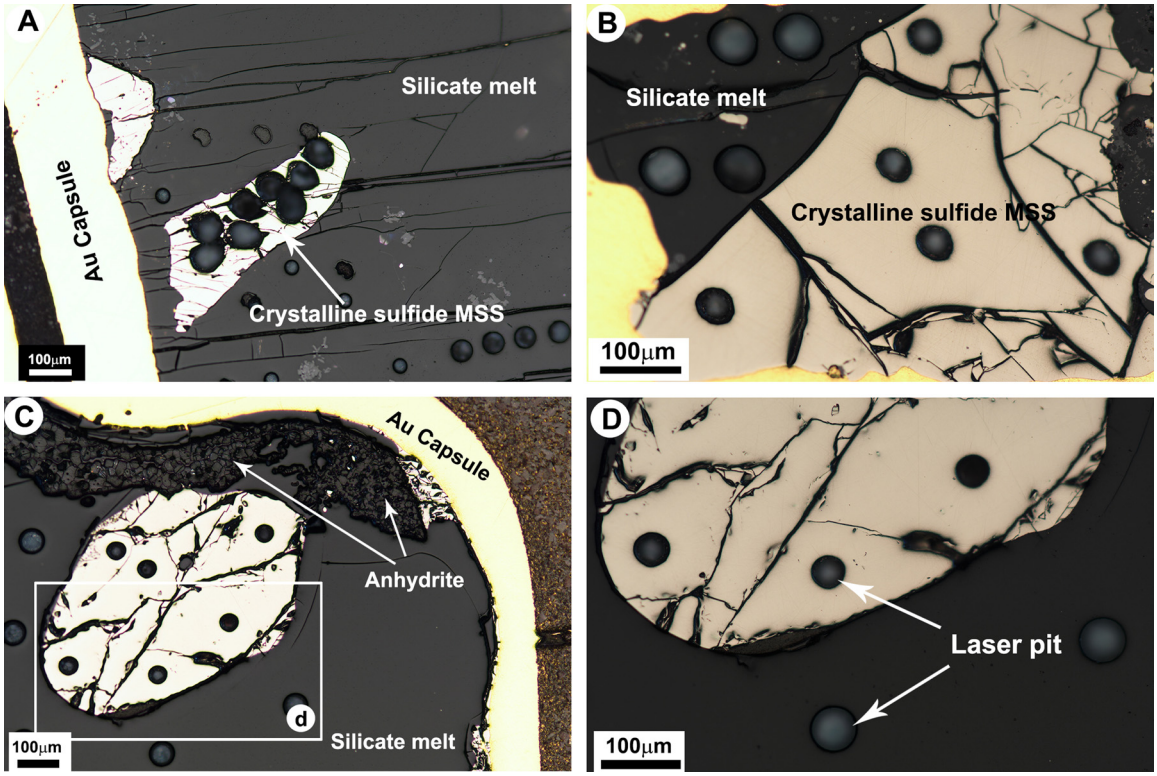



**Fig. 1.** Reflected-light photomicrographs of typical run products in gold capsules. (A) Run Sulf-4 (1040 °C, 2 GPa, dacitic melt), which shows the coexistence of silicate melt, crystalline sulfide (MSS), and very small silicate crystals. (B) Run Da-3A (1040 °C, 0.5 GPa, dacitic melt), which shows MSS coexisting with silicate melt. (C) Run Rh-1b (1040 °C, 0.5 GPa, rhyolitic melt), which shows the coexistence of silicate melt, crystalline sulfide (MSS), and anhydrite. (D) Close-up view of the crystalline sulfide shown in (C). Note that the crystalline sulfide MSS was quenched into homogeneous solid with a very smooth surface.

addition, the $Na_2O$ content in the silicate melts of the Set-4 experiments is significantly higher than the $Na_2O$ content in the starting silicates. The reason for this is not clear, but the contamination by NaCl-bearing pressure media appears to be impossible because the sample capsules were surrounded by MgO sleeve and spacer. Based on the differences in the EPMA totals to 100 wt.%, the water content in the silicate melts of all present experiments is ~0-12 wt.%, which is generally consistent with the proportion of water added in the starting materials. The water content in the silicate melts of the experiments that simulated slab melting at 1-3 GPa is ~7-12 wt.%.

### 3.3. Sulfur speciation in the silicate melts and estimation of sample $fO_2$

The sulfur content in the silicate melts at only sulfide-saturation (SCSS), sulfide-anhydrite-saturation (SCSAS), and only anhydrite-saturation (SCAS) is 40-3000 ppm, 280-5500 ppm, and 50-1030 ppm, respectively (Figs. S2-4). The $S^{6+}/S_{tot}$ in the silicate melts ranges from 0 to 0.96 (Table 1). The $S^{6+}/S_{tot}$ in the only sulfide-saturated silicate melts ranges from 0 to 0.68; whereas in the sulfide-anhydrite-saturated silicate melts it ranges from 0.61 to 0.96. For a given sulfide ± anhydrite and silicate melt system, the measured sulfur content in the silicate melts, in general, increases with increasing $S^{6+}/S_{tot}$ (Fig. S2A), except for the Set-4 experiments. In the Set-4 experiments, the sulfur content in the silicate melts is positively correlated with the $Na_2O$ content (Fig. S2B), which is consistent with the strongly positive effect of $Na_2O$ on SCSS (D'Souza and Canil, 2018).

The $fO_2$ of most of our experiments was not buffered by any $fO_2$ buffer. However, the relationship between $fO_2$ and $S^{6+}/S_{tot}$ in the quenched silicate melts provides an approach to estimate the $fO_2$ prevailing in our experiments. Several studies have calibrated $S^{6+}/S_{tot}$ in the quenched silicate melts as a function of $fO_2$ varying from FMQ-2 to FMQ+6 (Carroll and Rutherford, 1988; Jugo et al., 2005; Wallace and Carmichael, 1994) (see (Wilke et al., 2011) for a review), and these calibrations have been used to estimate the $fO_2$ of natural samples of different compositions by determining $S^{6+}/S_{tot}$ in the sample glasses (Metrich and Clocchiatti, 1996; Rowe et al., 2007; Rowe et al., 2009). In this study, we used a model from Jugo et al. (2005), which was calibrated on a large number of natural and synthetic samples of basaltic to dacitic compositions:

$$S^{6+}/S_{tot} = 1/(1 + 10^{A-B\Delta FMQ}) \quad (3)$$

in which A equals 1.22, B equals 0.95, and ΔFMQ is $fO_2$ relative to the FMQ buffer. The calculated $fO_2$ values for our unbuffered experiments that are only sulfide-saturated are between FMQ+0.6 and FMQ+1.6 (Table 1). For the dacitic and rhyolitic experiments that are saturated with both anhydrite and sulfide (Set-2 experiments), the calculated $fO_2$ values are between FMQ+1.5 and FMQ+2.7 (Table 1).

Several only sulfide-saturated experiments contain graphite (Table 1), and the maximum $fO_2$ of these experiments corresponds to the C-$CO_2$ buffer (~FMQ-1.7) (Hirschmann et al., 2008). Therefore, the $fO_2$ in our only sulfide-saturated experiments is between FMQ-1.7 and FMQ+1.6; while in the experiments that are saturated with both sulfide and anhydrite or anhydrite alone, the $fO_2$ is between FMQ+1.5 and FMQ+2.7. These $fO_2$ values are consistent with previous $fO_2$ values determined for the stabilization of sulfide and/or anhydrite in the andesitic-to-rhyolitic melts (see Parat et al., 2011 for a review). For example, Chang and Audétat (2018) show that their estimated $fO_2$ values for the andesitic melts that are saturated with both sulfide and anhydrite are between FMQ+2 and FMQ+2.6, which are well consistent with the $fO_2$ values (FMQ+1.8 to FMQ+2.7) estimated here for our sulfide-anhydrite-saturated dacitic melts. A further evaluation on the va-

lidity of using $S^{6+}/S_{tot}$ in the silicate melts to estimate sample $fO_2$ is provided in the Supplementary Materials.

In addition, we compared our measured SCSS and SCSAS values with the predicted SCSS values using a comprehensive parameterization of Smythe et al. (2017) (Fig. S3). Fig. S3 shows that our measured SCSS and SCSAS values are generally higher than the predicted SCSS values, which demonstrates that the $fO_2$ of most of our unbuffered, only sulfide-saturated experiments is in the $fO_2$ range required for the sulfide-sulfate transition in the silicate melts (see Supplementary Materials). Overall, the present experimental redox conditions well cover those conditions that are relevant for subduction-related magmatism (Frost and McCammon, 2008) and those at which the sulfide-sulfate transition occurs in the silicate melts (Jugo et al., 2005; Jugo et al., 2010).

### 3.4. Major element compositions of MSS and estimation of sample $fS_2$

The major element contents of MSS are listed in Table S3. The S and Fe contents in MSS of all sets of experiments range from 36.68 to 39.94 wt.% and from 51.22 to 61.88 wt.%, respectively. The O content in MSS ranges from below 0.2 to 0.7 wt.%, with one sample MSS containing 1.87 wt.% O. The Ni content in the Ni-Cu-bearing MSS ranges from 2.62 to 6.86 wt.%, with most values at ~5 wt.%. The Cu content in the Ni-Cu-bearing MSS ranges from 0.13 to 1.96 wt.%. Compared to the ~2 wt.% Cu in the starting sulfides, significant Cu was thus lost from the Cu-Ni-bearing MSS to the Au capsule walls, except for a few experiments in which a piece of $Au_{95}Cu_{05}$ alloy was added (Table S3). The Cu and Ni contents in FeS-pyrrhotite are low, which are 70-1430 ppm and 17-340 ppm, respectively.

Sample sulfur fugacity $\log fS_2$ was calculated based on the major element compositions of MSS, using an experimental calibration (Toulmin and Barton, 1964):

$$N_{FeS} = FeS/(FeS + S_2) \quad (4)$$

$$\log fS_2 = (70.0 - 85.83N_{FeS}) \times (1000/T - 1) + 39.30\sqrt{(1 - 0.9981N_{FeS})} - 11.91 \quad (5)$$

in which $N_{FeS}$ is the mole fraction of FeS in the FeS-$S_2$ system, and T is the temperature in K. For all $\log fS_2$ calculations, the measured oxygen in MSS was assumed to be present in the form of FeO, and $N_{FeS}$ was replaced by $N_{FeS+NiS+Cu_2S}$ for the Ni-Cu-bearing MSS (Mengason et al., 2010). The calculated $\log fS_2$ for all of the samples ranges from −2.17 to 2.08 (Table 1). Sample $\log fS_2$ was also calculated using a calibration in which the pressure effect was considered (Froese and Gunter, 1976), but we chose to use the $\log fS_2$ values calculated using the calibration of Toulmin and Barton (1964) (see Supplementary Materials).

### 3.5. Au solubility in the silicate melts

The solubility of Au in the silicate melts ($C_{Au}^{SM}$) varies by more than three orders of magnitude, from 0.012 to 55.3 ppm. Although a considerable fraction of sulfur in the only sulfide-saturated silicate melts is present as $S^{6+}$, as measured by the $SK_\alpha$ method of electron microprobe, $C_{Au}^{SM}$ shows a strong correlation with SCSS (Fig. 2A). However, in the experiments that are sulfide-anhydrite-saturated or only anhydrite-saturated, $C_{Au}^{SM}$ remains nearly constant as the variation of SCSAS or SCAS (Fig. 2A), indicating a negligible role for $S^{6+}$ in enhancing Au dissolution in the silicate melts. Fig. 2B further illustrates that for all of the only sulfide-saturated experiments, $\log(C_{Au}^{SM}$, μmol) is strongly correlated with log(SCSS, μmol), although the sample $fO_2$ varies from ~FMQ-1.7 to FMQ+1.6 in this study and from ~FMQ-0.5 to FMQ+2

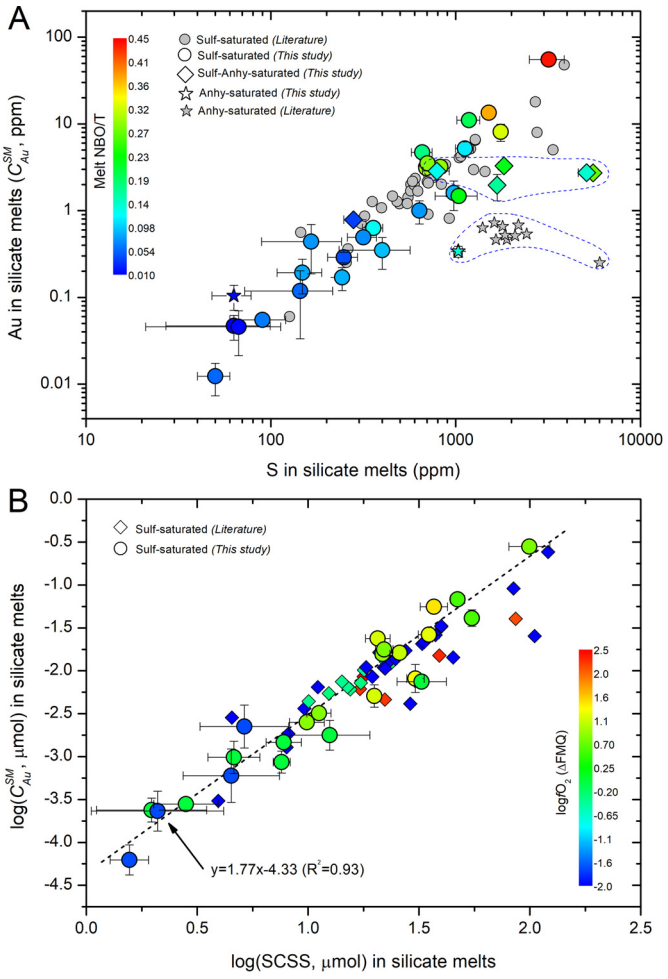



**Fig. 2.** The solubility of Au in silicate melts ($C_{Au}^{SM}$) as a function of the melt sulfur content. (A) $C_{Au}^{SM}$ and the melt sulfur content (SCSS) are strongly correlated in the only sulfide-saturated experiments; whereas in the sulfide-anhydrite-saturated or only anhydrite-saturated silicate melts, $C_{Au}^{SM}$ does not vary with the melt sulfur content (SCSAS or SCAS), indicating that $S^{6+}$ does not enhance Au dissolution in the silicate melts. (B) In the only sulfide-saturated experiments, $\log(C_{Au}^{SM}$, μmol) is a strong linear function of log(SCSS, μmol), although the sample $fO_2$ varies from ~FMQ-1.7 to FMQ+2, which indicates the enhancement of Au dissolution in the silicate melts by the formation of Au-sulfur species at reduced to moderately oxidized conditions. Note that $C_{Au}^{SM}$ and the melt sulfur content are generally higher in the silicate melts with higher NBO/T. The literature data were taken from Zajacz et al. (2013), Botcharnikov et al. (2011), Jégo and Pichavant (2012), and Jégo et al. (2010, 2016).

in previous studies. The correlation between $\log(C_{Au}^{SM}$, μmol) and log(SCSS, μmol) can be described as:

$$\log(C_{Au}^{SM}, \mu mol) = 1.77 \log(SCSS, \mu mol) - 4.33 \ (R^2 = 0.93) \quad (6)$$

These observations are consistent with previous studies (Jégo and Pichavant, 2012; Jégo et al., 2010; Zajacz et al., 2013; Zajacz et al., 2012) that imply the enhancement of $C_{Au}^{SM}$ in $S^{2-}$-bearing silicate melts. These observations are also consistent with studies of Botcharnikov et al. (2011) and Jégo et al. (2016) that show an increase of $C_{Au}^{SM}$ in the only sulfide-saturated silicate melts with increasing $fO_2$ over the range of ~FMQ-1.2 to FMQ+2, but the present study more precisely defined the correlation between $C_{Au}^{SM}$ and SCSS due to the largely extended experimental conditions. Jugo et al. (2010) show that over the $fO_2$ range of sulfide-sulfate transition, the abundance of $S^{2-}$ in the sulfide-saturated silicate melts remains constant, and the increase of SCSS with increasing $fO_2$ is due to the increased $S^{6+}$ content, which, however, does not complex with Au or enhance Au dissolution (Fig. 2A). Therefore, if the

study of Jugo et al. (2010) is right and if $S^{2-}$ is the only sulfur species that complexes with Au, $C_{Au}^{SM}$ for a given sulfide-saturated silicate melt system should remain constant, regardless of the $fO_2$ and melt sulfur content. In this context, Fig. 2B implies that in addition to $S^{2-}$, another sulfur species, which have an intermediate oxidation state and can enhance Au dissolution, may also exist in the only sulfide-saturated silicate melts.

In contrast to Jugo et al. (2010), Botcharnikov et al. (2011) found that the $S^{2-}$ content in the only sulfide-saturated silicate melts increases with increasing $fO_2$ over the range of FMQ-0.5 to FMQ+1.5. If this finding is correct, then the observation that $C_{Au}^{SM}$ is positively correlated with SCSS over the $fO_2$ range of ~FMQ-1.7 to FMQ+2 (Fig. 2B) could be explained by the formation of only Au-sulfide species in the silicate melts (Jégo et al., 2016). Species such as Au-Na/H-S (Zajacz et al., 2013) and $Au_2$-Fe-$S_2$ (Jégo and Pichavant, 2012) have been proposed to be the main Au-sulfide species in the silicate melts. However, the slope of 1.77 of Eq. (3), derived from experiments performed under different conditions of P-T-$fO_2$-melt composition, indicates that the Au-S species dissolved in the silicate melts may be more complicated than these. The actual sulfur and Au-S species dissolved in the sulfide-saturated silicate melts at different $fO_2$s await future in-situ spectroscopic measurements; however, more importantly, $C_{Au}^{SM}$ is strongly correlated with SCSS in the only sulfide-saturated silicate melts over an $fO_2$ range of ~FMQ-1.7 to FMQ+2 (Fig. 2B).

### 3.6. Au solubility in MSS

The solubility of Au in MSS ($C_{Au}^{MSS}$) varies from 130 to 2800 ppm and is positively correlated with the sample $\log fS_2$ (Fig. 3). The presence or absence of several wt.% of Ni and Cu in MSS appears not to affect $C_{Au}^{MSS}$ (Fig. 3A).

The dissolution of Au in MSS can be described by a reaction of

$$\text{Au (metal)} + \frac{1}{4}S_2 = \text{AuS}_{1/2}\ \text{(MSS)} \quad (7)$$

Since the activity of Au in pure Au-metal is one, the equilibrium constant (K) of Eq. (7) can be written as:

$$K = \frac{\alpha AuS_{1/2}}{f^{1/4}S_2} \quad (8)$$

which can be further arranged as:

$$\log K = \log \alpha \text{AuS}_{1/2} - 1/4 \log fS_2 \quad (9)$$

$$\log \gamma \text{AuS}_{1/2} X\text{AuS}_{1/2} = 1/4 \log fS_2 + \log K \quad (10)$$

In Eqs. (8)–(10), $\alpha$, $\gamma$, and X refer to the activity, activity coefficient, and mole fraction of Au in MSS. Assuming that $\gamma \text{AuS}_{1/2}$ does not change greatly with the temperature and small variation of MSS composition, Eq. (10) can be further written as:

$$\log(C_{Au}^{MSS}, ppm) = 1/4 \log fS_2 + C \quad (11)$$

in which C is a constant. Eq. (11) would imply that $\log(C_{Au}^{MSS}, ppm)$ increases with increasing $1/4 \log fS_2$, which is in a good agreement with the trend shown in Fig. 3B.

### 3.7. MSS-silicate melt partitioning of Au

The Nernst partition coefficient $D_{Au}^{MSS/SM}$, calculated from Au weight proportions in MSS and silicate melt, varies by more than three orders of magnitude, from 10 to 14000 (Fig. 4). Negative correlations exist between $D_{Au}^{MSS/SM}$ and the melt sulfur or Au content for all of the only sulfide-saturated experiments over the $fO_2$ range of ~FMQ-1.7 to FMQ+1.6 (Fig. 4). However, for the sulfide-anhydrite-saturated experiments, $D_{Au}^{MSS/SM}$ does not show any dependence on the melt sulfur content, which again indicates that the dissolved $S^{6+}$ does not enhance Au dissolution in the silicate melts. These experimental results thus reveal that the MSS-silicate melt partitioning of Au under reduced to moderately oxidized conditions ($fO_2 \leqslant$FMQ+1.6) depends significantly on SCSS. According to Fig. 4A, $D_{Au}^{MSS/SM}$ can be directly linked to SCSS in a quantitative way, as follows:

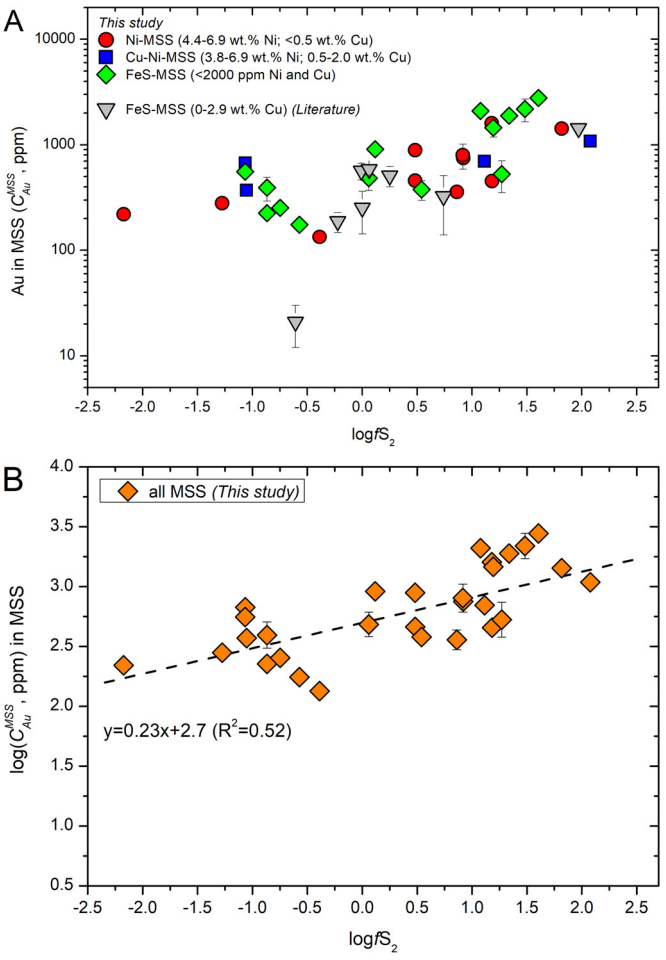



**Fig. 3.** The solubility of Au in monosulfide-solid-solution ($C_{Au}^{MSS}$) as a function of sulfur fugacity $\log fS_2$. Note that $C_{Au}^{MSS}$, in general, increases with increasing $\log fS_2$, and $C_{Au}^{MSS}$ is not considerably affected by the presence of different amounts of Ni and Cu in MSS. The literature data were taken from Botcharnikov et al. (2011) and Zajacz et al. (2013).

$$\log D_{Au}^{MSS/SM} = -1.63 \log(\text{SCSS, ppm}) + 7.03\ (R^2 = 0.86) \quad (12)$$

In addition, the combination of Eq. (6) and Eq. (11) by converting µmol into ppm in Eq. (6) would yield:

$$\log(C_{Au}^{MSS}, \text{ ppm}) - \log(C_{Au}^{SM}, \text{ ppm}) = 0.25 \log fS_2 - 1.77 \log(\text{SCSS, ppm}) + C \quad (13)$$

In Eq. (13), $\log(C_{Au}^{MSS}, \text{ ppm}) - \log(C_{Au}^{SM}, \text{ ppm})$ equals $\log D_{Au}^{MSS/SM}$, so Eq. (13) can be further written as:

$$\log D_{Au}^{MSS/SM} = 0.25 \log fS_2 - 1.77 \log(\text{SCSS, ppm}) + C \quad (14)$$

Eq. (14) implies that $D_{Au}^{MSS/SM}$ should be a function of $fS_2$ and SCSS. Regression of our $\log D_{Au}^{MSS/SM}$ data as a multiple linear function of $\log fS_2$ and log(SCSS, ppm) yielded:

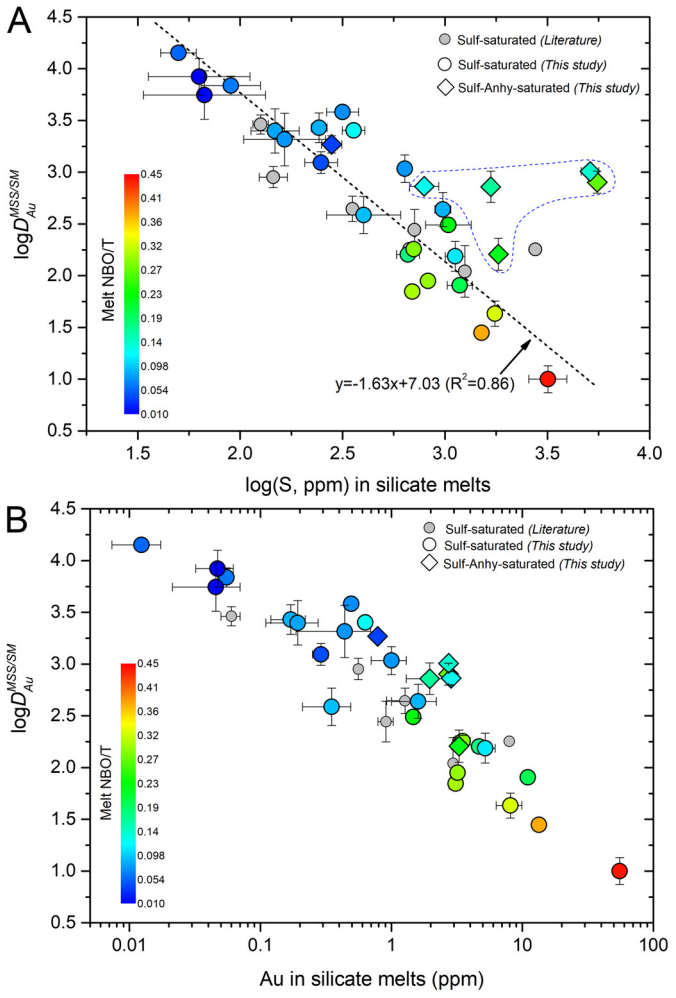



**Fig. 4.** MSS-silicate melt partition coefficient of Au ($D_{Au}^{MSS/SM}$) as a function of the melt sulfur/Au content for the only sulfide-saturated and sulfide-anhydrite-saturated experiments. (A) For the only sulfide-saturated experiments under reduced to moderately oxidized conditions (FMQ-1.7 < $fO_2$ < FMQ+1.6), the correlation between $D_{Au}^{MSS/SM}$ and the melt sulfur content (SCSS) can be described as $\log D_{Au}^{MSS/SM} = -1.63\log(\text{SCSS, ppm}) + 7.03$ ($R^2 = 0.86$). The independence of $D_{Au}^{MSS/SM}$ on the melt sulfur content (SCSAS) in the sulfide-anhydrite-saturated experiments indicates that $S^{6+}$ does not enhance Au dissolution in the silicate melts, as explained in Fig. 2A. (**B**) $\log D_{Au}^{MSS/SM}$ is strongly negatively correlated with the melt Au content for all sulfide-saturated and sulfide-anhydrite-saturated experiments. Note that $D_{Au}^{MSS/SM}$ varies by more than three orders of magnitude, and $D_{Au}^{MSS/SM}$ is generally lower for the experiments with higher NBO/T. The literature data were taken from Botcharnikov et al. (2011) and Zajacz et al. (2013).

$$\log D_{Au}^{MSS/SM} = 0.27\log fS_2 - 1.64\log(\text{SCSS, ppm}) + 7.03\ (R^2 = 0.94) \quad (15)$$

The coefficients for $\log fS_2$ and log(SCSS, ppm) in Eqs. (14) and (15) are nearly identical. Accordingly, the large variation of $D_{Au}^{MSS/SM}$ observed in this study appears to be fully explained by the combined $fS_2$ and SCSS, but $D_{Au}^{MSS/SM}$ depends more heavily on SCSS. To further test the model of Eq. (15), all present and literature $D_{Au}^{MSS/SM}$ data (total data points $n = 49$ as compiled in Fig. S1) were fitted as a multiple linear function of $fS_2$ and SCSS, which yielded:

$$\log D_{Au}^{MSS/SM} = 0.28\log fS_2 - 1.23\log(\text{SCSS, ppm}) + 5.89\ (R^2 = 0.74) \quad (16)$$

A comparison between the experimentally measured $\log D_{Au}^{MSS/SM}$ and the predicted $\log D_{Au}^{MSS/SM}$ using Eq. (16) is provided in Fig. S5, which illustrates that more than 90% of the $\log D_{Au}^{MSS/SM}$ data can be predicted within 0.5 log units.

## 4. Discussion

### 4.1. Factors that affect the MSS-silicate melt partitioning of Au

The above results, as summarized in Fig. 4A and Eqs. (12) and (15), demonstrate that the melt sulfur content (SCSS) and $fS_2$ strongly control the MSS-silicate melt partitioning of Au under reduced to moderately oxidized conditions. However, SCSS is a multiple function of the temperature, pressure, $fO_2$, melt composition, and melt water content (Jugo et al., 2010; Smythe et al., 2017), and $fS_2$ is positively correlated with $fO_2$ in $fS_2$-unbuffered, sulfide-saturated experiments (Botcharnikov et al., 2011; Li and Audétat, 2012). The SCSS at $fO_2$ of the sulfide-sulfate transition is up to one order of magnitude higher than the SCSS at $fO_2$ below FMQ (Jugo et al., 2010). Mafic-to-intermediate melts, in general, have higher SCSS than the felsic melts (Clemente et al., 2004), and alkaline melts have particularly high SCSS as shown in Fig. S2 and by D'Souza and Canil (2018). For a hydrous melt of basaltic andesite at 1250 °C and 1 GPa, increasing per wt.% of $Na_2O$ would increase the SCSS by ~560 ppm (D'Souza and Canil, 2018); increasing the per wt.% of $H_2O$ would increase the SCSS by ~100 ppm in the basaltic to rhyolitic melts (Fortin et al., 2015). Therefore, the sulfide-silicate melt partitioning of Au is indirectly controlled by all of the factors that control the SCSS and $fS_2$. The large variation of $D_{Au}^{MSS/SM}$ from 10 to 14000, as compiled in Fig. S1, can be indirectly ascribed to the variation of physical and chemical parameters such as the experimental temperature, pressure, $fO_2$, silicate melt composition, and melt water content, because a variation of any of these parameters can cause a variation in SCSS and, consequently, a variation in $D_{Au}^{MSS/SM}$. For example, the $D_{Au}^{MSS/SM}$ values obtained from the sulfide-andesitic melt system are lower than those obtained from the sulfide-rhyolitic melt system because of the higher SCSS in andesitic melts (Fig. 4A). For a given sulfide-silicate melt system, the $D_{Au}^{MSS/SM}$ values obtained under moderately oxidized conditions are lower than those obtained under reduced conditions because of the enhanced SCSS under moderately oxidized conditions (Table 1). Apparently, the $D_{Au}^{MSS/SM}$ for hydrous and moderately oxidized mafic to intermediate melts could be sufficiently low owing to the large SCSS, in such a way that fractionation of MSS may sequester very limited amounts of Au. Whereas, fractionation of a small amount of MSS could potentially sequester most of the Au for a rhyolitic system owing to the small SCSS (see below).

The sulfide-silicate melt partitioning of many chalcophile elements, such as Ni, Re, Mo, and Pb, is a strong function of the melt FeO content or both the melt FeO content and $fO_2$, as summarized by Eqs. (1) and (2) and discussed previously, because these metals dissolve as different metal oxide species in the silicate melts (Feng and Li, 2019; Kiseeva and Wood, 2013, 2015; Li, 2014; Li and Audétat, 2012, 2015). Eqs. (6), (12), and (15), and Figs. 2 and 4 as well, demonstrate that, compared to many other chalcophile elements, Au has a remarkably distinct dissolution mechanism in the sulfide-saturated silicate melts (mainly as Au-S species) and, consequently, a distinct partitioning behavior in the sulfide-silicate melt systems. Eqs. (12) and (15) also explain the observed lack of correlation between $D_{Au}^{MSS/SM}$ and the melt FeO content or $fO_2$ (Fig. S1), because neither the melt FeO content nor $fO_2$ is the only factor that determines SCSS and/or $fS_2$ (Jugo et al., 2010; Smythe et al., 2017).

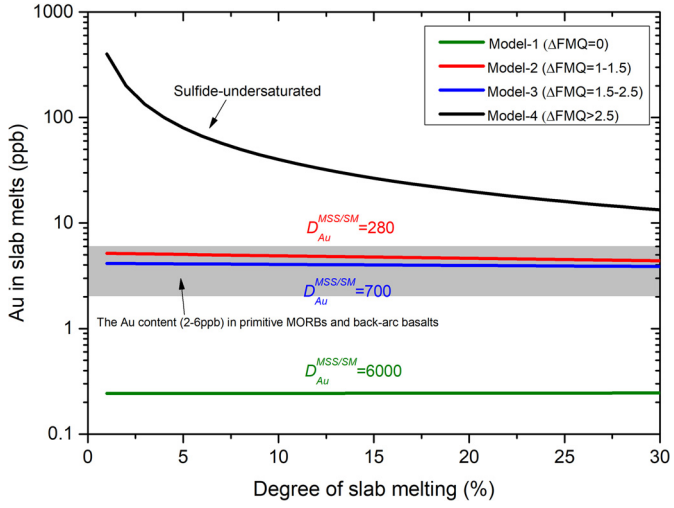



**Fig. 5.** Modeled Au content in the slab melts as a function of the degree of slab melting at various redox states using a batch melting model. The Au content in primitive MORBs and back-arc basalts (Jenner et al., 2010) was taken for comparison with the modeled Au content in the slab melts. The $fO_2$ during slab melting increases from Model-1 to Model-4. The slab melting temperature is assumed to be 1000 °C, under which condition most of the experiments were performed to determine the SCSS in the slab melts (Fig. S4). See text for a detailed description of each model calculation.

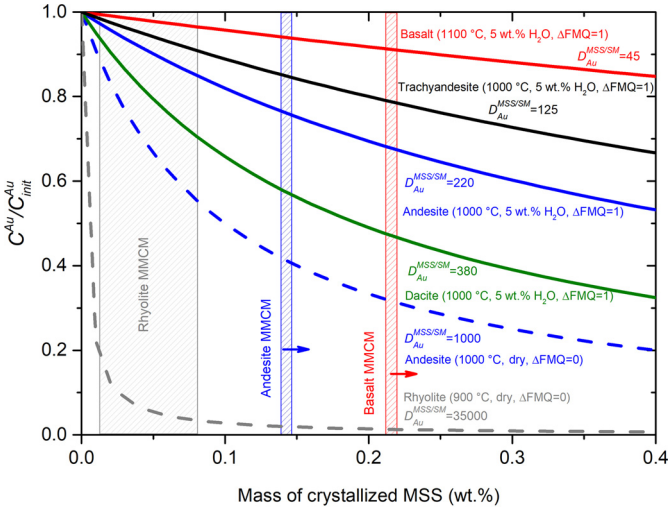



**Fig. 6.** Variation of the Au content in arc magmas induced by MSS crystallization. Equilibrium crystallization of MSS is used for all of the calculations. The model of D'Souza and Canil (2018) was used for calculating the SCSS in trachyandesite at 0.2 GPa, and the SCSS for other types of arc magmas is calculated at 0.2 GPa using the model of Smythe et al. (2017). For magmas at $fO_2$ of FMQ+1, the melt sulfur content equals twice the calculated SCSS owing to the positive effect of $fO_2$ on SCSS (Botcharnikov et al., 2011; Jugo et al., 2010); otherwise it equals the calculated SCSS. $D_{Au}^{MSS/SM}$ is calculated for each type of arc magma using the melt sulfur content and Eq. (12) by assuming $\log fS_2 = 0$. The maximum mass of crystallized MSS (MMCM) for each type of magma is defined based on the observed range of sulfur contents in the corresponding arc magma (50-300 ppm for rhyolite, 500-2000 ppm for andesite, and 800-3000 ppm for basalt) (Wallace and Edmonds, 2011), by assuming that all sulfur in the magma crystallized as FeS-sulfide. The arrows mean that the MMCM for andesite and basalt is larger than the dashed area due to the large range of sulfur contents in arc andesite and basalt. $C^{Au}/C_{init}^{Au}$ denotes ratio of the Au content in the magma after and before MSS crystallization. Note that the small effect of MSS crystallization on the Au content in moderately oxidized mafic to intermediate magmas with a high-water content is due to the high sulfur content in the silicate melt.

### 4.2. Fate of Au during slab melting and deep Au cycle

The above results can be used to constrain the fate of Au during slab melting and the deep Au cycle in subduction zones via modelling the efficiency of Au extraction by slab melts. The redox state of the altered oceanic crust plus sediments could have plausibly varied from being reduced to oxidized through geological time (Evans and Tomkins, 2011), so we considered four different slab melting models to calculate the Au content in the slab melts (Fig. 5). In each model, concentrations of 1000 ppm sulfur and 4 ppb Au were assumed in the slab as in the primitive MORBs (Jenner et al., 2010). In Model-1, the slab $fO_2$ is ~FMQ, and SCSS in the slab melts is ~100 ppm, as determined at 850-1050 °C and 2-3 GPa (Jégo and Dasgupta, 2013, 2014), which correspond to a $D_{Au}^{MSS/SM}$ value of ~6000 (Fig. 4A; Eq. (12)), while sulfur is present as pyrrhotite in the slab (Jégo and Dasgupta, 2013). In Model-2, the slab is moderately oxidized, with $fO_2$ between FMQ+1 and FMQ+1.5, and SCSS in the slab melts is ~700 ppm, as determined in this study and Jégo and Dasgupta (2014) (Fig. S4), which correspond to a $D_{Au}^{MSS/SM}$ value of ~280, while the sulfur is still present as pyrrhotite. We also considered one highly oxidized model (Model-3; FMQ+1.5<$fO_2$<FMQ+2.5). In Model-3, we assumed that half of the slab sulfur is sulfide and the other half is sulfate during slab melting, despite the fact that the coexistence of sulfide and sulfate minerals in modern altered oceanic crust (Alt and Shanks, 2011; Evans, 2012) does not necessarily mean the presence of this much sulfate during slab melting. In this model, the minimum $D_{Au}^{MSS/SM}$ value (700) of those obtained from the sulfide-anhydrite-saturated experiments at 2 GPa is used (Table 1). In Model-4, the slab $fO_2$ is assumed to be exceedingly high ($fO_2$>FMQ+2.5), in such a way that only sulfate is present during slab melting. In this model, Au is thought to be perfectly incompatible during slab melting due to the absence of sulfides. Fig. 5 shows that the calculated Au content in the slab melts from Model-1 to Model-3 is below 5 ppb, and efficient Au extraction by slab melts occurs only when all of the sulfur is present as sulfate during slab melting (Model-4).

Fig. 5 illustrates that slab melts of both ancient (>2.5 Ga) and modern subduction zones can transport less than 25% of slab Au to the subarc mantle, if the degree of slab melting is not higher than 20%. Before the rise of oxygen in Earth's atmosphere at ~2.2-2.5 Ga (Lyons et al., 2014), sulfur occurs mainly as sulfide in the altered oceanic crust and the $fO_2$ during slab melting is not higher than FMQ (Evans and Tomkins, 2011; Prouteau and Scaillet, 2012). Therefore, partial melting of the ancient slab must lead to a negligible transfer of slab Au and sulfur to the subarc mantle due to the very small SCSS in the slab melts (Model-1 of Fig. 5). The redox state of the modern subducting slab remains debated. The oxidized nature of arc magmas could be inherited from oxidized materials of the subducting slab (Kelley and Cottrell, 2009; Mungall, 2002); however, similar V/Sc and Fe/Zn systematics in primitive MORBs and arc basalts suggest that the subducting slab may not be more oxidized than the oceanic mantle ($fO_2 \leqslant$FMQ) (Lee et al., 2005; Lee et al., 2010). Anhydrite together with pyrite was found in fluid inclusions of eclogitic vein assemblages (Zhang et al., 2008); whereas there are lines of evidence for the ubiquitous presence of sulfides in subduction-related eclogites (Aulbach et al., 2012; Evans et al., 2014). The sulfide abundance is much greater than the sulfate abundance in modern altered oceanic crust (Alt and Shanks, 2011; Evans, 2012), which is suggestive of more sulfur in the reduced species that enter the subduction zones. Because pressure causes the reduction of an iso-chemical silicate assemblage (Stagno et al., 2013), most of the sulfur present during slab melting at the subarc depth could be in the form of pyrrhotite and subducted efficiently into the deep mantle (Jégo and Dasgupta, 2013), which well explains the imbalance between the sulfur input and output in modern subduction zones - more than two thirds of the sulfur in modern subduction zones entering the deep mantle but not sourced by arc volcanism (Evans, 2012; Jégo and Dasgupta, 2013).

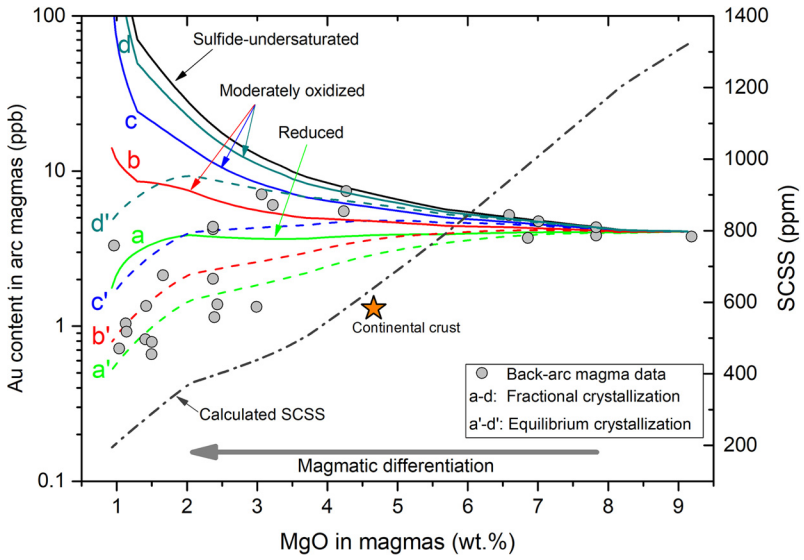



**Fig. 7.** Modeled Au content in MSS-saturated arc magmas differentiating from a MORB-like basalt with 2 wt.% water to a felsic residual magma. The magmatic differentiation trend was modeled from 1200 °C and 0.4 GPa using Rhyolite-MELTS (Gualda et al., 2012), and the modeled major elements were used to calculate the SCSS (dot-and-dash dark curve) in silicate melts of the differentiating arc magmas, using the model of Smythe et al. (2017). For differentiation under reduced conditions ($fO_2$=FMQ) (a-a' curves), the melt sulfur content equals the calculated SCSS; whereas, for differentiation under moderately oxidized conditions (FMQ<$fO_2$<FMQ+1.5), it equals two times (b-b' and c-c' curves) and four times (d-d' curves) the calculated SCSS, by assuming 50% and 25% of sulfur present as $S^{2-}$ in the moderately oxidized silicate melts, respectively. The corresponding $D_{Au}^{MSS/SM}$ used for modeling was calculated using the melt sulfur content and Eq. (12). A content of 4 ppb Au was assumed in the initial MORB-like basalt (Jenner et al., 2010). The mass of crystallized MSS for each step of crystallization was determined by variation of the calculated SCSS for a-a', c-c', and d-d' curves and by variation of twice the calculated SCSS for b-b' curves, by assuming that all sulfur is removed as FeS-sulfide. Note that for b-b' curves, all of the sulfur, including $S^{2-}$ and $S^{6+}$, is removed as FeS-sulfide, which could be caused by magnetite crystallization (Jenner et al., 2010) and/or degassing (Moussallam et al., 2016) for example. The modeled Au content in sulfide-undersaturated differentiating magmas, and the Au content in the continental crust (Rudnick and Gao, 2014) and back-arc magmas of the Eastern Manus basin (Jenner et al., 2010; Sun et al., 2004) were plotted for comparison.

Therefore, the extreme case, Model-4 of Fig. 5, cannot be realistic for any of the subduction zones. In addition, even if the slab is moderately oxidized or highly oxidized, as assumed in Model-2 and Model-3, the calculated Au content in the slab melts is not higher than the Au content in the primitive MORBs and arc basalts (Fig. 5). Accordingly, Fig. 5 implies that, although the capacity of slab melts in transporting Au depends on $fO_2$, the slab melts of both ancient and modern subduction zones overall have a low capacity in transporting slab Au to the subarc mantle. A low capacity for slab melts in transporting Au would imply that most of the slab Au which is coupled with sulfides is subducted into the deep mantle, and the slab melts contribute insignificant Au to the arc basalts. The observation (Jenner et al., 2010) that subduction-related, back-arc basalts have similar Au contents as MORBs may corroborate these conclusions, although the slab fluids thus far cannot be excluded from being a medium to transfer slab Au to the subarc mantle.

### 4.3. Au-enrichment and ore potential of MSS-saturated arc magmas

Our partitioning data also provide new constraints on the Au-enrichment and ore potential of the differentiating arc magmas. The depletion of Cu in variously evolved arc magmas and the continental crust indicates the fractionation of MSS during arc magmatic differentiation (Jenner, 2017; Lee et al., 2012; Li, 2014; Li and Audétat, 2013; Wang et al., 2018). To evaluate the effect of the fractionation of MSS on the Au content in the differentiating arc magmas, we have calculated the Au content in silicate melts of various compositions, melt water contents, and oxidation states as a function of the mass of crystallized MSS (Fig. 6). Fig. 6 illustrates that MSS crystallization has a very limited effect on the Au content in moderately oxidized mafic to intermediate magmas with high-water contents, but the effect can be significant for dry and reduced magmas, felsic magmas in particular. In addition, the Au content in the alkaline magmas (trachyandesite) appears to be less affected by MSS crystallization compared to the normal andesite, which can be ascribed to the higher SCSS caused by the higher $Na_2O$+$K_2O$ content in trachyandesite (D'Souza and Canil, 2018). To further investigate the effect of fractionation of MSS on the Au content in the differentiating hydrous arc magmas under reduced to moderately oxidized conditions, we have also calculated the SCSS and the corresponding $D_{Au}^{MSS/SM}$ for a series of magmas, differentiating from basaltic to granitic compositions at the saturation of MSS; the calculated SCSS and $D_{Au}^{MSS/SM}$ values were then used to calculate the Au content in the differentiating magmas as a function of MgO (Fig. 7). Fig. 7 shows that MSS crystallization would not cause depletion of Au in hydrous mafic-to-intermediate magmas (>3 wt.% MgO) under moderately oxidized conditions, and Au prefers to accumulate in the residual magmas if the magmatic crystallization follows a fractional crystallization model. Though not shown in Fig. 7, the enrichment of Au in the residual arc magmas can be further enhanced if the magmas are rich in alkali metals, because the oxides of alkali metals in magmas can significantly increase SCSS but decrease $D_{Au}^{MSS/SM}$ as discussed above and shown in Fig. S2B. Fig. 7 also illustrates that sulfide-undersaturation would sufficiently cause Au-enrichment in the differentiating arc magmas, but it is not a necessary condition to generate Au-enrichment. Previous studies (Mungall, 2002; Sillitoe, 1997) suggest that exceedingly high $fO_2$ is required to generate Au-enrichment in magmas via suppressing the saturation of sulfides; however, it should be noted that sulfide-saturation is a globally common phenomenon in arc magmas of mafic-to-felsic compositions (Chiaradia, 2014; Lee et al., 2012).

The above results (Figs. 6 and 7) have important implications for the formation of magmatic-hydrothermal Au deposits. The magmas that are formed under moderately oxidized conditions and that have high contents of sulfur, alkali metal, and water would potentially have a high content of Au. In an aqueous fluid-magma system under moderately oxidized conditions, Au complexed with sulfur partitions strongly into the fluid phase

(Zajacz et al., 2012), particularly when the aqueous fluids are rich in alkali metals and chlorine (Zajacz et al., 2010). Therefore, Au, sulfur, water, chlorine, and alkali metals are indeed interplayed in a moderately oxidized aqueous fluid-magma system. All of the factors that favor the formation of Au-enrichment in the magmas would essentially favor the magma to fluid transfer of Au and consequently, the formation of Au-enrichment in the aqueous fluids. Accordingly, the mafic to intermediate hydrous magmas, alkaline magmas in particular, under moderately oxidized conditions would have a high potential to form magmatic-hydrothermal Au deposits. These findings explain the strong genetic link observed between large to giant Au deposits and alkaline magmas (Müller and Groves, 2016; Sillitoe, 1997; Sillitoe, 2002), which are a type of magmas that are generated by small degrees of partial melting of the metasomatized subarc mantle and show high contents of alkali metals, sulfur, water, chlorine, and Au (D'Souza and Canil, 2018; Li and Audétat, 2013; Müller and Groves, 2016).

It is worthwhile to further point out that, although an exceedingly high $fO_2$ does render high Au contents in the differentiating magmas via suppressing sulfide-saturation (Fig. 7), it does not favor an efficient magma-to-fluid transfer of Au, which may hinder the formation of magmatic-hydrothermal Au deposits. This is because sulfur occurring as oxidized species (*e.g.*, $SO_2$) in oxidized fluids does not favor the partitioning of Au into the aqueous fluids (Zajacz et al., 2012; Zajacz et al., 2010). In addition, although Au-enrichment can also occur in moderately oxidized felsic magmas (<1.5 wt.% MgO, >70 wt.% $SiO_2$; Fig. 7) if the crystallization follows the fractional crystallization model, the low sulfur contents or SCSS of these magmas, as observed in natural felsic arc magmas (Wallace and Edmonds, 2011) and shown in Fig. 7, may limit their potential to form magmatic-hydrothermal Au deposits of large-to-giant sizes.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2019.115850.

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