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# Volcanic Processes and the Genesis of Porphyry and Epithermal Ore Deposits

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## Supplementary Information

### Geological Context

Merapi volcano was most active within the last 40,000 years (Camus et al., 2000). Since the beginning of the 20th century, Merapi has alternated between periods of quiescent degassing and lava dome growth and occasional collapse, typically lasting a few years, and periods of explosive activity, with St-Vincent - type explosions, pyroclastic flows and surges, typically lasting several months. From September 2002 to March 2006, the volcano was in a phase of quiescent degassing. From March to July 2006, it went through a phase of explosive activity, with its plume reaching an altitude of 3.7 km and erupting about  $1.07 \times 10^{10}$  kg of rock (Ratdomopurbo et al., 2013). On May 27th 2006, a magnitude 6.3 earthquake occurred about 50 km SW of Merapi at a depth of about 10 km, resulting in a three-fold increase of volcanic activity (Global Volcanism Program of the National Museum of Natural History – Smithsonian Institution (GVP); United States Geological Survey, consulted online in June 2015). From July 2006 and until October 2010, it went back to a phase of quiescence. In 2010, the volcano had its greatest eruption since 1872. From October to November 2010, Merapi erupted about  $3.1 \times 10^{11}$  kg of rock and degassed about  $0.44 \times 10^9$  kg of SO<sub>2</sub> (GVP; Surono et al., 2012). Although the initial explosion occurred 19 hours after a magnitude 7.7 earthquake 1200 km NW of Merapi, any links between this seismic event and the major eruption of 2010 are difficult to prove. Volcanic vapours at Merapi emanate from distinct fumarole fields. Gendol was the highest temperature fumarole field, with temperature reaching up to 900°C (Le Guern, 1979), until it was destroyed by the eruption in 2006. Woro was a lower temperature fumarole field, reaching up to 710°C (Le Guern et al., 1982), until it was destroyed by the 2010 eruption. In this paper we used only the volcanic vapour data from Woro as they were the only dataset that could be compared between 2004 and 2006 and because vapours from distinct fumarole fields cannot be compared directly.

### Supplementary Methods

#### *Condensates of volcanic vapor*

Volcanic vapours were sampled by inserting meter-long fused silica tubes into fumaroles and connecting the quartz tubes to condensers filled with ice and pumping the vapour slowly through the condenser using a hand-held pump. The liquid that collected in the condenser was stored in Teflon bottles and analyzed at Actlabs Inc., Canada, by a combination of inductively coupled plasma mass spectrometry (ICP-MS), ICP optical emission spectrometry (OES), neutron activation (INAA) and ion chromatography.

### *Sublates of volcanic vapor*

The sampling of vapor condensates was complemented by inserting meter-long, fused silica tubes into the fumaroles immediately after the condensates had been collected and waiting until sufficient solid had precipitated on the inner walls of the tubes (Le Guern et al., 1982). In 2004, tubes were inserted for periods varying between four and six days. In 2006, tubes were in place for a period of 22 days. The sampling was done during the dry season to avoid dissolution and redistribution of sublates by rain. Temperatures were measured along the tube centerlines at 10 cm intervals using a meter-long thermocouple and the tubes were subsequently cut into sections representing increments of 10 to 20°C. The sublates were scraped off and a fraction of each sublate was mounted on a glass slide and polished. As several of the sublate phases are water soluble (e.g., halite and sylvite), the polishing agent (aluminium oxide or diamond powder) was suspended in alcohol rather than water. The phases in the polished sections were analysed chemically using a JEOL JXA-8900L electron microprobe (EMPA) at McGill University. A second fraction of sublate was scanned using a Siemens D500 X-ray diffractometer equipped with a Co tube and a Si detector at the Université du Québec à Montréal. The diffraction patterns were analyzed using Jade software at McGill University for identification of major phases.

## Supplementary Tables

**Table DR1. Mineralogy and temperature distribution of volcanic vapour sublimates collected from Merapi volcano in 2004-2006**

Mineral	Formula	Year	Max	Min
Anglesite	PbSO <sub>4</sub>	2004	470	440
Anhydrite	CaSO <sub>4</sub>	2004	500	225
Arsenic	As	2004	350	190
Barite	BaSO <sub>4</sub>	2004	470	460
Bismuthinite	Bi <sub>2</sub> S <sub>3</sub>	2006	500	340
Challacolloite	KPb <sub>2</sub> Cl <sub>5</sub>	2006	560	320
Cotunnite	PbCl <sub>2</sub>	2006	590	300
Fe-Cr alloy	Fe,Cr	2006	590	340
Galena	PbS	2006	560	300
Halite	NaCl	2004, 2006	580	420
Hematite	Fe <sub>2</sub> O <sub>3</sub>	2004, 2006	600	320
Ilmenite	FeTiO <sub>3</sub>	2004	470	460
Penfieldite	Pb <sub>2</sub> Cl <sub>3</sub> (OH)	2004	450	380
Powellite	CaMoO <sub>4</sub>	2004	470	460
Pyrite	FeS <sub>2</sub>	2006	590	300
Salamoniac	NH <sub>4</sub> Cl	2004	420	190
Smythite	Fe <sub>9</sub> S <sub>11</sub>	2006	480	380
Sulfur	S	2004, 2006	560	190
Sylvite	KCl	2004, 2006	580	440
Tsugaruite	Pb <sub>4</sub> As <sub>2</sub> S <sub>7</sub>	2006	340	320
Wurtzite	(Zn,Cd,Fe)S	2006	590	340
Greenockite	CdS	2006	590	340

**Table DR2. Compilation of volcanic vapour condensates**

A total of 282 samples of vapour condensates from subduction zone stratovolcanoes with trace element concentrations were compiled from the literature (Fig. 2). Data were taken from Arenal, Costa Rica (Stoiber and Rose, 1970), Augustine, Alaska (Symonds et al., 1990), Cerro Negro, Nicaragua (Gemmel, 1987; Stoiber and Rose, 1970), Colima, Mexico (Taran et al., 2001), Fuego, Guatemala (Stoiber and Rose, 1970), Izalco, El Salvador (Stoiber and Rose, 1970), Kawa Ijen, Indonesia (Berlo et al., 2014), Kudryavy, Russia (Wahrenberger et al., 2002; Taran et al., 1995), Masaya, Nicaragua (Gemmel, 1987), Merapi, Indonesia (this research; Symonds et al., 1987), Momotombo, Nicaragua (Gemmel, 1987), Mutnovsky, Kamchatka (Zelensky et al., 2005), New Tolbachik, Kamchatka (Menyailov and Nikitina, 1980), Pacaya, Guatemala (Stoiber and Rose, 1970), Poas, Costa Rica (Gemmel, 1987), Santiagito, Guatemala (Stoiber and Rose, 1970), Satsuma Iwojima, Japan (Hedenquist et al., 1994), Showa Shinzan, Japan (Oana, 1962; Mizutani, 1970; Symonds et al., 1996) and St-Helens, USA (Bernard et al., 1990). The concentrations of S, Cl, Pb, Cu, Zn, Mo, Y, Au and U were normalized to Na to neutralise the effect of dilution by H<sub>2</sub>O. The concentration of these elements did not show any correlation with the silica content nor with the alkalinity of the associated volcanic rocks. Conversely, a correlation was observed between their composition and temperature. The samples were thus separated into five temperature groups, i.e., 85-200°C (n=23), 201-400°C (n=109), 401-600°C (n=55), 601-800°C (n=44) and 801-1020°C (n=19). These results are reported in “violin plots”, using NCSS statistical software, showing the median (black dot), the interquartile range (central vertical line extending from the 25th to 75th percentile) and the total distribution (gray envelopes; width representing the amount of data).

Most of the violin plots show normal distributions, with medians near the centres of the interquartile bars and the latter approximately in the middle of the total distribution, except for some plots of the low temperature group with abnormal distributions, due to limited data. Uranium, Y, and Au to a lesser extent, also have limited data and show a limited temperature distribution and inconsistent statistical values. Sulphur and Cl have the highest concentrations of the elements in the volcanic vapour condensates other than H and O. Concentrations of S range from 2 ppm to 2.7 wt.% and Cl from 10 ppm to 6.6 wt.%, values which are significantly higher than those of the base metals (Pb-Cu-Zn-Mo), which vary between 0.01 ppb and 21.9 ppm, and trace metals (REE, Au, U) which vary between 0.001 ppb and 0.22 ppm (Gemmel, 1987).

The temperature distribution of the volatile and metallic elements results in convex-upward patterns with maxima at intermediate values (usually around 400-800°C) and lower values at lower (85-400°C) and higher (800-1020°C) temperatures. Copper has a maximum concentration in vapours at 200-400°C, whereas Mo is most concentrated in vapours at 200-400°C and 600-800°C. Although very little data is available for Y, Au and U, Y appears more concentrated in vapours of medium temperature (400-600°C), whereas Au appears to be preferentially concentrated in vapours of lower temperature, 200-400°C.

Table DR2. Compilation of volcanic vapour condensates

magmatic system	type	Na	Cu	Zn	Mo	Pb	Reference
Bajo de la Alumbrera Cu-Au porphyry	b	78000	6500			1420	Seo et al., 2009
Bajo de la Alumbrera Cu-Au porphyry	v	24000	1800			210	Seo et al., 2009
Bajo de la alumbrera Cu-Au porphyry	b	160000	7600	14000	70	4500	Ulrich et al., 1999
Bajo de la alumbrera Cu-Au porphyry	v	17000	33000	1200		200	Ulrich et al., 1999
Bajo de la alumbrera Cu-Au porphyry	b	106000	100	6000	140	1700	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	50000	300	6000		1800	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	92000	200				Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	105000	100	6000	30	2000	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	219000	1700				Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	105000	10000	18300	220	4400	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	243000	3700				Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	252000	2300	20			Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	124000	4800	7400	70	3300	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	100000	500	8900		2800	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	107000	1200	12000	120	3600	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	123000	2200	4600		1600	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	81000	3200	9500	40	2600	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	65000	3200	6000	80	1500	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	198000	1000				Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	80000	5500	9900	90	2400	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	110000	2600	5400	130	1700	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	104000	2000	9000	60	2000	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	100000	5200	5700	50	1800	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	97000	700	5000		1200	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	100000	500	1200		1500	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	33000		1000		200	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	20000	300	1300		1600	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	9500	100	200		90	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	b	4700		300		110	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	11000	500				Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	3000	1100	200		70	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	7000	900	700		200	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	11000	1200	400		140	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	3000	300	100		30	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	6000	3000	300		100	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	14000	6000	800		170	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	9800	2500	1000		250	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	30000	30000	6800		620	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	13000	29000	1000		40	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	21000	26000	1300		180	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	17000	33000	1200		230	Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	7900	5200				Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	3900	1800				Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	3900	500				Ulrich et al., 2002
Bajo de la alumbrera Cu-Au porphyry	v	3900	1700				Ulrich et al., 2002
Bingham Cu-Au-Mo porphyry	b	123000	26000	2900	45	2400	Landtwing et al., 2005

Bingham Cu-Au-Mo porphyry	b	102000	22000	4100	270	3800	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	108000	15000	2800	94	3800	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	132000	15000	2700	60	3100	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	112000	6200	4400		3600	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	113000	3500	3500	1060	2900	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	125000	3200	3300	400	3300	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	110000	2500	4500	70	3700	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	113000	2100	3800	140	3300	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	107000	1300	4000	620	4100	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	123000	700	2100		2100	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	116000	600	2100		1800	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	102000	400	3700	44	2900	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	116000	8100	2500	150	3800	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	106000	7100	3100	49	3200	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	980000	6520	3100		3600	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	105000	4500	3300		2500	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	115000	3000	2200		2000	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	960000	2000	3500	21	3200	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	112000	1450	2100		2600	Landtwing et al., 2005
Bingham Cu-Au-Mo porphyry	b	97000	7600		450	2800	Seo et al., 2009
Bingham Cu-Au-Mo porphyry	b	129000	18900		33	3000	Seo et al., 2009
Bingham Cu-Au-Mo porphyry	b	117000	1190		88	3800	Seo et al., 2009
Bingham Cu-Au-Mo porphyry	v	16800	4200		51	390	Seo et al., 2009
Bingham Cu-Au-Mo porphyry	v	23000	10800		18.3	440	Seo et al., 2009
Bingham Cu-Au-Mo porphyry	v	22000	300		21	540	Seo et al., 2009
Butte Cu-Mo porphyry	b	68000	5900	12000		1200	Rusk et al., 2004
Butte Cu-Mo porphyry	b	110000	170	3300		1000	Rusk et al., 2004
Butte Cu-Mo porphyry	b	100000		5600		1000	Rusk et al., 2004
Butte Cu-Mo porphyry	b	55000		9500			Rusk et al., 2004
Butte Cu-Mo porphyry	b	100000	380	4700		1000	Rusk et al., 2004
Butte Cu-Mo porphyry	b	110000	81	4000		860	Rusk et al., 2004
Butte Cu-Mo porphyry	b	110000	1000	4300		1100	Rusk et al., 2004
Butte Cu-Mo porphyry	b	91000	800	5800		810	Rusk et al., 2004
Butte Cu-Mo porphyry	b	100000	1100	4500		800	Rusk et al., 2004
Butte Cu-Mo porphyry	b	80000	88	6900		1300	Rusk et al., 2004
Butte Cu-Mo porphyry	b	100000	140	8300		1600	Rusk et al., 2004
Butte Cu-Mo porphyry	b	97000	440	12000		2000	Rusk et al., 2004
Butte Cu-Mo porphyry	b	83000	150	9800		1400	Rusk et al., 2004
Butte Cu-Mo porphyry	b	96000	760	15000		1700	Rusk et al., 2004
Butte Cu-Mo porphyry	b	97000		7900		1300	Rusk et al., 2004
Butte Cu-Mo porphyry	b	74000		6400		840	Rusk et al., 2004
Butte Cu-Mo porphyry	b	91000	850	7100	16	1500	Rusk et al., 2004
Butte Cu-Mo porphyry	b	100000	2400	2800		790	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6300	4400	130		32	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7800	2100				Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6100	3800	64			Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7800	3400	170	5	20	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	5900	5600	100		8	Rusk et al., 2004

Butte Cu-Mo porphyry	sc	6500	5600	150		24	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	5200	3800	140		10	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6300	10100	140		35	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	4000	13400	81			Rusk et al., 2004
Butte Cu-Mo porphyry	sc	5100	6600	120		19	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8900	1100	28			Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6500	6000	100		9	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8200	1800	160		19	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6700	2200				Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8100	1500	170			Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8600	1200	150	8	14	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6900	5000	160		22	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6600	3600	160		17	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7800	2300	110		22	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7900	2200	170		23	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	10000	51	43		30	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	4300	2000	140		11	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8800	320	100		48	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	5200	2300	100		9	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6400	160	90		15	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8200	130	140		58	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8000	1000				Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7600	1200	100			Rusk et al., 2004
Butte Cu-Mo porphyry	sc	13000		230		76	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7200	940	190		93	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	9400	600	340		62	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	5700	12000	200		50	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7000	9900	140			Rusk et al., 2004
Butte Cu-Mo porphyry	sc	5800	10000	460	37	63	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	9100	3100	560	38	83	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8700	2200	390		48	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7900	5000	300	343	66	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6100	7300	240		42	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	10000	360			61	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6000	12000			77	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	9800		60		26	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8100	4300	290		46	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8600	1800	690		63	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8600	4400	110		52	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8100	5200			59	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7100	11000	70		35	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8300	7900				Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8500	3400	1500		35	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	9700	330	470		100	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	10000				54	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6500	11000	210		52	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	9600	890	300		88	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6900	10000	210		44	Rusk et al., 2004

Butte Cu-Mo porphyry	sc	8600	1300	640		81	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	8900	4600			40	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6200	18000	1600		75	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7200	12000	300		23	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7700	13000		42	61	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	10000	5500				Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7100	15000	210			Rusk et al., 2004
Butte Cu-Mo porphyry	sc	9900	7200	200		100	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	12000	2100				Rusk et al., 2004
Butte Cu-Mo porphyry	sc	9500	8100	330		68	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	4500	18000	350		59	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	6400	14000	270		56	Rusk et al., 2004
Butte Cu-Mo porphyry	sc	7900	8000	1100			Rusk et al., 2004
El Teniente porphyry Cu-Mo	b	96900	820	2600	4	650	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	112400	450	2600	11	520	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	104600	260	6600	8	2100	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	139500	9600	4800	17	760	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	92400	4900	4400	12	1000	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	86600	2800	4100	55	750	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	114200	5000	4300	760	620	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	152000	4600	1300	660	460	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	159800	7900	1700	1200	610	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	200700	3900	1100	830	220	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	166200	29100	1400	1300	550	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	176400	7400	1300	1000	520	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	177600	4200		1800	400	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	189700	730		610	610	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	97800	400	1700	17	640	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	81000	420	2300		460	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	75300	400	23700	8	800	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	98400	620	910	120	270	Klemm et al., 2007
El Teniente porphyry Cu-Mo	b	96100	2100	4500	60	1000	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	37800	370	1600	80	220	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	34700	1500	980	6	240	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	5400	1400	220		50	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	8600	3300	240	15	40	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	10200	14400	300	17	50	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	13200	4300	220	8	50	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	5100	21100	110		13	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	15400	4500	150	11	75	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	15500	2500			50	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	14400	2800	250		65	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	11800	6200	270	6	55	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	17300	4600	460	8	75	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	8100	8700	120	7	19	Klemm et al., 2007
El Teniente porphyry Cu-Mo	sc	20800	1700	190		59	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	8800	5800	260	60	35	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	900	260	12	6	9	Klemm et al., 2007

El Teniente porphyry Cu-Mo	v	2900	350	55	3	11	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	2200	3200			20	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	7500	9700	140	3	35	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	1200	3700				Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	1900	1500	100	4	16	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	2800	10900	80	8	15	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	3000	23200	90	5	14	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	6800	18800	270	19	50	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	14200	7200	290	55	70	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	6400	16200	220	25	35	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	8600	7900		12	60	Klemm et al., 2007
El Teniente porphyry Cu-Mo	v	14400	3200		7		Klemm et al., 2007
Famatina Cu-Au porphyry / HS epitherm b	b	196000	1500		190	1700	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm b	b	128000	880		50	1100	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm b	b	169000	50		40	930	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm b	b	110000	240		360	1200	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm b	b	85000	820		30	940	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm b	b	96000	4600			610	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm b	b	97000	3000			550	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm b	b	114000	3800			540	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	8000	670		40	90	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	5000	270		6	60	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	4000	1100			60	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	9000	580			70	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	34000	3300		70	200	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	8000	2100		20	110	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	9000	5500			70	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	7000	390		10	90	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	7000	1500			90	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	5000	5400			150	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	10000	1300			110	Pudack et al., 2009
Famatina Cu-Au porphyry / HS epitherm v	v	1000	440			8	Pudack et al., 2009
Rosia-Poieni porphyry Cu-Au	b	111628	3009	29240		13251	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	112692	2761	28718		13300	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	109324	3161	31545		14192	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	115614	3370	23792		11069	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	117970	2571	20567		12104	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	117141	1392	20818		9503	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	118096	2366	20364		11002	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	126933	16441	4370		2000	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	119053	13997	3845		1453	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	126294	10272	4176		1079	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	116054	2102	22745		11145	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	108437	8874	30565		14115	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	110684	3970	31198		15865	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	129053	1516	9976		4890	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	113825	2621	24544		12579	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	115400	1487	19633		16947	Kouzmanov et al., 2010

Rosia-Poieni porphyry Cu-Au	b	113836	3170	25023		12461	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	117696	2019	22070		7277	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	120260	2314	16677		10056	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	118632	1860	18853		10462	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	119786		13816		26325	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	122163	1885	17538		10794	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	119590	1317	21814		11815	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	115808	1057	25452		14115	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	105602	1748	39610		17722	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	97573	2581	43213		20343	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	107373	2986	35954		19660	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	108885	3725	34765		19574	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	109691	5232	34364		18912	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	105348	5147	33324		17606	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	94639	139	26504		10189	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	101573	113	23176		10715	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	101142	194	19817		11812	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	107724	244	30213		17146	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	105114	337	5946		3760	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	101035	319	6591		4178	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	102399	235	7808		4189	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	b	96803	167	16573		4911	Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1675					Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1642	30	31	1.7		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1957		24			Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1821		3.5			Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1961	47		0.5		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1935	1332	33	13		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1963	67				Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1567		531	153		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1941		40	0.7		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	785		211			Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1664		172	33		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1386		134	9.3		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1617		809	23		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1952		28			Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1014					Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1870			1.4		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1936		4.1	1.5		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1967					Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1226		27	15		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1816					Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1581	113	76	3.8		Kouzmanov et al., 2010
Rosia-Poieni porphyry Cu-Au	v	1252	303	832	625		Kouzmanov et al., 2010
Santa Rita Cu (Mo-u) porphyry	b	67900	2300	3400	800		Audébat et al., 2008
Santa Rita Cu (Mo-u) porphyry	b	68100	2700	2800	13	590	Audébat et al., 2008
Santa Rita Cu (Mo-u) porphyry	b	75000	2200			780	Audébat et al., 2008
Santa Rita Cu (Mo-u) porphyry	b	74300	2800	2300	42	830	Audébat et al., 2008

Santa Rita Cu (Mo-u) porphyry	b	61800	1700	2800		840	Audébat et al., 2008
Santa Rita Cu (Mo-u) porphyry	b	64900	620		380		Audébat et al., 2008
Santa Rita Cu (Mo-u) porphyry	v	50000	7800	2500	5	410	Audébat et al., 2008
Santa Rita Cu (Mo-u) porphyry	v	50800	8800	1300		390	Audébat et al., 2008
Santa Rita Cu (Mo-u) porphyry	v	28400	4100			200	Audébat et al., 2008
Santa Rita Cu (Mo-u) porphyry	v	50000	3800	1400	15	420	Audébat et al., 2008

**Table DR3. Compilation of fluid inclusion data**

A total of 292 analyses of fluid inclusions from seven porphyry Cu ± Mo ± Au deposits with trace element concentrations and physical phase descriptions (supercritical fluid, brine or vapour inclusions) were compiled from the literature (Fig. 4). The data are from Bajo de la Alumbrera Cu-Au porphyry, Chile (Seo et al., 2009; Ulrich et al., 2001), Bingham Cu-Au-Mo porphyry, USA (Landtwing et al., 2005; Seo et al., 2009), Butte Cu-Mo porphyry, USA (Rusk et al., 2004), El Teniente Cu-Mo porphyry, Chile (Klemm et al., 2007), Famatina Cu-Au porphyry-epithermal, Argentina (Pudack et al., 2009), Rosia-Poieni Cu-Au porphyry, Romania (Kouzmanov et al., 2010) and Santa Rita Cu (Mo) porphyry, New Mexico (Audétat et al., 2008). Only Pb, Cu, Zn and Mo are reported here because S, Cl, Au, REE, Au, U and other elements were almost never reported. The concentrations of Pb, Cu, Zn and Mo were normalized to Na to neutralise the effect of dilution by H<sub>2</sub>O and to enable comparison between volcanic vapours and fluid inclusions. The Pb/Na, Cu/Na, Zn/Na and Mo/Na ratios are displayed as violin plots for supercritical fluid-, brine- and vapour inclusions and the ratios for volcanic vapours are displayed beside them.

The Pb/Na ratio is smallest for supercritical fluid inclusions, averaging about 0.006 (note that the calculated averages and the medians shown on violin plots are not necessarily identical), and is progressively higher for vapour and brine inclusions. Volcanic vapours have a large range of Pb/Na values that encompass all the fluid inclusion data and reach values much higher than the latter, averaging around 0.6. The Cu/Na ratios are similar for supercritical fluid and vapour inclusions, with values averaging around 0.8. Brine and volcanic vapours also have similar ratios averaging of 0.03 and 0.05, respectively. The distribution of Zn/Na is very similar to that of Pb/Na; values are smallest for supercritical fluid inclusions, averaging around 0.035, and are gradually higher in vapour and brine inclusions. The Zn/Na ratio reaches a maximum average value of about 0.26 in volcanic vapours, where it also has the greatest range, again encompassing that of most fluid inclusions. Finally, Mo/Na ratios show the highest values (average 0.4) and the greatest variations in volcanic vapours like for Pb/Na and Zn/Na. Vapour, supercritical fluid and brine inclusions have gradually lower Mo/Na ratios ranging between 0.005 and 0.002.

**Mass balance calculations**

An actively forming porphyry system of intermediate size associated with an overlying volcano that erupts every 5 years would cycle 20,000 times during 100 ka. Assuming an intermediate-sized porphyry deposit containing 1 Gt of Cu, 50 t of Cu should be deposited during each cycle. If 50 wt. % of the Cu present in the basalt is deposited in each cycle, 1.67 Gt of basalt containing 60 ppm Cu (a normal value; see georoc database at [georoc.mpch-mainz.gwdg.de/georoc](http://georoc.mpch-mainz.gwdg.de/georoc)) needs to be injected during each cycle. Given a density of 2800 kg/m<sup>3</sup>, this represents a volume of ~ 600 million m<sup>3</sup>, which is a reasonable size for a mafic injection in the shallow part of subduction zone magma system (Pallister et al., 1992).

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