

1 **Revision 1**

2 **Behavior of gold in a magma at sulfide-sulfate transition: Revisited**

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24 **ABSTRACT**

25 We have investigated experimentally the partitioning of Au between solid and liquid
26 sulfide phases and basaltic melts at 200 MPa, at redox conditions close to the sulfide-sulfate
27 transition, over temperatures between 1050 and 1200 °C which span the monosulfide solid
28 solution (MSS) - sulfide liquid (SuL) solidus. The measured MSS/basalt partition coefficient
29 of Au ($D^{\text{MSS-sil}}_{\text{Au}}$) is about 100-200, whereas the partition coefficient of sulfide liquid/basalt
30 ($D^{\text{SuL-sil}}_{\text{Au}}$) is approximately ten times larger at 2200. Although we find that temperature,
31 pressure, and oxygen fugacity ($f\text{O}_2$) exert relatively weak controls on Au partitioning, they
32 exert major indirect influences on Au behavior by controlling the identity of the condensed
33 sulfide phase and by affecting S solubility. These observations have important implications
34 for the behavior of Au in the processes of partial melting in the mantle and magma
35 crystallization in the crust. The occurrence of natural magmas with elevated concentrations of
36 Au and presumably other highly siderophile and chalcophile elements requires predominance
37 of MSS over SuL in the source or/and oxidizing conditions close to or above the sulfide-
38 sulfate transition in the magma.

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41 *Running Title: Behavior of Au in a magma*

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43 *Key words: gold, sulfur, sulfide, solubility, partitioning, enrichment, magma, basalt*

44 INTRODUCTION

45 Sulfide liquid (SuL) and monosulfide solid solution (MSS), are key phases that
46 dominate the behavior of highly siderophile elements (HSE) such as Au during magma
47 generation and evolution. It is therefore generally thought that Au-rich magmas cannot form
48 in the presence of residual sulfide in their mantle sources unless it is removed from the source
49 by high degrees of melting (Hamlyn et al. 1985; Solomon 1990), by melting at fO_2 above that
50 of the oxidation reaction that replaces sulfide with sulfur oxide (SSO buffer; Mungall 2002),
51 or by melting at moderately oxidizing conditions (Mungall et al. 2006; Botcharnikov et al.
52 2011) where the presence of sulfate vastly increases the solubility of sulfur and hastens its
53 exhaustion from the mantle restite. Experiments at reducing conditions and high temperatures
54 have determined that the sulfide/silicate partitioning coefficient $D^{\text{sulfide-silicate}}_{\text{Au}}$ is as high as
55 10,000 (e.g., Fleet et al. 1999). Botcharnikov et al. (2011) measured much smaller $D^{\text{sulfide-}}$
56 $^{\text{silicate}}_{\text{Au}}$ of only 100-200 at 1050 °C and fO_2 near SSO, concluding that fO_2 at sulfide saturation
57 has a pronounced effect on the solubility of Au in basaltic and andesitic melts. However,
58 recent experiments between 1050 and 1250 °C and at $P=200$ MPa (Beermann et al. 2011)
59 showed that MSS melts to sulfide liquid over this temperature range (e.g., Bockrath et al.
60 2004). Since the behavior of HSE and gold is strongly controlled by the nature of the sulfide
61 phase present (e.g., Li et al. 1996; Ballhaus et al. 2001; Barnes et al. 2001; Bockrath et al.
62 2004; Mungall et al. 2005; Li and Audetat 2012), this finding raises the question about the
63 importance of P - T - fO_2 conditions for metal mobility during magma generation and evolution.

64 In this study we revisit our earlier results by presenting new experimental
65 measurements of Au partitioning between sulfide phases and basaltic silicate melts at 200
66 MPa in the temperature range 1050 – 1200 °C. We present a revised model of Au behavior
67 during magma generation to take into account the relative importance of SuL and MSS as the
68 restite sulfide phase during mantle melting, and show that melting at relatively low
69 temperature can release Au-rich magmas even in the presence of residual sulfide.

70 **EXPERIMENTAL APPROACH**

71 Silicate melts of basaltic composition (natural basalt from Mt.Etna, Beermann et al.
72 2011) and ferrobaltic composition (Skaergaard intrusion, Botcharnikov et al. 2008;
73 synthetic composition SC1 after Toplis and Carroll 1995) were equilibrated with H₂O- and S-
74 bearing fluids and/or S-rich phases at pressure of 200 MPa and temperature in the range from
75 1050 to 1200°C in Internally Heated Pressure Vessels (IHPV).

76 Experiments at 1050 °C were conducted in gold capsules that are relatively resistant to
77 the reaction with S using starting material composed of dry glass, elemental S and H₂O. At
78 higher T the starting H₂O-bearing basaltic glass of Mt.Etna or the dry ferrobaltic glass
79 (+H₂O) were placed with a sulfide phase in containers made of San Carlos olivine within
80 Au₈₀Pd₂₀ capsules (following the method described in Beermann et al. 2011).

81 The basaltic glass from Mt.Etna contained natural concentrations of trace elements and
82 S-bearing phase was added as natural pyrrhotite (provided by J.Schuessler, Schuessler et al.
83 (2007)). The ferrobaltic glass was doped with trace elements including PGEs and Au using
84 standard ICP-MS solutions; the S-bearing phase added to the glass was synthetic HSE-doped
85 pyrrhotite (~50 µg/g Au; synthesized following the procedure described in Wohlgemuth-
86 Ueberwasser et al. 2007).

87 The redox conditions were adjusted by the Ar-H₂ gas mixture in the IHPV as
88 controlled by a Shaw-membrane and monitored by the analysis of content and speciation of
89 volatiles and of ferric-ferrous ratio in the quenched glasses. The nominal redox conditions
90 varied from $\log fO_2 = \Delta FMQ - 0.4$ to +3.3 (where FMQ is the oxygen fugacity buffered by the
91 fayalite-magnetite-quartz solid assemblage). We note that internal redox reactions involving
92 the olivine containers resulted in fO_2 different from that expected from the redox state
93 imposed by the IHPV in 24-56-hour experiments of Beermann et al. (2011). The exact redox
94 conditions were not determined in the two 86-hour ferrobaltic experiments; for these we
95 have fO_2 calculated from the imposed fH_2 assuming $a_{H_2O} \sim 1$ and taking into account the high

96 S content of the silicate melt (Table 1 in the main text) which points to significant
97 contribution from sulfate.

98 The quenched run products consisted mainly of H₂O- and S-bearing glass, fluid and
99 sulfide phases. Several basaltic samples at 1050°C (close to liquidus in H₂O-rich basalt) also
100 contained small amounts of olivine, magnetite, clinopyroxene and plagioclase (see
101 Botcharnikov et al. 2011 and Beermann et al. 2011).

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103 **ANALYTICAL METHODS**

104 The analytical approaches were reported previously in Botcharnikov et al. (2011) and
105 Beermann et al. (2011) and are briefly reiterated below. Major element concentrations, Ni and
106 S contents were determined using Electron Probe Micro Analysis (EPMA). Water content
107 was evaluated using FTIR spectroscopy or the difference to 100% of the EPMA total. The Au
108 distribution between glasses and solid phases was quantified by laser-ablation inductively
109 coupled plasma mass spectrometry (LA-ICP-MS; Botcharnikov et al. 2011). In this study, we
110 used a 193 nm excimer laser (Coherent GeoLas Pro) with a Zurich Large Volume ablation
111 cell coupled to a quadrupole-based ICP-MS (Agilent 7500cs) at the Institute of Geosciences,
112 CAU Kiel, Germany. In situ-micro-sampling was done with 80 µm pit size and 15 Hz pulse
113 frequency at 10 J·cm⁻² for silicate glass and with 20-80 µm pit size and 5 Hz pulse frequency
114 at 3 J·cm⁻² for sulfide phases. Silicate glass (NIST610 with 23.6 µg/g Au) and sulfide (PGE-
115 A, NiS sulfide with 274 µg/g Au, Gilbert et al. 2012) standards were used for the external
116 calibration of the LA-ICP-MS signal. Silicon and nickel analysed by EPMA were used as
117 internal standards for silicate glasses and sulfide phases, respectively. Glasses were analysed
118 using profiles with the movement rate of 3 µm/s, whereas sulfides were analysed using spot
119 analysis. Micronuggets of Au, typical for quenched silicate glasses obtained in high pressure
120 experiments, were considered as experimental artefacts (e.g., Botcharnikov et al. 2010; Jago

121 et al. 2010; Jegou and Pichavant 2012; Zajacz et al. 2012) and filtered out from the LA-ICP-
122 MS spectra.

123 Small sulfide phases quenched from 1050°C experiments were present as rounded
124 phases with almost homogeneous appearance in BSE images (see Fig.1a). The EPMA
125 analytical data using a focused and defocused beam did not show significant difference for the
126 quenched sulfide phase (MSS) from 1050°C experiments, indicating the presence of a
127 chemically homogeneous phase which could be quenched without phase separation. On the
128 other hand, large sulfide blobs found in experiments at $T > 1050^\circ\text{C}$ showed obvious quench
129 effects and formation of quench phases (see Fig.1b,c) pointing to the existence of a liquid
130 phase at these experimental conditions (e.g., Mungall et al. 2005). Ni was analysed with
131 EPMA (15 kV, 100 nA beam current, calibrated on NiO) using a defocused 20 μm electron
132 beam to overcome heterogeneity of the quenched sulfide liquid (Fig. 1c). The variation in Ni
133 concentration is $< 4\%$. Thus, the size of the beam was large enough to be representative of
134 the bulk composition of the quench sulfide phase existing at high temperature.

135

136 **RESULTS AND DISCUSSION**

137 The sulfide phases produced in our experiments at 1050°C were originally interpreted
138 as droplets of quenched sulfide liquid by Botcharnikov et al. (2011) owing to their rounded
139 shapes (Fig.1a). However, the homogeneous texture and composition of the sulfide phase
140 indicate that it is MSS rather than quenched SuL. In contrast, in high-T experiments (above
141 1050 °C) Energy Dispersive X-ray (EDX) analysis showed qualitatively the presence of
142 oxygen in quench-textured sulfides from high-T experiments (Fig.1b,c), supporting our
143 interpretation that they were oxygen-bearing sulfide liquids at run conditions. The presence of
144 MSS at 1050 °C and of SuL at $T > 1050^\circ\text{C}$ is also in agreement with the phase diagram
145 reported by Bockrath et al. (2004).

146 Figure 2 compares our measured $D^{\text{sulfide-silicate}}_{\text{Au}}$ with previously published values for
147 both MSS and SuL. It must be noted that the data of earlier studies have been obtained using
148 bulk analytical techniques for the determination of Au concentrations resulting in wide
149 scattering of the data presumably due to contamination by metal micronuggets. The
150 application of laser ablation techniques provides much more reliable results because it allows
151 filtering of micronugget spikes from the spectrum. The spike-free parts of the LA ICPMS
152 spectra should theoretically correspond to the parts of the sample which are free of Au
153 particles, because any tiny metal particle should result in a very strong signal compared with
154 very low (ppb to ppm level) Au concentration in the silicate glass. The absence of
155 micronugget effect for sulfide phases is more difficult to prove because the concentrations of
156 dissolved Au are one to two orders of magnitude higher than that in silicate melts. Based on
157 the precision of the determined Au concentrations and on the reproducibility of the repeated
158 measurements for each individual sample, we assume that any micro/nanonugget effect (if
159 present) on the determined partition coefficients is minimized by the signal filtering and is
160 included in the bulk uncertainty. The validation of this assumption is not trivial and requires
161 additional specific study which is technically quite challenging and is not possible based on
162 the experimental results we have. Thus, for the purposes of this study we postulate that the
163 sulfide-silicate partitioning equilibrium is controlled by Au species dissolved in the sulfide
164 and silicate phases and that this equilibrium is not affected by the presence of micro- or nano-
165 particles of Au in either phase.

166 The $D^{\text{sulfide-silicate}}_{\text{Au}}$ for MSS-saturated ($D^{\text{MSS-sil}}_{\text{Au}}$) basalts determined in this study
167 varies from 110 to 280, with an average value of 170 ± 78 ($n = 4$), and is in excellent
168 agreement with our earlier results (Botcharnikov et al. 2011) and the experimental results of
169 Li and Audetat (2012) obtained for systems with different bulk compositions and at much
170 higher P and T (1.5-3 GPa, 1175-1300 °C) where both MSS and sulfide liquid coexisted. The
171 dependence of the partitioning behavior of Au on the redox conditions is not well constrained,

172 yet. The data obtained using LA ICPMS analysis (this study and the work of Li and Audetat,
173 2012) show no dependence within uncertainty in the investigated range of fO_2 .

174 Two examples of basaltic melts at 1150 °C and two examples of ferrobaltic melts at
175 1100 and 1150 °C are consistent within uncertainty and show $D^{\text{SuL-sil}}_{\text{Au}}$ values >1000 (the
176 average value is 2205 ± 485 , $n = 4$). A single low $D^{\text{SuL-sil}}_{\text{Au}}$ value of 358 ± 34 was determined
177 for sample S8 equilibrated at 1200 °C. Both the LA-ICPMS spectra for silicate glasses and the
178 spectra for sulfides collected in this sample showed well-reproducible patterns from several
179 analyses, resulting in a relatively low uncertainty. However, although the concentration of Au
180 in the quenched sulfide is similar to that found in other high- T Etna basalt samples, the
181 concentration of Au in the silicate glass is significantly higher, leading us to suppose that
182 there may have been widely dispersed microdroplets of SuL or Au micronuggets within the
183 glass phase, leading to a spuriously low calculated $D^{\text{SuL-sil}}_{\text{Au}}$. If this experiment is not
184 considered, then the $D^{\text{SuL-sil}}_{\text{Au}}$ values for the systems with SuL are about 20 times higher than
185 the values for MSS-saturated systems, in agreement with the results of Li and Audetat (2012).

186 The good correspondence between several independent datasets shown in Figure 2,
187 obtained using different experimental methods and analytical laboratories, implies that
188 temperature in the range from 1050 to 1350 °C, pressure in the range from 0.2 bar to 3 GPa,
189 basaltic melt composition and redox conditions in the range from $\Delta\text{FMQ}-3$ to $\Delta\text{FMQ}+1.3$ do
190 not have decisive effects on $D^{\text{sulfide-silicate}}_{\text{Au}}$ in basaltic systems. Rather, the main factor which
191 governs Au partitioning is the nature of the sulfide phase present in the system and, if both
192 MSS and SuL coexist, the relative proportions of these phases (Li and Audetat 2012).

193 The other key factor controlling the comportment of Au during mantle melting is the
194 solubility of S, as dictated by T , P , melt composition, and fO_2 (e.g., O'Neill and Mavrogenes
195 2001; Jugo et al. 2005; Liu et al. 2007; Moune et al. 2009; Beermann et al. 2011;
196 Botcharnikov et al. 2011). As predicted by modelling (Moretti and Baker 2008) and
197 demonstrated experimentally (e.g., Beermann et al. 2011; Botcharnikov et al. 2011) we find

198 that the solubility of S at sulfide saturation in basaltic melts has a positive correlation with fO_2
199 due to the concomitant increase in fS_2 and fO_2 in the system. Moreover, at the fO_2
200 corresponding to that of the sulfide-sulfate transition, the solubility of S increases
201 significantly due to the presence of sulfate species with higher solubility than that of sulfide
202 species (e.g., Jugo et al. 2010). Thus, enhanced S solubility observed at the sulfide-sulfate
203 transition may dramatically affect dissolution and extraction of S-bearing phases from mantle
204 rocks during partial melting or the precipitation of S-bearing phases during magma
205 crystallization.

206 In Figure 3 we present the results of some simple models of non-modal fractional
207 melting of the mantle (according to Shaw 1970) to test the effects of the identity of the restite
208 sulfide phase, temperature and fO_2 on Au distribution between mantle and basaltic melt.

209 The concentration of Au in the silicate liquid (C_{Au}) representing the instantaneous
210 fractional non-modal melt of the mantle source was modelled by the expression $C_{Au} =$
211 $C_{oAu}/D_o(1-PF/D_o)^{(1/P-1)}$, where C_{oAu} is the bulk concentration of Au in the source prior to
212 melting, D_o is the bulk partition coefficient for the original solid phases before the onset of
213 melting, P is the bulk distribution coefficient of the minerals that produce the melt, and F is
214 the weight fraction of melt produced (see eq.13 in Shaw 1970 for details). Since sulfides have
215 predominant control on Au behavior, D_o and P are dependent on the abundances of sulfides
216 and Au in the source, on the solubility of sulfides in the melt and on $D^{\text{sulfide-silicate}}_{Au}$. We
217 assume that Au is perfectly incompatible with silicate minerals, so that the D_o and P terms
218 depend only on the sulfide/silicate partition coefficient and the fraction of sulfide that enters
219 the silicate melt in the melting reaction (i.e., its solubility). Pooled melts were modeled with
220 the expression $C_{Au} = C_{oAu}/F[1-(1-PF/D_o)^{1/P}]$ (eq. 14 in Shaw 1970) with all terms defined as
221 above.

222 The initial concentration of Au in the mantle is assumed to be about 1 ng/g, and the
223 abundance of S present in the mantle as sulfides is considered to be about 250 $\mu\text{g/g}$ S

224 (McDonough and Sun 1995; 690 $\mu\text{g/g}$ sulfide, assuming a sulfide phase composed mainly of
225 FeS). The exact S content of the mantle source depends presumably on the tectonic
226 environment, i.e, whether the mantle has been depleted by previous melt extraction or
227 enriched by metasomatic reactions with S-bearing fluids. The depleted mantle that is first
228 encountered by fluids in nascent arcs probably has about 120 ppm S (Salters and Stracke
229 2004) but then S is added in unknown quantities as arc system evolves (e.g., Mungall 2002,
230 Richards 2009), hence any S concentration can be chosen. Thus, here we use an average S
231 value for pyrolite mantle for simplicity. The variation in the amount of sulfide phase present
232 in the mantle source at given bulk Au content may influence the absolute concentrations of
233 Au in the produced melts but the relative effects of MSS and SuL on the partitioning will not
234 be affected. Higher initial S contents in the mantle will correspond with higher initial modal
235 abundance of the condensed sulfide phase and will require greater degrees of melting before
236 sulfide exhaustion from the restite, but the fundamental control of Au concentration will
237 remain the physical state of the sulfide phase.

238 The calculations were done for temperature of 1100°C which is at the lower limit of
239 partial melting temperatures for arc magma generation at 1 GPa, that is for the mantle
240 containing certain amount of water and relevant for the stability of MSS (Bockrath et al.
241 2004). Temperature of 1200°C is relevant for the melting of dry peridotite at 1 GPa where
242 sulfide liquid only is stable. The dissolution reaction of sulfide is constrained by our estimate
243 of the solubility of S in basaltic melt at 1100 and 1200°C using extrapolation and
244 interpolation of experimental data for basalts obtained in the studies of Jugo et al. (2005), Liu
245 et al. (2007), Beermann et al. (2011) and Botcharnikov et al. (2011). The effect of pressure on
246 S solubility in basaltic melts is relatively small (e.g., Mavrogenes and O'Neill 1999; Moune et
247 al. 2009) and assuming isobaric melting we do not consider any pressure effect. The $D^{\text{sulfide-}}$
248 $^{\text{silicate}}_{\text{Au}}$ is assumed to be independent of T , P , $f\text{O}_2$, and melt composition and was taken to be

249 170 and 2200 for MSS and SuL, respectively (average values determined in this study, Table
250 1).

251 Two principal controls are apparent on Au compartment in Figure 3; the identity of the
252 sulfide phase in the restite and the oxidation state at which melting occurs. At 1100 °C all
253 sulfide is present as MSS, which has a low enough $D^{\text{MSS-sil}}_{\text{Au}}$ to allow significant
254 concentration of Au in the melt even while sulfide remains stable in the restite. However at
255 1200 °C sulfide is present in liquid form, with a much larger $D^{\text{SuL-sil}}_{\text{Au}}$. The concentration of
256 Au in basalt is very low while SuL remains in the restite, rising to high values only in the last
257 infinitesimal stages of melting prior to complete sulfide exhaustion. The instantaneous
258 fractional melts approach a singularity at that point before falling to zero Au thereafter,
259 whereas the pooled melts rise to join the curve representing all S-undersaturated melts
260 (including those formed at $f\text{O}_2$ above SSO where sulfide is never a stable restite phase). The
261 significance of the identity of the sulfide phase is that depending on the bulk S content of the
262 mantle Au-rich magmas can form at arbitrarily low degrees of melting if MSS is in the restite,
263 whereas Au-rich magmas in equilibrium with sulfide liquid can only be generated if the
264 degree of melting is sufficient to completely dissolve SuL into the basaltic melt.

265 The second key control on Au in basalts is $f\text{O}_2$, due to the dramatic effect it has on S
266 solubility. High S solubility leads to rapid exhaustion of the sulfide phase from the restite,
267 whether it is MSS or SuL, allowing melt compositions to join the sulfide-absent curve
268 (dashed lines, Fig. 3c, 3d). Whereas more than 8% fractional melting is required to exhaust
269 sulfide from the source at FMQ, the sulfide has been completely dissolved after less than 3%
270 melting at FMQ+1.5.

271 Also shown for comparison in Figure 3 are the compositions of unusually Au-rich
272 alkaline mafic rocks from Hawaii (Sisson 2003), which were produced by small degrees of
273 melting of phlogopite garnet lherzolite at about 1350 °C, 3.0 GPa (Sisson et al. 2009) at
274 ΔFMQ between 0.5 and 1.5. For each sample containing > 10 wt% MgO, the melt fraction F

275 was calculated using the measured Zr concentrations and assuming that $D_{\text{oZr}} = 0.033$ and C_{oZr}
276 = $8.9 \mu\text{g/g}$ (e.g., Sisson et al. 2009) for pooled modal melts (eq. 10 in Shaw 1970). Although
277 the data are rather scattered, it is evident that even the highest Au values reported by Sisson
278 (2003) would be unremarkable if melting occurred in the presence of MSS, whereas some
279 low-degree melts contain an order of magnitude too much Au to have been generated in the
280 presence of residual sulfide liquid. The MSS solidus occurs close to $1350 \text{ }^\circ\text{C}$ at 3 GPa
281 (Bockrath et al. 2004), lending some support to our inference that the Hawaiian basalts were
282 generated at a temperature below the MSS solidus.

283

284 CONCLUSIONS

285 New experimental and analytical data illustrate that the nature of sulfide phase present
286 in magmatic source during magma generation or evolution exerts a major control on the
287 partitioning of Au between sulfides and silicate melt. Partition coefficients found for systems
288 saturated with monosulfide solid solution (MSS) are at least order of magnitude lower than
289 those observed in systems coexisting with sulfide liquids (SuL), implying that Au-enriched
290 magmas are expected to be formed at lower temperatures or at higher pressures, when MSS is
291 stable. Thus, the predominance of MSS over SL in the source or/and oxidizing conditions
292 close to or above the sulfide-sulfate transition are prerequisite factors governing occurrence of
293 Au-enriched magmas.

294

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414 FIGURE CAPTIONS

415

416 **Figure 1.** Back-scattered electron images illustrating the appearance of sulfide phases
417 in experiments at 1050°C (a) and 1150°C (b,c). (a) Sulfide, olivine and silicate melt phases in
418 the experimental product from run 0-15-2-red (Table 1). The sulfide phase is monosulfide
419 solid solution (MSS). The MSS is commonly in direct contact with olivine (OL) and fluid
420 bubbles (black) pointing to nucleation and equilibration processes during the experiment. (b)
421 Experimental product from experiment S19 illustrating coexistence of sulfide liquid, fluid
422 bubble, silicate melt and olivine container. Sulfide liquid experienced quench modifications
423 as evident from detail view in (c) representing the area outlined by the dashed line in panel
424 (b).

425 **Figure 2.** Partition coefficients of Au between sulfide phases and silicate melt. Grey
426 symbols represent literature data for the systems with sulfide liquid (St90 is after Stone et al.,
427 1990; Be94 is after Bezmen et al., 1994; Cr97 is after Crocket et al., 1997; Fl99 is after Fleet
428 et al., 1999; Li12 is after Li and Audetat, 2012); open circles are the data of Li and Audetat
429 (2012) for the partitioning between MSS and silicate. Black squares and open triangles are the
430 data from this study for SuL/silicate and MSS/silicate coefficients, respectively.

431 **Figure 3.** The model of Au extraction in an instantaneous fractional melt during
432 melting of the mantle containing 1 ng/g Au and 250 µg/g S. The model takes into account the
433 redox conditions, the degree of partial melting (F) and the nature of sulfide phase present: (a)
434 for MSS at 1100°C and (b) for sulfide liquid at 1200°C. The grey rectangles illustrate the
435 redox conditions and the range of Au concentrations in bulk rocks for basanitic magmas from
436 Kilauea (Sisson, 2003). The solid vertical lines define the stability field of sulfides as a
437 function of fO_2 . The long-dashed lines show the expected concentration of Au in the oxidized
438 melts with 5% melting at complete sulfide exhaustion. Panels 3c and d show the dependence
439 of melt Au on degree of melting at various oxygen fugacities, showing both instantaneous
440 (short-dashed lines) and pooled (solid) fractional melts; dashed lines show the compositions
441 of melts produced after sulfide exhaustion either due to melting above the SSO buffer or due
442 to complete dissolution of sulfide in the silicate melt. Since a condensed sulfate phase does
443 not form until S concentrations reach approximately 1% in the melt, we neglect sulfate phases
444 in our restite assemblage, assuming that all S in the mantle assemblage is either MSS or SuL.
445 Black dots are the data on Au content in basanitic magmas (see text).

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449 Table 1. Experimental conditions at P=200 MPa and analytical results.
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Run	S6 *	S36 *	S41 *	0-15-2-red §	BOL6	S19 ^b	S20 §	BOL5	S8 §
T, °C	1050	1050	1050	1050	1100	1150	1150	1150	1200
logfO ₂	-9.2	-10.1	-10.5	-9.7	-8.1 **	-8.4	-8.6	-8.0 **	-7.8
ΔFMQ	0.9	-0.1	-0.4	0.3	1.3 **	0.3	0.1	0.7 **	0.3
S in melt, μg/g	2760±60	1250±60	710±40	1200±100	8190±350	3100±600	2700±700	6110±260	3000±400
H ₂ O in melt, wt%	4.5	4.3	2.7	4.8	4.6	3.2	3.1	2.8	3.4
Fe in sulfide, wt%	59.59±0.24	61.43±0.34	62.21±0.49	60.87±0.40	58.73±0.54	60.35±0.59	60.33±1.03	55.61±0.76	59.78±0.73
S in sulfide, wt%	41.01±0.28	38.14±0.22	37.76±0.17	38.76±0.19	34.49±0.84	34.26±0.33	33.98±0.33	35.67±1.23	34.66±0.59
Ni in sulfide, μg/g	n.d.	1254±130	818±61	1734±367	11498±304	6152±144	4639±163	27192±817	5377±142
Au in melt, μg/g	7.97±0.03	2.96±0.22	0.91±0.12	13.04±2.61	0.22±0.05	0.76±0.16	0.52±0.10	0.38±0.08	6.096±0.309
Au in sulfide, μg/g	1431±103	326±186	253±110	1499±328	371±64	2098±174	1268±45	737±98	2185±176
D _{Au} sulfide/silicate	179±13	110±63	278±126	115±34	1694±467	2764±607	2438±464	1924±468	358±34
D _{Au} MSS average	170±78								
D _{Au} SuL average						2205±485			

451 Notes:

452 n.d. - not determined;

453 * - samples from Botcharnikov et al. (2011), reanalysed for sulfide composition;

454 § - samples from Beermann et al. (2011), reanalysed for sulfide composition and for Au
 455 concentrations in sulfides and silicate melt;

456 ** - redox conditions were estimated from the conditions imposed by Ar-H₂ mixture of the
 457 IHPV.

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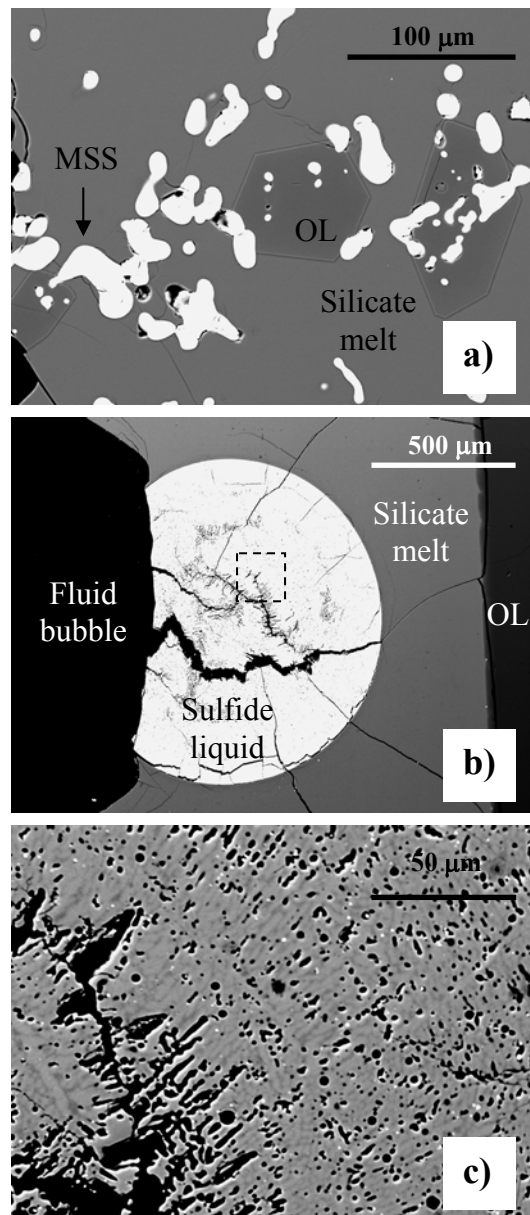


Figure 1. Botcharnikov et al.

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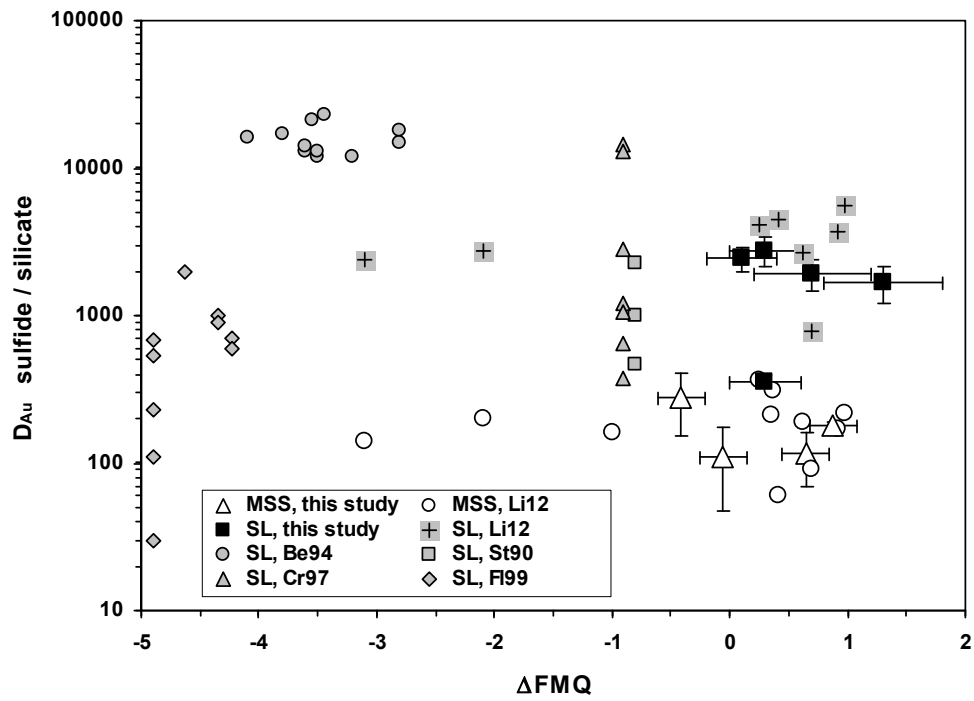


Figure 2. Botcharnikov et al.

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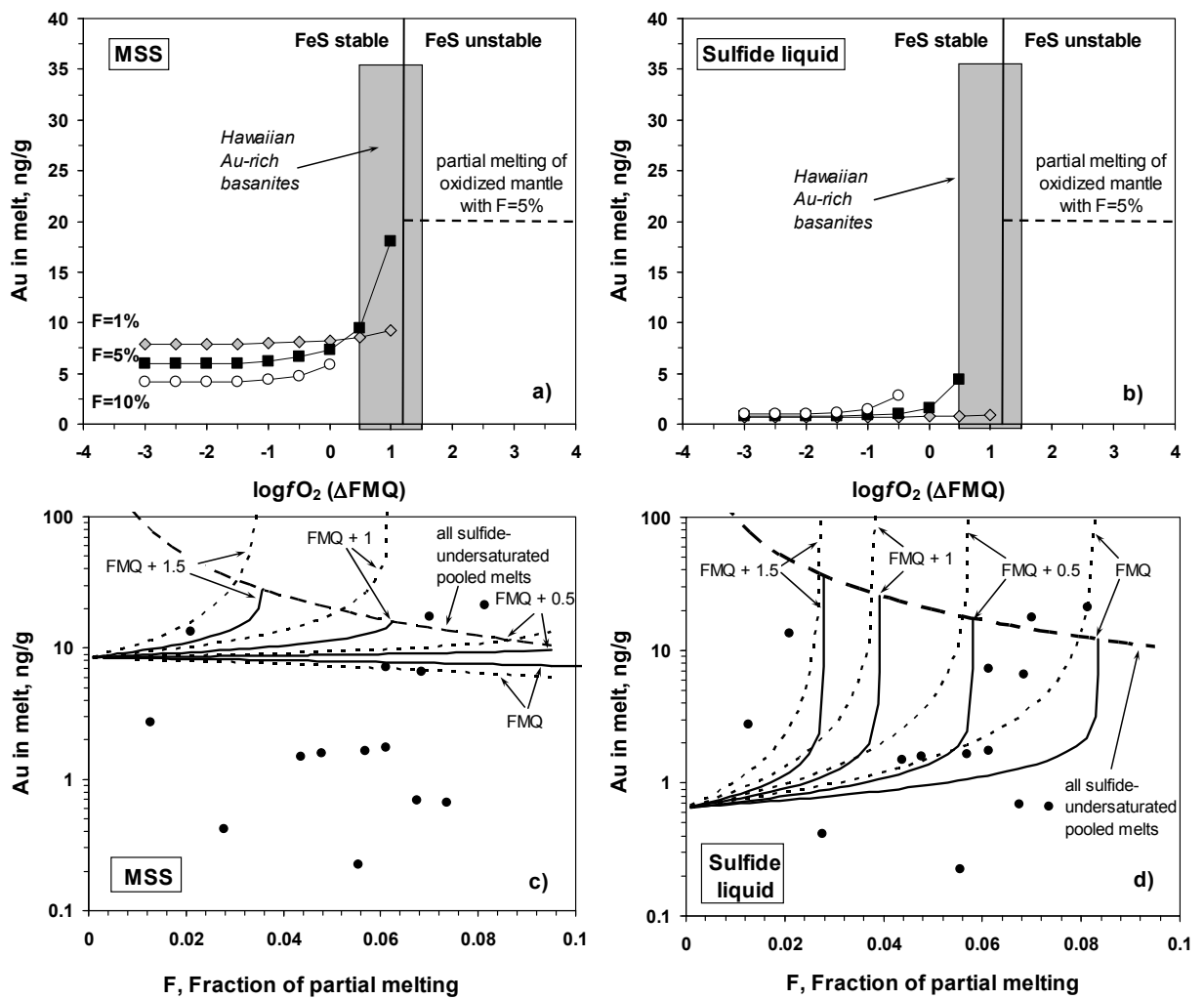


Figure 3. Botcharnikov et al.