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## SUPPLEMENTARY INFORMATION

## Sample description

In total five samples were collected for analysis, representing mafic composition with varying degree of open-system degassing. The Kilauea samples consist of two samples of pahoehoe tholeiitic basalts from the ongoing 61g flow at the Pu'u O'o crater of East Rift Zone (ERZ) (KL-1, 19.33264°N 155.04158°W and KL-2, 19.32979°N 155.04308°W) collected roughly 1 meter beneath the tumuli center (Fig. 1). They are highly vesicular (50% -60% for KL-1, and 70%-80% for KL-2) with aphanitic texture in the host basalt. KL-1's vesicles (0.5-0.9 cm in diameter) are larger than those in KL-2 (0.1-0.3 cm in diameter). No olivine phenocrysts were observed in hand sample observation. Under the scanning electron microscope (SEM), both samples displayed a moderately glassy texture, with abundant microcrystallites of plagioclase, pyroxene, and dendritic magnetite.

The Mauna Loa samples consist of two samples from a'a alkalic basalt from a 1907 flow at Southwest Rift Zone (SWRZ), collected along Highway 11 (ML-1 and ML-2, 19.18°N 155.276°W). They have a vesicular and porphyritic texture, with 1-5 mm olivine phenocrysts embedded in finegrained groundmass. Unlike the Kilauea samples, ML-1 and ML-2 contain fewer vesicles and are dominated with much larger, titanium-rich iron oxides when observed under SEM. Together with the frequent olivine phenocrysts it suggests a more extensively crystallized magma composition before eruption.

One MORB pillow basalt sample from the Chile Ridge in the southeast Pacific was also examined (45.8°S, 78.3°W; Klein and Karsten, 1995). In previous studies it was reported to have chemical composition more similar to that of arc volcanoes instead of other MORBs, which may be attributed to contamination by marine sediment and altered oceanic crust in the mantle source (Klein and Karsten, 1995). The sample exhibits a fresh interior with glassy texture in hand sample, and small vesicles with irregular shapes and size (from circular vesicles with 10 microns in diameter to large

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irregular vugs of open space >50 microns across) present when examined under SEM. Klein and Karston (1995) reported no abnormal values of Cu, Ag and Au in the bulk composition of the Chile Ridge samples. It is unlikely that our sample here is contaminated by sediment or altered oceanic crust, at least with regards to the metals of question in our study.

# Methods:

#### **Electron microprobe analysis**

Polished and carbon-coated thin sections were made for each sample and they were scanned with Cameca CAMEBAX electron microprobe at Duke University. The original objective was to look for variations in Cu/S ratios in sulfide minerals as a proxy for sulfur loss to degassing, and some native copper and silver were indeed found associated with sulfide. However, it was quickly observed that the most effective way to locate native metals was by their relative brightness in back-scattered electron imagery (BSE), as native metals have a higher bulk average atomic number than typical iron oxides and other common igneous minerals. Energy dispersive spectrometry (EDS) analysis was carried out on such grains to obtain the specific composition of the mineral. If the grain indeed displayed a metal peak on the EDS spectrum, X-ray composition map was constructed to record the specific mineral and textural environment proximal to the native metal. Each thin section was scanned at least twice to locate as many native metal grains as possible, as well as to affirm previous findings as unequivocally in-situ deposit instead of surface debris. Many grains were too small to get a clean EDS spectrum without including some of the surrounding silicate matrix. These mixed phase analyses were typically enriched in Cu, Ag, or Au (>10 wt.% but <50 wt%), but were counted as metal phase based on their high backscattered electron brightness (= high atomic number) of the backscatter image.

During the thin-section preparation stage, the samples were not exposed to any external equipment that may hold high concentration of silver or gold. On the other hand, the samples were exposed to copper-rich alloy polishing laps (mainly brass and bronze residue from thin-section preparation) during the prep stage and chips of brass and bronze embedded in the epoxy of the thinsection are surprisingly common. These contaminants were readily detected with by their unusually

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large size, angular nature, suspicious position in epoxy, and an abnormal Sn or Zn peak along with enriched Cu in the probe analysis. They were excluded in the final data.

To further confirm the primary origin of the native metals, we made thin-sections of the same rock sample (KL-2) in two different locations (Duke University and Texas Petrographic Services, Inc.) and we found native metals and metal alloys in both thin-sections. We also took one of the thinsection (KL-2) and scrubbed it clean with towel, brush and tap water, before recoating it with carbon coat. The recoated thin section still contains native metals and metal alloys when examined under the microprobe.

## Whole-rock analysis

Each rock sample was powdered, digested and analyzed on a VG PQ3 ICP-MS at Duke University following the protocols adapted from those described in Meurer et al. (1999) and Stewart et al. (2002). Three separate analyzing vials were prepared for each rock sample. The digested solutions were analyzed at 1:2000 dilution for minor and rare earth element concentration. The detection limit (DL) for silver on the PQ3 for the duration of analysis was 0.002 ppb in solution as calculated following the procedures of Taylor (2001). This was comparable to the 0.001 ppb for Ag reported for the PG3 (e.g. Taylor, 2001). DL for Au was not determined but was expected to be similar to Ag based on the high-mass sensitivity curve of the PQ3 (e.g. Taylor, 2001). The dilution level applied in this study yields an effective DL of ~2-4 ppb (ng/g) for Au and Ag in the solid rock samples. The detection of Ag in the ICP-MS was further complicated by two zircon oxides, <sup>91</sup>Zr<sup>16</sup>O and <sup>92</sup>Zr<sup>16</sup>O<sup>1</sup>H, which were constantly being produced in the IC-Plasma. These two zircon oxides have the same atomic numbers as the two Ag ions of interest, <sup>107</sup>Ag and <sup>109</sup>Ag, and made the otherwise small Ag signal (~90 ppb in a typical Hawaiian basalt, Greaney et al., 2017) even harder to detect, despite of the fact that the bulk concentration of Ag in our samples should be higher than the effective DL of 2-4 ppb. This problem of interference was not an issue for Au, as the potential interfering agent for <sup>197</sup>Au, <sup>181</sup>Ta<sup>16</sup>O, was present at minor amount at best given the low Ta content (0.4-1ppm) in our samples.

## Metal enrichment modeling

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To illustrate the metal enrichment during crystallization and degassing, we constructed a simple partitioning model under Rayleigh fractionation conditions (Ohara *et al.*, 1981):

$$C_{liq} = C_0 \times F^{\overline{D}-1} \tag{1}$$

where  $C_{liq}$  and  $C_0$  represent the concentration of metal in the silicate liquid and its initial concentration, respectively,  $\overline{F}$  represents the weight fraction of liquid in the system.  $\overline{D}$  is the bulk partition coefficient of metal in the system:

$$\overline{D} = D_{vapor/liq} \times X^{vapor} + \sum \left( D_{xtal/liq}^{i} \times X^{i} \right)$$
(2)

 $D_{vapor/liq}$  is the vapor/liquid partition coefficient,  $D_{xtal/liq}^{i}$  the crystal/liquid partition coefficients for each mineral phase *i*, and  $X^{i}$  and  $X^{vapor}$  are the weight fraction of crystals *i* and vapor separating from the liquid, respectively. For the metals consider here, they are incompatible in most common silicate and oxide phases and thus  $D_{xtl/liq}^{i} = 0.0$ . Using equation 2 for the evolving liquid composition and the vapor/liq partition coefficient, the concentration of the metal in the vapor as crystallization proceeds is given by:

$$C_{vapor} = C_0 \times F^{D-1} \times D_{vapor/liq} \tag{3}$$

Allard *et al.* (2000) have reported an enrichment of 10 for Au in vapor relative to silicate liquid. While no partition coefficient between vapor and basaltic melt has been investigated for Ag, Simon et al. (2007) has reported  $D_{vapor/melt}(Ag) = 32$  in a rhyolite system. If we take  $X_{melt} = 0.99$ ,  $X_{vapor} = 0.01$ , and  $D_{vapor/melt} = 10$  as a conservative value for both Au and Ag, assuming they are incompatible to other silicate/oxides crystalizing minerals as note above, then the metal concentration in the vapor as crystallization proceeds is given by

$$C_{vapor} = C_0 \times F^{-0.9} \times 10 \tag{4}$$

Au will reach saturation in Hawaiian systems when  $F \le 0.0054$  and  $F \le 0.00046$  in MORB. Ag will reach saturation in Hawaiian systems when  $F \le 0.015$  and  $F \le 0.003$  in MORB (Table 2 for specific initial metal concentrations in silicate liquid used in calculation).

Additional figure examples



Figure S1: Native copper (Cu) found at the junction between plagioclase (Pl) and pyroxene (Px) in KL-1. a) back-scattered electron image. b) X-ray composite composition map, with EDS analysis spectrum that shows a strong Cu peak and a minor Ag peak.



Figure S2: Native gold (Au) sitting in the cracks along pyroxene (Px) grain boundaries in KL-2. a). Back-scattered electron image. b) X-ray composite composition map.



Figure S3: Electrum (Au-Ag alloy) in KL-2. a) back-scattered electron image. b). X-ray composite composition map. C) Fe X-ray map. D) Mg X-ray map.



Figure S4: Metal enrichment of silicate liquid and evolving vapor as a function of fraction of liquid remaining for Ag (redrawn after Wernette et al., in prep). The metal concentrations for the silicate liquid (red) and co-existing vapor (blue) are shown for a range of initial liquid composition encompassing Hawaiian basalt and MORB following a Rayleigh fractionation enrichment. The horizontal red dashed line marks the saturation level of Ag in silicate liquid (6 ppm, Zajacz et al., 2013).



Fig. S5: Vesicle profile of a 3m lava flow cross-section adapted from Sahagian et al. (2002) with two proposed models for vesicle disappearance after metal precipitation. A) Matrix collapse: After the vesicle is completely degassed, the partially solid surrounding matrix collapses into the vesicle and preserves the precipitated metals between voids or between minerals grains that moved into the vesicle, as seen in some of the native gold in the Kilauea samples and especially the a'a flow samples. b) Late liquid inflow: during degassing, the crystal framework surrounding the vesicle may be rigid but porous enough such that only evolved interstitial liquid flows into the vesicle (Philpotts and Carroll, 1996). The open vesicle will continuously attract degassing evolved liquids. The inflow liquid and concurrent degassing will push or localize metal precipitation to the vesicle center. The Mg-rich pyroxene in Fig. 2 crystallizes from an early cooling liquid, whereas the magnetite-rich assemblage near the silver is the late-crystallizing, more evolved liquid that infilled the vesicle.



Figure S6: Open vesicle in KL-2. Note the dendritic magnetite crystals scattered along the vesicle rim with similar morphology to magnetite in infilled vesicles shown in Fig. S3 and Fig. 2.

# Table S1: The distribution of native metals in all analyzed samples with different flow

Sample	Flow type	Native Cu	Cu-Fe- S± O	Cu-O ± Fe	Native Ag	Ag- Au	Ag-S- (O)	Ag- (O)	Native Au
KL-1	Dahaahaa	5	2	5	5	-	-	-	-
KL-2	Panoenoe	2	1	1	8	1	1	-	28
ML-1	۸'۵	4	3	3	2	-	-	-	1
ML-2	A a	-	1		-	-	1	-	-
Chile	Pillow								
Ridge MORB	basalt	2	3	-	8		-	-	2

morphology.

Metal	C <sub>0</sub> (pp)	m)	Saturation	Temperature	Pressure	Oxidation
	Hawaiian	MORB	(ppm)	( <b>°</b> °)	(MPa)	condition
Au	$0.0027^{a}$	0.00023 <sup>b</sup>	0.49 <sup>c</sup>	1050 <sup>°</sup>	200 <sup>c</sup>	FMQ <sup>c</sup>
Ag	0.09 <sup>d</sup>	0.0178 <sup>b</sup>	6 <sup>e</sup>	800-1030 <sup>e</sup>	$200^{\rm e}$	NNO-0.8 <sup>e</sup>
Cu	133 <sup>a</sup>	72.29 <sup>f</sup>	600 <sup>g</sup>	1245 <sup>g</sup>	0.1 <sup>g</sup>	FMQ <sup>g</sup>

**Table S2.** The initial bulk composition of metals in a Hawaiian and MORB basalt and saturation concentrations.

Notes. a. Fresh basalt from Episode 15, eruption of Pu'u O'o from Crocket, 2000; b. Fresh interior of T3-72D254-16-4 from Keays and Scott, 1976; c. Bell et al., 2011; d. Whole rock powder composition in Greaney et al., 2017; e. Zajacz et al., 2013; f. average whole-rock analysis value from Klein and Karsten, 1995; g. Ripley et al., 2002

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All concentrations in ppm except P205, which is wt %. Zr data should be considered with caution, digestion process does not necessarily completely dissolve zircons. Values are relative to pre-LOI weights of samples and standards.

Sample	Vial	P2O5 L	.i	Ве	Sc	v	Cr	Co I	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Cs	Ва	La	Ce	Pr	Nd	Sm	Eu '	Гb (	Gd D	)y ⊦	lo E	۲١	۲b I	u I	Hf '	Та	Pb 1	Th (	IJ
KL-1	IC14	0.2	5.3	0.9	31.6	302.4	254.4	76.8	78.7	150.3	115.7	8.1	328.6	27.1	151.2	13.7	0.1	104.8	11.7	28.8	4.3	19.2	5.4	1.8	0.9	5.7	6.0	1.0	2.5	2.2	0.3	3.7	1.0	0.9	0.9	0.3
KL-1	T44	0.2	5.1	0.9	30.6	291.9	251.3	69.5	76.4	147.1	113.3	8.0	318.0	26.4	121.0	13.3	0.1	102.4	11.5	28.0	4.2	18.6	5.3	1.8	0.9	5.7	5.9	1.0	2.5	2.1	0.3	3.6	1.0	0.8	0.9	0.3
KL-1	AR21	0.2	5.1	0.9	30.2	298.7	255.6	69.7	76.0	140.6	110.5	8.0	326.6	26.8	123.6	13.6	0.1	103.5	11.5	28.2	4.2	19.0	5.3	1.7	0.9	5.7	5.9	1.0	2.5	2.2	0.3	3.7	1.0	0.9	0.8	0.3
KL-2	BO34	0.2	4.8	0.8	30.2	282.6	292.7	84.0	88.3	129.7	105.6	7.3	312.8	24.2	121.4	12.3	0.1	97.9	10.6	26.3	3.9	17.6	4.9	1.6	0.9	5.4	5.6	0.9	2.3	1.9	0.3	3.4	0.9	0.8	0.8	0.2
KL-2	JW34	0.2	5.0	0.8	30.5	285.7	303.2	86.7	89.8	132.7	107.7	7.4	320.0	25.0	138.9	12.5	0.1	97.6	10.7	26.4	4.0	17.8	4.9	1.6	0.9	5.4	5.5	0.9	2.3	2.0	0.3	3.6	0.9	0.8	0.8	0.2
KL-2	L11	0.2	5.0	0.9	30.6	286.7	310.7	72.2	96.0	139.1	112.0	7.6	323.4	25.4	115.5	13.0	0.1	99.2	10.8	26.6	4.0	17.8	5.0	1.6	0.9	5.3	5.5	0.9	2.3	2.0	0.3	3.4	1.0	0.8	0.8	0.3
ML-1	JW32	0.2	4.2	0.7	25.7	222.9	642.1	107.5	520.7	116.8	112.3	6.2	282.9	21.7	97.7	8.0	0.1	78.8	8.1	20.7	3.2	14.8	4.2	1.4	0.8	4.6	4.9	0.8	2.0	1.7	0.3	2.9	0.7	0.7	0.5	0.2
ML-1	JW35	0.2	4.2	0.7	24.6	229.2	565.9	111.0	546.3	115.4	110.3	6.1	283.9	22.0	96.3	8.1	0.1	76.4	8.0	20.3	3.1	14.2	4.1	1.4	0.7	4.5	4.8	0.8	2.0	1.7	0.2	2.9	0.6	0.7	0.5	0.2
ML-1	IC18	0.2	4.4	0.7	25.7	235.9	567.5	115.0	558.4	115.8	111.2	6.2	287.3	22.3	98.0	8.3	0.1	77.7	8.1	20.6	3.1	14.7	4.2	1.4	0.8	4.5	4.7	0.8	2.0	1.7	0.2	2.9	0.7	0.7	0.5	0.2
ML-2	JW29	0.2	4.2	0.7	26.1	217.1	667.4	143.2	456.3	79.3	111.9	6.2	284.0	21.7	96.0	8.2	0.1	79.2	8.1	20.8	3.2	14.8	4.1	1.4	0.8	4.7	5.0	0.8	2.0	1.7	0.3	3.0	0.8	1.2	0.5	0.2
ML-2	T5	0.2	4.3	0.7	26.1	220.5	669.8	145.8	461.7	80.2	115.0	6.5	292.2	22.3	109.1	8.3	0.1	81.3	8.4	21.2	3.3	15.0	4.3	1.4	0.8	4.7	5.0	0.8	2.1	1.8	0.3	3.0	0.8	1.2	0.5	0.2
ML-2	IC25	0.2	4.2	0.7	25.2	222.5	526.6	140.8	450.2	77.5	110.9	6.2	280.5	21.4	93.8	7.9	0.1	77.2	7.9	20.2	3.1	14.5	4.1	1.4	0.7	4.6	4.9	0.8	1.9	1.7	0.2	3.0	0.8	1.1	0.5	0.2
MORB	X5	0.2	7.4	0.8	37.2	300.0	159.7	89.0	78.2	58.5	96.7	0.8	131.6	44.4	128.5	3.2	0.0	10.4	4.7	15.4	2.7	14.4	4.9	1.6	1.2	6.7	8.5	1.6	4.4	4.3	0.6	3.7	0.4	0.6	0.2	0.1
MORB	BO28	0.2	7.7	0.8	38.6	313.7	167.3	91.9	81.0	60.7	155.2	1.1	145.3	46.7	146.5	3.3	0.0	11.9	5.0	16.1	2.8	14.9	5.1	1.6	1.2	6.9	8.8	1.7	4.5	4.5	0.7	3.9	0.4	0.6	0.2	0.1
MORB	BO19	0.2	8.0	0.8	38.5	317.9	170.0	95.7	81.4	61.8	100.9	0.9	138.1	46.3	160.1	3.3	0.0	11.2	5.0	16.0	2.8	14.7	5.2	1.7	1.2	6.8	8.7	1.6	4.5	4.5	0.7	3.9	0.4	0.6	0.2	0.1