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Selective copper diffusion into quartz-hosted vapor inclusions: evidence from other host minerals, driving forces, and consequences for Cu-Au ore formation

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Abstract

Recent experimental studies have raised concerns that Cu concentrations in quartz-hosted fluid inclusions from magmatic-hydrothermal ore deposits do not represent pristine concentrations in the trapped fluids, but are modified by post-entrapment diffusional exchange through the host quartz. New microanalyses of fluid inclusions hosted in topaz and garnet show significantly lower Cu concentrations in vapor inclusions, compared to otherwise identical inclusions hosted by coexisting quartz, whereas coeval brine (hypersaline liquid) inclusions are very similar independent of host mineral in one sample. Sulfur is present as a major component in all vapor inclusions, as in most porphyry-related vapor inclusions, and Cu never exceeds S, but commonly matches the S content at a molar ratio of $\text{Cu:S} \leq 2$ in vapor inclusions hosted by quartz.

Univalent ions with a radius smaller than $\sim 1\text{\AA}$ are known to diffuse rapidly through the channels of the quartz structure, parallel to its crystallographic *c* axis. Since only Cu concentrations differ between topaz- and quartz-hosted inclusions, we hypothesize that Cu^+ and H^+ re-equilibrate by diffusional ion exchange through these channels, while all other element concentrations remain

essentially unchanged. A thermodynamic model considering charge-balanced $\text{Cu}^+ - \text{H}^+$ exchange and diffusive H_2 re-equilibration of an initially Cu-poor but S-rich vapor inclusion with a typical rock-buffered fluid environment outside the host crystal demonstrates a strong chemical driving force for Cu^+ to migrate from the surrounding rock into the fluid inclusion during cooling of the system. The driving force for Cu diffusion, against the gradient in total Cu concentration, is the abundant H^+ liberated inside the inclusion by dissociation of HCl and particularly by the precipitation of CuFeS_2 by reaction with the initially trapped H_2S and/or SO_2 . Gold is not only a much larger ion, but is subject to an opposing driving force, suggesting that high concentrations of this larger ion analyzed in vapor inclusions probably represent true gold concentrations in magmatic-hydrothermal vapor.

These findings imply that brine – vapor separation in porphyry deposits does not cause selective Cu transfer to the vapor, but is more likely to destabilize Cu complexes and promote copper ore deposition during decompression and unmixing of the two fluid phases. By contrast, Au may be selectively transferred into the vapor phase, allowing its transport through the deeper porphyry copper deposits to form epithermal gold deposits closer to the earth's surface.

1. Introduction

Quartz has been the favored host mineral for fluid inclusion studies of magmatic and other hydrothermal ore deposits, because of its common association with ore minerals, its transparency and its chemically simple composition. Quartz veins and euhedral quartz crystals from high-temperature magmatic-hydrothermal deposits and miarolitic cavities in granitoids contain large fluid inclusions in diverse assemblages, which preserve distinct and internally consistent compositions and densities among numerous individual coeval inclusions. Magmatic-hydrothermal fluid inclusions in petrographically controlled context therefore provide abundant information about high-temperature processes including pressure-temperature evolution, phase state of fluids, metal transportation and precipitation, and the segregation of elements during phase separation into fluids of different densities (Cloke and Kesler, 1979; Eadington, 1983; Roedder, 1984; Cline and Bodnar, 1991; Bodnar and Vityk, 1994; Audétat et al., 1998). Fluid densities as well as salinity are important factors for the mobility of metals as well as volatiles in magmatic-hydrothermal environments. Selective metal transportation in immiscible two-phase fluids, a high-density hypersaline aqueous liquid (brine) coexisting with a vapor phase of lower density and salinity, has been of particular interest in ore deposit research and related experimental studies (Krauskopf, 1964; Henley and McNabb, 1978; Eastoe, 1982; Heinrich et al., 1992; Pokrovski et al., 2005; Williams-Jones and Heinrich, 2005; Simon et al., 2006; Pokrovski et al., 2008; Seo et al., 2009; Frank et al., 2011).

Copper has long been known to be highly concentrated in low-density vapor inclusions hosted in quartz from magmatic-hydrothermal systems. Vapor inclusions in magmatic-hydrothermal quartz veins (i.e., inclusions that trapped the vapor as a homogeneous fluid sample at high temperatures and pressures) commonly contain chalcopyrite daughter crystals after cooling that are similar or even larger in size than those in coexisting brine inclusions. High Cu concentrations in the vapor inclusions were initially estimated based on the size of the chalcopyrite daughter crystals (Sawkins

and Scherkenbach, 1981; Roedder, 1984). Micro-PIXE (Proton Induced X-ray Emission) and LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) analyses of individual inclusions in distinct assemblages allowed quantification of the selective enrichment of Cu, As, and Au in low-density vapor inclusion, whereas major salt components and trace elements such as Na, K, Fe, Mn, Zn, Rb, Cs, and Pb were shown to be enriched in coexisting brine inclusions (Heinrich et al., 1992; Ryan et al., 1993; Damman et al., 1996; Heinrich et al., 1999; Ulrich et al., 1999; Baker et al., 2004). This chemical separation was interpreted to result from volatile sulfur complexing of Cu and Au at magmatic-hydrothermal fluid conditions, consistent with recent observations that the Cu-rich vapor inclusions also contain an equivalent or even larger enrichment of S (Seo et al., 2009). Hydrothermal experiments with S-bearing two-phase fluids confirmed relatively elevated Cu concentrations in the vapor phase, compared to the vapor in S-free fluid systems (Simon et al., 2006; Nagaseki and Hayashi, 2008; Pokrovski et al., 2008; Frank et al., 2011), but only the study of Nagaseki and Hayashi (2008) using synthetic fluid inclusion in quartz reported higher absolute concentrations of Cu in vapor compared to coexisting brine.

Recent experiments have shown that Cu concentration in melt and fluid inclusions can be modified after their entrapment in quartz. Zajacz et al. (2009) and Li et al. (2009) demonstrated significant compositional modification of fluid and melt inclusions hosted in quartz, by selective diffusional exchange with surrounding hydrothermal fluids of Li^+ , Na^+ , Cu^+ and Ag^+ through the host mineral. Such quantitative experiments in cold-seal bombs quantified earlier suspicions reported by Kamenetsky and Danyushevsky (2005). Lerchbauer and Audétat (2012) recently performed systematic re-equilibration experiments using brine and vapor inclusions coexisting in individual quartz samples, which were loaded into a pressure vessel with an external fluid of variable composition. The authors showed that the initial S content of quartz-hosted fluid inclusion can promote inward diffusion of Cu from the external hydrothermal fluid, by precipitation of a Cu-sulfide crystal inside the inclusion. The proposed inward diffusion provides Cu until the activities of Cu^+ , H^+ , and H_2S in the inclusion reach a chemical equilibrium with the external fluid (Lerchbauer and Audétat, 2012), which allows the internal precipitation of CuFeS_2 consistent with the observed positive correlation of 1:2 molar ratios of Cu and S in many natural quartz-hosted inclusion assemblages from magmatic-hydrothermal ore deposits (Seo et al., 2009).

Here, we complement these experimental data with new results of LA-ICP-MS microanalysis of natural topaz- and garnet-hosted fluid inclusions. We chose topaz and garnet, because they are mechanically strong and have generally lower chemical diffusivity compared to quartz (Brady and Cherniak, 2010). Due to their different crystal structures, these minerals are expected to be less, or at least differently, affected by post-entrapment diffusional exchange (Ingrin and Blanchard, 2006) and therefore provide an independent test for the proposed, element-specific behavior of quartz as an inclusion host.

2. Samples and Analytical Methods

The topaz samples are from wolframite-bearing quartz – topaz greisen of the Fielders Hill deposit located in a roof pendent of the Mole Granite, Australia (Eadington, 1983; Audétat et al., 2000). The

garnet sample is from the Dongguashan skarn Cu deposit, which is spatially related to a subeconomic porphyry deposit in the Tongling district, China (Yang et al., 2009). Cogenetic assemblages of single trails (healed microcracks) comprising coeval brine and vapor inclusions (traditionally termed 'boiling assemblages') were analyzed in topaz. Consistently large bubble/liquid proportions in the vapor inclusions and constant bubble/liquid/halite proportions in the brine inclusions at room temperature indicate that each inclusion type approximates a homogeneous fluid phase. The two fluids coexisted at elevated pressures and temperatures and were isolated from each other by rapid healing of microcracks in the host minerals. A boiling assemblage hosted in quartz in the same sample was also analyzed for comparison, in addition to quartz data from the same location reported previously by Audétat et al. (2000) and Seo et al. (2009). We were not successful in finding individual inclusion trails crossing a grain boundary between quartz and topaz. Nevertheless, the close intergrowth of both minerals in sample Fiel_32b and the similarity of fluid inclusion associations in samples from the same and other localities in the Mole Granite indicate that we are comparing coeval brine and vapor inclusions in the two host minerals. The garnet from the Dongguashan skarn contains vapor inclusions only, which cannot be reliably correlated with quartz-hosted inclusions in the spatially associated porphyry-style mineralization in the same deposit (Yang et al., 2009).

Representative fluid inclusion assemblages (FIA) comprising 5-12 individual inclusions of each type, hosted in topaz, garnet and quartz, were selected by detailed petrography. Microthermometry was conducted to determine halite dissolution and homogenization temperatures of brine inclusions. Obtaining ice melting temperatures to determine salinities of most vapor inclusions was difficult because of the thin layer of aqueous liquid around the walls of inclusions, which were generally much smaller ($\sim < 25 \mu\text{m}$) than those hosted in quartz from the Mole Granite. Brine inclusions in quartz and topaz have essentially identical properties, but in light of the incomplete microthermometric data for most vapor inclusions we report our data in terms of element ratios. These are determined directly by LA-ICP-MS and can be calibrated quantitatively, without any assumptions (Günther et al., 1998). We normalized elements concentrations with Pb rather than Na because Pb can be measured more precisely by LA-ICP-MS due to its greater abundance sensitivity, and Pb is exclusively chloride complexed in high-temperature hydrothermal fluids (Seward, 1984). Na concentrations in quartz-hosted fluid inclusions may also be subject to modifications by post-entrapment diffusion (Li et al., 2009; Zajacz et al., 2009; Lerchbaumer and Audétat, 2012).

We measured singly-targeted fluid inclusions in representative fluid inclusion assemblages using the ETH-prototype LA-ICP-MS system (Günther et al., 1998). A limited number of isotopes, ^7Li , ^{23}Na , ^{32}S , ^{35}Cl , ^{39}K , ^{57}Fe , ^{65}Cu , ^{66}Zn , ^{75}As , ^{95}Mo , ^{107}Ag , ^{133}Cs , ^{197}Au , and ^{208}Pb were measured, applying an increased dwell time on selected elements (50-100 ms for ^{197}Au , 20 ms for ^{95}Mo , 20 ms for ^{32}S and ^{35}Cl , and 10 ms for other elements). A small flux of H_2 gas (5 ml/min) was added to the He carrier gas (1.1 l/min) to enhance sensitivity for heavier elements such as Cu, Au, and Mo (Guillong and Heinrich, 2007). Energy densities between 30 and 40 J/cm² on the sample surface with 10 Hz pulse frequency allowed controlled sampling of most quartz- and garnet-hosted fluid inclusions, while higher repetition rates of 20 Hz pulse frequency were applied for topaz-hosted fluid inclusions

analysis. An iris aperture was gradually opened during analysis to a spot size allowing complete excavation of the fluid inclusion without the loss of daughter crystals. We used a natural scapolite as an external standard reference material (SRM) for ^{35}Cl (Seo et al., 2011), while NIST SRM 610 was used for all other elements. Quantification of elements followed the data reduction procedures of Günther et al. (1998) and Heinrich et al. (2003) using the SILLS software (Guillong et al., 2008). The average and 1σ variation within each assemblage is calculated from all quantifiable inclusion signals for each element, to give an estimate of realistic analytical uncertainty of each fluid composition represented by an assemblage (Heinrich et al., 2003; Table 1).

3. Results

Copper concentrations in the vapor inclusions can be compared by normalizing the analysed element ratios to a previously measured salinity of 3 wt% NaCl eqv. of many vapor inclusion assemblages in the Mole Granite (Audétat et al., 2000; Seo et al., 2009). Copper ranges from 56 ± 18 $\mu\text{g/g}$ to 160 ± 98 $\mu\text{g/g}$ in several topaz-hosted assemblages of vapor inclusions, and from 66 ± 34 $\mu\text{g/g}$ to 74 ± 24 $\mu\text{g/g}$ in the garnet-hosted vapor inclusion assemblages. These values are comparable to typical Cu concentrations expected experimentally predicted for a high-temperature magmatic vapor of moderate salinity, exsolving from a moderately reduced andesitic melt (Zajacz et al., 2011). Sulfur concentrations in vapor inclusion assemblages range from $\sim 1,000$ $\mu\text{g/g}$ to $9,900 \pm 1,900$ $\mu\text{g/g}$ in topaz-hosted and from $8,200 \pm 2,900$ $\mu\text{g/g}$ to $11,000 \pm 4,900$ $\mu\text{g/g}$ in garnet-hosted assemblages. Copper concentrations in topaz-hosted brine inclusion assemblages vary from 700 ± 83 $\mu\text{g/g}$ to $1,100 \pm 270$ $\mu\text{g/g}$, and S concentrations are from 230 ± 14 $\mu\text{g/g}$ to $1,100 \pm 800$ $\mu\text{g/g}$. In topaz and garnet, vapor inclusion assemblages contain S in excess compared to Cu, whereas brine inclusions have similar or even higher Cu than S. Such Cu excess compared to S has never been found in quartz-hosted fluid inclusions (Cauzid et al., 2007; Seo et al., 2009; Seo et al., 2011).

Gold was not detected in the transient signals of the topaz- and garnet-hosted vapor inclusions, whereas some brine inclusions hosted in topaz contain Au between 0.06 ± 0.00 $\mu\text{g/g}$ and 0.28 ± 0.24 $\mu\text{g/g}$, which is comparable to the gold concentrations in quartz-hosted brine inclusions (Table 1). Detection of Au, especially in vapor inclusions hosted by topaz is hampered by the small total fluid mass and the small inclusion size, compared with the typically larger quartz-hosted inclusions. According to individually calculated limits of detection, the gold concentration in topaz-hosted vapor inclusions may be as high as in those hosted by quartz.

The cogenetic brine and vapor inclusions trapped in the single healed crack (boiling assemblage) hosted in topaz show no selective Cu enrichment in the vapor inclusions compared to the coexisting brine inclusions. By contrast, As and S are relatively enriched in vapor inclusions (Fig. 1), to a similar degree as shown by the quartz-hosted inclusions. Boiling assemblages hosted in coexisting quartz, by contrast, show a high degree of selective Cu enrichment in the vapor inclusions, which correlates with that of S, similar to numerous other quartz-hosted vapor – brine assemblages worldwide. When the ratios of Cu to other ore and alkali metals are compared between topaz- and quartz-hosted boiling assemblages, up to three orders of magnitude of discrepancy is found in the Fielders Hill samples (Fig. 1). We also found minor differences for Li and Ag ratios, whereas the

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element ratios between vapor and brine, for all other metals including Na, are not significantly different between the host minerals.

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Table 1

Composition of natural brine and vapor inclusions coexisting in different host minerals. Salinities (equivalent NaCl wt.%), homogenization temperatures (T_h), and LA-ICP-MS microanalysis ($\mu\text{g/g}$) of eight cogenetic brine and vapor inclusions hosted in topaz and quartz, and two vapor-rich inclusion assemblages hosted in garnet. “Fiel” and “Boyd” samples are from quartz-topaz greisen, and “gold” sample is from Bi-rich quartz vein associated with Mole Granite, Australia (Audétat et al., 2000; Seo et al., 2009). “54-5” sample is from Cu-rich garnet skarn at Dongguashan porphyry-skarn Cu deposit, China (Yang et al., 2009). Salinities of some vapor-rich inclusion assemblages are assumed to be 3 wt.% NaCl eqv. Detection limits of Au are reported when no reliable Au peak from LA-ICP-MS transient signals of fluid inclusion are found.

	Host mineral	Sample # FI #	Phase	Salinity wt.% NaCl eqv.	T_h	^7Li $\mu\text{g/g}$	^{23}Na $\mu\text{g/g}$	^{32}S $\mu\text{g/g}$	^{35}Cl $\mu\text{g/g}$	^{39}K $\mu\text{g/g}$	^{57}Fe $\mu\text{g/g}$	^{65}Cu $\mu\text{g/g}$	^{66}Zn $\mu\text{g/g}$	^{75}As $\mu\text{g/g}$	^{95}Mo $\mu\text{g/g}$	^{107}Ag $\mu\text{g/g}$	^{133}Cs $\mu\text{g/g}$	^{197}Au $\mu\text{g/g}$	^{208}Pb $\mu\text{g/g}$
AV	Topaz	Fiel_1.1_1	Vapor	3.0	n.d.	440	6700	1400	6000	4100	5900	56	400	170	0.5	1.9	350	<0.63	100
STD		TP1	(boil)	Assum.		54	510	960	3000	680	1100	18	130	56	0.2	0.7	100		34
AV			Brine	36.0	n.d.	1200	72,000	230	100,000	64,000	88,000	710	6200	400	2.3	39.0	5400	<0.75	1800
STD			(boil)	0.2		310	4600	14	18,000	6100	6000	160	1500	180	1.0	3.6	1300		250
AV	Topaz	Fiel_1.1_1	Vapor	3.0	n.d.	380	7000	2400	5800	3100	6300	74	370	400	0.6	2.3	300	<0.54	98
STD		TP6	(boil)	Assum.		56	480	1500	1900	790	620	13	160	260	0.6	1.5	88		36
AV			Brine	35.3	n.d.	1300	67,000	420	100,000	62,000	96,000	1100	4900	370	1.6	31.0	3100	<1.29	1800
STD			(boil)	0.2		210	5800	300	19,000	8300	5800	180	850	52	0.4	3.9	600		140
AV	Topaz	Fiel_1.1_1	Vapor	3.0	n.d.	400	7100	1000	6100	3800	5700	64	330	230	1.1	2.2	190	<0.11	58
STD		TP2	(boil)	Assum.		85	680	1100	1800	830	1000	14	83	110	0.3	0.8	50		10
AV			Brine	31.3	n.d.	1700	68,000	260	90,000	54,000	67,000	700	4000	690	7.4	37.0	2300	<0.10	680
STD			(boil)	0.1		290	3100	170	13,000	3600	5000	83	450	140	6.6	3.5	610		130
AV	Topaz	Fiel_32b_1	Vapor	3.0	n.d.	2300	6400	9200	13,000	3400	8700	110	410	3000		3.8	110	<0.36	51
STD		TP1	(boil)	Assum.		390	500	3900	6400	990	1500	17	200	450		3.2	29		17
AV			Brine	33.6	546.7	1700	60,000	1100	73,000	65,000	97,000	860	7500	820	3.9	54.0	6700	0.28	2100
STD			(boil)	0.1	7.6	980	4000	800	16,000	5900	8900	270	2200	590	2.2	25.0	840	0.24	210
AV	Topaz	Fiel_32b_1	Vapor	3.0	n.d.	3200	6900	9900	18,000	3700	8300	160	500	3200		4.5	140	<1.72	70
STD		TP2	(boil)	Assum.		830	1300	1900		1500	2500	98	230	1400		1.9	58		21
AV			Brine	35.0	544.7	900	66,000	460	100,000	69,000	93,000	1100	5200	370	8.5	48.0	3600	0.06	1200
STD			(boil)	1.6	7.5	160	4300	340	33,000	7800	5900	270	880	93	5.8	12.0	1200	0.00	550
AV	Topaz	Fiel_1.1_1	Vapor	3.0	n.d.	420	7300	4400	8300	3600	5300	100	310	420	1.5	1.6	130	<1.18	92
STD		V7	(non-boil)	Assum.		170	870	2500	3900	1800	2700	53	140	170	0.7	0.8	49		41
AV	Garnet	54-5_2	Vapor	3.0	n.d.	170	9700	11,000	53,000	5100		66	460				16	<1.40	100
STD		TP1	(non-boil)	Assum.		140	590	4900	8300	1400		34	360				7		41
AV	Garnet	54-5_2	Vapor	3.0	n.d.	320	8100	8200	93,000	9100		74	450			13.0	38	<3.34	210
STD		V2	(non-boil)	Assum.		200	1900	2900	16,000	5500		24	360			2.4	30		120
AV	Quartz	Gold_1.2.2	Vapor	2.4	n.d.	450	7600	9800	10,000	2500	3400	5400	260	410	1.0	9.6	86	0.32	220
STD			(boil)	0.5		160	1000	8000	6200	690	1400	3600	130	370	0.4	8.8	34	0.25	120
AV			Brine	37.4	356.0	480	85,000	340	360,000	77,000	120,000	290	8800	310	1.4	59.0	3400	0.04	8900
STD			(boil)	0.4	19.0	110	16,000	140	23,000	17,000	23,000	130	2000	230	0.8	6.2	970	0.03	2600
AV	Quartz	BoydB_1	Vapor	3.3	n.d.	100	10,000	12,000	13,000	3300	4000	8200	390	130	5.8	26.0	140	0.38	180
STD			(boil)			72	1000	8800	3000	1100	1100	11,000	190	140	6.5	22.0	28	0.19	74
AV			Brine	39.6	n.d.	550	96,000	710	370,000	79,000	110,000	240	6500	260	4.4	48.0	3800	0.13	3900
STD			(boil)	0.4		370	19,000	370	44,000	12,000	12,000	150	1300	340	8.8	7.9	1400	0.25	1200
AV	Quartz	Fiel_32b_2	Vapor	3.0	n.d.		9200	1200	16,000	3700	5400	370	950	26		2.7	250	<2.28	310
STD		TP1	(boil)	Assum.			930	660	9400	1100	2100	550	350	14			76		130
AV			Brine	40.5	263.7	76	110,000	1500	290,000	58,000	91,000	120	15,000	360		37.0	5300	0.35	4600
STD			(boil)	1.6	5.5		21,000		62,000	15,000	19,000	34	4300	110		19.0	1700	0.17	1400

AV and STD represent average and standard deviation (1σ) of 5–12 single fluid inclusion analyses in an inclusion assemblage of petrographically identical and coeval inclusions; where 1σ is similar or even slightly greater than the average, the average value data still indicate the correct order of magnitude among clearly detected element signals. ‘Boil’ and ‘non-boil’ denote boiling assemblage and single-phase fluid inclusion assemblage, respectively. n.d. represent no data.

Figure 1. Partitioning of elements between co-genetic vapor and brine inclusion assemblages hosted in topaz (red and yellow) and quartz (gray and white) in several ore deposits associated with the Mole Granite (Australia) including quartz-hosted boiling assemblages reported by Seo et al. (2009), first described by Audétat et al. (2000). Element concentrations are normalized to Pb, which is most strongly enriched in the high-salinity brine and most analytically robust, and then plotted as ratios between vapor and brine to emphasize differences in relative enrichment. In quartz-hosted fluid inclusions, Ag, Cu, As, Au, and S are enriched in the vapor inclusions relative to Pb, Zn, Cs, Fe, K and Na. Topaz-hosted fluids inclusions, however, show that Cu does not partition preferentially into the vapor, while S and As are strongly enriched in the coexisting vapor irrespective of host mineral.

4. Post-entrapment Cu diffusion into quartz-hosted vapor inclusions

To understand and assess post-entrapment modification in quartz-hosted vapor inclusions, we need to consider our new data from topaz and garnet in combination with the following published analytical and experimental observations:

- (1) In hydrothermal experiments allowing separate sampling of coexisting saline liquid and vapor, Cu always fractionates in favor of the saline liquid (Pokrovski et al., 2005), but the addition of H₂S causes a 10 to 100-fold enrichment of Cu in vapor relative to other chloride salts (Pokrovski et al., 2008).
- (2) In contrast to these autoclave experiments, Cu concentrations in quartz-hosted vapor inclusions commonly exceed those in coeval brine inclusions, in many natural samples as well as synthetic-inclusion experiments with S-rich fluid systems (Nagaseki and Hayashi,

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2008), but natural vapor inclusions in coeval topaz and garnet in this study do not show this enrichment.

(3) Copper enrichment in natural quartz-hosted vapor inclusions correlates with their sulfur content, with most assemblages showing a molar Cu:S concentration greater or equal to 1:2. This ratio is consistent with the presence of a sizeable CuFeS_2 crystal in such inclusions (Sawkins and Scherckenbach, 1981; Seo et al., 2009).

(4) Copper can be added at laboratory timescales by selective diffusion into natural vapor assemblages, and the extent of Cu introduction is enhanced by high initial sulfur and high acid concentrations in the vapor inclusions (Lerchbaumer and Audétat, 2012). Earlier experiments have shown that molecular H_2 exchange between quartz-hosted fluid inclusions and external fluids occurs at laboratory time scales, allowing effective redox re-equilibration of aqueous inclusions with the surrounding fluid (Mavrogenes and Bodnar, 1994; Hall and Sterner, 1995).

(5) Microanalytical data for gold indicate selective enrichment in some natural S-rich vapor inclusions hosted by quartz (Ulrich et al. 1999; Seo et al., 2009). In contrast to Cu, preferential partitioning of Au into S-rich vapor has been confirmed experimentally, with $K_d = \text{Au}_{\text{vapor}}/\text{Au}_{\text{brine}}$ up to 7.5 at 450°C and 500bar, provided that the vapor is acidic and contains ~ 1 wt% H_2S (Pokrovski et al., 2008).

Selective transport of Cu into and out of existing quartz-hosted fluid inclusions depends on two essential factors: an element- and mineral-specific diffusion mechanism, and a chemical driving force for Cu to exchange with an external reservoir, which we now discuss in turn.

4.1. Charge-Balanced Ion Migration through Quartz

Rapid diffusion of ions has long been known from experiments applying an electric potential difference between two aqueous electrolyte solutions separated by a quartz plate that is cut perpendicular to the c-axis of the crystal (Harris and Waring, 1937; Verhoogen, 1952). This electrolytic ion migration is highly directional and thought to occur through the staircase-like channels in the quartz structure. This channel between oxygen atoms has an approximate radius of 1 Å, through which Li^+ (effective ion radius 0.76 Å) and Na^+ (1.02 Å) can be rapidly transported at 300-500°C, whereas K^+ transport is far slower (1.38 Å; Harris and Waring, 1937). The former three elements, as well as Cu^+ (0.77 Å) and possibly Ag^+ (1.15 Å; effective ion radii after Shannon, 1976) have been shown to be transported in and out of quartz-hosted fluid and melt inclusions using hydrothermal equilibration experiments (Li et al., 2009; Zajacz et al., 2009; Lerchbaumer and Audétat, 2012). Since the Au^+ ion (1.37 Å) is much larger than these cations, Au is not expected to readily diffuse through quartz. No electrolytic diffusion experiments for H^+ have been reported to our knowledge, but exchange experiments by Zajacz et al. (2009) and Li et al. (2009) indicate that H^+ is at least as mobile in quartz as Li^+ and Cu^+ . Measurements of the typical time-decrease of direct-current conductivity through natural Na-Li-H-Al-bearing quartz (Kronenberg and Kirby, 1987) and self-diffusion experiments for oxygen in the presence of H_2O (Elphick and Graham, 1988)

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indicate that interstitial H^+ in quartz is partly coupled to Al^{3+} replacing Si^{4+} and thus rather immobile, whereas additional H^+ (supplied for example by an acidity gradients of the surrounding fluid) may contribute to much greater H^+ diffusivity in the direction of the c axis of quartz.

Post-entrapment diffusion of Cu into quartz-hosted vapor inclusions requires a complementary ion diffusion to maintain charge balance. To explain excess concentrations on the order 1 wt % Cu, as analyzed in many low-salinity porphyry-related vapor inclusions in which Cu is one of the major dissolved elements, requires balancing species of equal concentration. This confines possible exchange reactions to species within the major-component system Na-K-Fe-Cu-Cl-S-O-H, because no other element is present in a concentration that is high enough to charge-balance such major Cu addition. Given the experiments summarized above and our analytical data indicating that M/Na ratios are not significantly host-mineral dependent, H^+ appear to be the most likely specie for outward diffusion to balance inward diffusion of Cu^+ (Lerchbaumer and Audétat, 2012).

4.2. *Driving Force for Cu Migration: Cu^+H^{+1} Exchange Dominated by Sulfur Geochemistry*

Inward diffusion of Cu into natural fluid inclusions trapped at high temperatures and pressures in ore veins seems paradoxical at first, considering that Cu concentration in the residual pore fluid surrounding the inclusion-hosting quartz is decreasing as a result of Cu-Fe-sulfide precipitation upon fluid cooling and eventual dilution by invading meteoric water (Crerar and Barnes, 1976; Herzarkhani and Williams-Jones, 1998). In this section, we show that a gradient in chemical potential for Cu^+H^{+1} exchange is expected to be established as a result of overall cooling of natural fluid – rock systems, and that this gradient is capable of driving the observed quantities of Cu^+ from the surrounding rock-buffered fluid into S-rich vapor inclusions.

To quantify this effect, the thermodynamic dataset compiled in Heinrich (2005) was applied to a simple scenario for a quartz-hosted fluid inclusion cooling within a porphyry-Cu-Au ore environment. Our analytical data comparing garnet and topaz-hosted inclusions with earlier data from coeval quartz-hosted inclusions indicate that all major-element concentrations including Na, K and Fe as well as Cl-complexed trace elements such as Pb maintain their concentrations in coexisting high-salinity brines and low-salinity vapor inclusions. Although we cannot exclude some Na^+ diffusion out of the inclusion, we explore the limiting possibility that the inclusion system is open to only two types of major-element transfer: the ion exchange of Cu^+H^{+1} and the diffusion of elemental H_2 between the fluid inclusion and the surrounding rock and its local pore fluid. Driving forces for the transfer of these two components in- or outward will be determined by multicomponent reactions in the system Na-K-Fe-Cu-Cl-S-O-H. The speciations of minor elements in the vapor inclusions, including Au, are likely to be dominated by equilibria among the major-element species.

Chemical equilibria inside the fluid inclusions include the following important reactions (and their combinations), which tend to proceed from left to right with decreasing temperature:

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Chemical equilibria in the rock-buffered pore fluid outside the inclusions are subject to complex fluid–mineral buffering reactions, which we can express in simplified terms by:

whereby 'FeO' stands for biotite and other ferrous silicates, in rocks that are typically affected by potassic alteration (K-feldspar, biotite, magnetite) with a partial overprint by phyllic alteration (muscovite, chlorite; using the empirical calibration for 'FeO' from Giggenbach, 1992; see table 4 in Heinrich, 2005). These pH- and redox-controlling equilibria in turn fix the concentrations of Fe, Cu, Au and S dissolved in the pore fluid in equilibrium with in the surrounding rock, if saturation with chalcopyrite, pyrite and gold is assumed (Heinrich, 2005). The rock system therefore acts as an unlimited reservoir or sink of the mobile components Cu^+ , H^+ and H_2 , whose activities are buffered by an excess of saturating minerals, i.e., albite + K-feldspar + muscovite + quartz + 'FeO' + magnetite + pyrite + chalcopyrite or bornite + gold.

To predict the possible extent of chemical modification of a low-salinity vapor inclusion in this environment, we chose a starting composition based on high-temperature vapor inclusions from the Grasberg porphyry Cu-Au deposit, where high gold as well as variably high copper concentrations were analyzed (Ulrich et al., 1999). In contrast to earlier papers inferring a high original Cu content from the average of all vapor analyses in a boiling assemblage (1.2 wt% Cu as analyzed by Ulrich et al., 1999), we here consider the possibility that the copper content may have initially been near the lower end of the analyzed range, i.e. ~ 500 ppm ($0.008m \text{ Cu}_{\text{tot}}$), which is consistent with estimations based on experimental data in S-rich fluid systems (Zajacz et al., 2011). We assume that the inclusions trapped and maintained a high concentration of ~ 2 % total sulfur, assumed to be initially present in equal proportions of SO_2 and H_2S ($0.3m$ each). This sulfur concentration is slightly higher than the maximum measured in the present study of garnet and topaz inclusions, but typical for low-salinity vapor inclusions in porphyry copper systems such as Bingham Canyon (Seo et al., 2009, 2012) and Bajo de la Alumbrera (Heinrich et al., 2011). Initial acid concentration ($\text{H}^+ + \text{HCl}$) was taken as $0.03m$ (HCl partitions into the vapor at high P-T; Palmer et al., 2004; Williams-Jones and Heinrich, 2005) but this value turns out to be of minor importance so long as it is lower than total H_2S and SO_2 concentration.

In a series of free-energy minimization experiments we used the ETH-modified CSIRO-THERMOCALC package of Turnball and Wadsley (1986) to compute the bulk composition and speciation inside this idealized fluid inclusion, assuming that Cu^+ , H^+ and H_2 can freely exchange between the inclusion and the surrounding rock. Charge-balanced exchange of Cu^+ and H^+ between the inclusion interior and the surrounding rock-dominated environment is then described by the reaction

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$$\text{Cu}^+_{\text{inclusion}} + \text{H}^+_{\text{rock}} = \text{Cu}^+_{\text{rock}} + \text{H}^+_{\text{inclusion}} \quad (6)$$

with

$$\begin{aligned} \Delta G_r = & -\mu^0_{\text{Cu}^+, \text{inclusion}} - RT \ln a_{\text{Cu}^+, \text{inclusion}} - \mu^0_{\text{H}^+, \text{rock}} - RT \ln a_{\text{H}^+, \text{rock}} + \\ & + \mu^0_{\text{Cu}^+, \text{rock}} + RT \ln a_{\text{Cu}^+, \text{rock}} + \mu^0_{\text{H}^+, \text{inclusion}} + RT \ln a_{\text{H}^+, \text{inclusion}} \end{aligned} \quad (7)$$

The standard potentials μ^0_i in the inclusion and the surrounding rock are equal, if we assume thermal equilibrium and ignore pressure effects between the isochoric system forming a bubble in the inclusion, and the external environment that may not necessarily follow the boiling curve of the cooling fluid (the external fluid more likely cools at constant pressure and thereby evolves to a single-phase liquid; Heinrich et al., 2004). If the inclusion interior and the surrounding rock system attain a state of exchange equilibrium with regard to reaction (6), then $\Delta G_r = 0$ and eq. (7) simplifies to

$$(a_{\text{Cu}^+} / a_{\text{H}^+})_{\text{rock}} = (a_{\text{Cu}^+} / a_{\text{H}^+})_{\text{inclusion}} \quad (8)$$

In the numerical equilibration experiments, redox potential was fixed at $\log f_{\text{O}_2} = \text{NNO}+2$, which constrains a_{H_2} outside as well as in the inclusion to the same value, close to the hematite + magnetite equilibrium at temperatures between 440 and 250 °C. In a first step, a rock-buffered external system was equilibrated to calculate $(a_{\text{Cu}^+} / a_{\text{H}^+})_{\text{rock}}$ at each temperature in steps of 10°, at a high ratio of minerals to fluid containing the same total chloride concentration as the inclusion. Speciation inside the fluid inclusion was subsequently computed iteratively for each temperature, varying the bulk composition by exchanging Cu^+ for H^+ until $(a_{\text{Cu}^+} / a_{\text{H}^+})_{\text{inclusion}}$ matched the activity ratio $(a_{\text{Cu}^+} / a_{\text{H}^+})_{\text{rock}}$. Figure 2 compares the initial concentration of major components in the inclusion (= assumed trapping composition marked on the right-hand axis) with the resulting concentrations in the re-equilibrated inclusion at each temperature (heavy lines and symbols) and the corresponding concentrations in the rock-buffered pore fluid (thinner lines with equivalent symbols and colors). The total Cu content of the inclusion increases with decreasing equilibration temperature of the $\text{Cu}^+ - \text{H}^+$ exchange, because most of the inward-diffusing Cu precipitates as Cu-Fe-sulfide (heavy red line with round symbols). Bornite + pyrite are stable at re-equilibration temperatures above 360°C, but increasing amounts of chalcopyrite are formed from 340 down to 250°C. Even the dissolved copper concentration in the aqueous phase of the inclusion is higher than the assumed starting concentration, with a maximum near 350°C, for the following reason. Although significant H^+ is removed in exchange for added Cu^+ to adjust charge balance (equilibrium 8), the total acid concentration ($\text{H}^+ + \text{HCl}$) in the inclusion fluid increases with decreasing re-equilibration temperature, in contrast to its counterpart in the external rock-buffered pore fluid, which is progressively neutralized by feldspar hydrolysis (eq. 4). Acidity inside the inclusion is produced, beyond the initial 0.03m, by the precipitation of Cu-Fe-sulfides (eq. 3), being ultimately derived from H_2S . Due to the moderately high H_2 fugacity imposed by the redox buffer in the rock, any initial SO_2 becomes reduced to H_2S (eq. 2), contributing to Cu-Fe-sulfide precipitation. More oxidized conditions would generate additional acidity inside the inclusions by the

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disproportionation reaction (1), thus equally contributing to H^+ diffusion outward and Cu^+ diffusion inward. In real geological systems, some of the excess H^+ produced within the model inclusion will probably diffuse outward in exchange for some inward diffusion of Na^+ , but this will only contribute to further minimization of the total free energy of the system compared to the limiting case modeled here.

In summary, inward diffusion of Cu^+ indeed occurs against the gradient in Cu^+ activity and total dissolved copper concentration, driven by the even steeper outward gradient in H^+ activity. This acidity gradient in turn results from the cooling of acid sulfur species and the generation of H^+ associated with internal precipitation of Cu-Fe-sulfide, caused by the large initial excess of S inside the fluid inclusion while the activities of all S species in the surrounding rock-buffered fluid decrease steeply with falling temperature. The magnitude of predicted Cu introduction therefore explains the microanalytical observations of Cu $\sim$ 1 wt% at similar or somewhat higher S contents in many natural vapor inclusions (Fig. 2).

Gold has been modeled in the same equilibration calculations, as a trace-element whose solubility is determined by activities of H^+ , H_2 and the two ligands HS^- and Cl^- (Stefansson and Seward, 2004). If our model fluid in the inclusion contained 10 ppm as analyzed in the Grasberg vapor inclusions, gold is predicted to precipitate inside the inclusion upon cooling, but the activities of the solubility-determining bisulfide species inside the inclusion will be higher than those in the rock-buffered environment outside, where aqueous sulfide is consumed by sulfidation of Fe from rock-forming silicates (e.g., Sillitoe, 2010). This creates a driving force for Au to migrate out of the inclusion, but never to diffuse into a fluid inclusion after entrapment. We conclude, therefore, that high Au concentrations analyzed in porphyry-hosted vapor inclusions are likely to be correct or even minimum estimates for actual trapping concentrations. In contrast to the small Cu^+ ion, the large Au^+ ion (1.37 Å) is also less likely to diffuse through the quartz structure, and therefore would be retained within the inclusion.

While species concentrations in this model are subject to uncertainties in thermodynamic data, the predicted direction of chemical driving forces shown in Figure 2 are robust, because they are dominated by mass balance in the S-O-H subsystem and do not depend critically on accurate representation of ore mineral solubility and aqueous Cu and Au speciation. They explain the extreme enrichment of Cu in S-rich vapor inclusions, by a mechanism that will affect coexisting brine inclusions to a smaller extent, because these are depleted in sulfur species (H_2S and/or SO_2). We cannot predict the post-entrapment behavior of brine inclusions for lack of thermodynamic data, but if their composition is dominated by chloride salts, any post-entrapment modification of element ratios should be detectable by microanalytical techniques. Studies by Hall and Sterner (1993) and Audétat and Günther (1999) suggest that post-entrapment loss of H_2O from brine inclusions is more likely than modification of element ratios, with the notable exception of minor Li. If cooling ores are dominated by residual brines remaining in the pore space of the rock after removal of buoyant vapor, their excess concentration in base metals compared to their low S content may further assist diffusion of Cu into S-rich vapor inclusions.

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Figure 2. Multicomponent thermodynamic reaction model predicting the bulk composition and internal speciation of a quartz-hosted vapor inclusion that initially trapped a high concentration of sulfur but comparatively little Cu, like a typical high-temperature vapor fluid in a porphyry-Cu-Au deposit (compositional parameters except Cu similar to the Grasberg vapor analyzed by Ulrich et al., 1999, modeled with data for the Na-K-Fe-Cu-Cl-S-O-H system as in Heinrich, 2005). Allowing diffusive re-equilibration of H_2 activity and charge-balanced exchange equilibrium of Cu^+ for H^+ with a rock-buffered fluid existing outside the host quartz can explain the extent of Cu enrichment observed in the Grasberg vapor inclusions after cooling. By contrast, Au has no driving force for inward transport, tentatively indicating that high Au concentrations analyzed in high-T vapor inclusions are unmodified trapping concentrations.

5. Geological implications for Porphyry-style and Epithermal ore formation

Total Cu concentrations in excess of 1 wt% in intermediate-density and vapor-like inclusions of low salinity, hosted by quartz veins in magmatic-hydrothermal systems, are likely to exceed the true trapping concentrations if a molar equivalent of sulfur or an excess of sulfur over copper is

present in the inclusion. Our earlier mass-balance estimates proposing that Cu introduced into a deposit as a single-phase fluid first partition into the vapor upon decompression, and then precipitates dominantly from the vapor phase (Landtwing et al., 2010; Seo et al., 2012) clearly needs to be revised (Lerchbaumer and Audétat, 2012). However, significant transport of Cu and particularly Au in S-rich vapor-like fluids remains an important natural process (Zajacz et al., 2010; Zajacz et al., 2011), compared to Fe, Zn, Pb that are invariably enriched in Cl-rich brines. The conclusion is still valid that porphyry-type deposits (especially Cu-Au-rich systems formed at low pressure and shallow depths) are dominated by vapor in terms of fluid mass and volume (Henley and McNabb, 1978; Hedenquist et al., 1998), accompanied by condensation of a smaller amount of hypersaline brine (Williams-Jones and Heinrich, 2005; Landtwing et al., 2010; Sillitoe, 2010; Richards, 2011). In contrast to our earlier interpretations emphasizing the dominant role of vapor (Heinrich et al., 1999; Landtwing et al., 2010), copper is probably transported in comparable proportions by vapor and brine, after fluid phase separation at high temperature (Lerchbaumer and Audétat, 2012). Fluid inclusion distribution in zoned ore shells (Landtwing et al., 2012) and a recent hydrological model for the physical evolution of ascending magmatic fluids in porphyry systems (Weis et al., 2012) indicate that copper ore deposition occurs well above the region of phase separation, from two-phase fluids that together cool and expand across the boundary from the hot lithostatically-pressured fluid domain towards the hydrostatically-pressured environment, thus forming a confined copper ore shell.

Gold concentrations at ppm-levels in sulfur-rich vapor inclusions require additional confirmation, ideally by microanalytical data from diverse host minerals in addition to quartz. Based on the presently available evidence, preferential partitioning of Au into S-rich acidic vapor at near-magmatic pressures and temperatures is not a geological artifact created by post-entrapment modification of fluid inclusions. If confirmed, this implies that the widespread separation of two fluid phases in the porphyry environment leads to chemical separation of Au from Cu. This would enhance the possibility of selective transport of Au out of the porphyry environment into the surrounding, cooler and hydrostatically-pressured near-surface domain. There, the gold-rich vapor (and aqueous fluids derived by its cooling and contraction) will become powerful agents for gold mineralization in various types of epithermal ore deposits (e.g., Muntean et al., 2011).

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References

- Audétat, A., Günther, D., Heinrich, C.A., 1998. Formation of a magmatic-hydrothermal ore deposit: Insights with LA-ICP-MS analysis of fluid inclusions. *Science* 279, 2091-2094.
- Audétat, A., Günther, D., 1999. Mobility and H₂O loss from fluid inclusions in natural quartz crystals. *Contributions to Mineralogy and Petrology* 137, 1-14.
- Audétat, A., Günther, D., Heinrich, C.A., 2000. Causes for large-scale metal zonation around mineralized plutons: Fluid inclusion LA-ICP-MS evidence from the Mole Granite, Australia. *Economic Geology* 95, 1563-1581.
- Baker, T., Van Achterberg, E., Ryan, C.G., Lang, J.R., 2004. Composition and evolution of ore fluids in a magmatic-hydrothermal skarn deposit. *Geology* 32, 117-120.
- Bodnar, R.J., Vityk, M.O., 1994. Interpretation of Microthermometric data for H₂O-NaCl fluid inclusions, in: De Vivo, B., Frezzotti, M.L. (Eds.), *Fluid inclusions in minerals: Methods and applications*. Virginia Tech, Blacksburg, pp. 117-130.
- Brady, J.B., Cherniak, D.J., 2010. Diffusion in Minerals An Overview of Published Experimental Diffusion Data, in: Zhang, Y.X., Cherniak, D.J. (Eds.), *Diffusion in Minerals and Melts*, pp. 899-920.
- Cauzid, J., Philippot, P., Martinez-Criado, G., Menez, B., Laboure, S., 2007. Contrasting Cu-complexing behaviour in vapour and liquid fluid inclusions from the Yankee Lode tin deposit, Mole Granite, Australia. *Chemical Geology* 246, 39-54.
- Cline, J.S., Bodnar, R.J., 1991. Can economic porphyry copper mineralization be generated by a typical calc-alkaline melt. *Journal of Geophysical Research-Solid Earth and Planets* 96, 8113-8126.
- Cloke, P.L., Kesler, S.E., 1979. Halite trend in hydrothermal solutions. *Economic Geology* 74, 1823-1831.
- Crerar, D.A., Barnes, H.L., 1976. Ore solution chemistry 5. Solubilities of chalcopyrite and chalcocite assemblages in hydrothermal solution at 200° to 350°C. *Economic Geology* 71, 772-794.
- Damman, A.H., Kars, S.M., Touret, J.L.R., Rieffe, E.C., Kramer, J., Vis, R.D., Pintea, I., 1996. PIXE and SEM analyses of fluid inclusions in quartz crystals from the K-alteration zone of the Rosia Poieni porphyry-Cu deposit, Apuseni mountains, Rumania. *European Journal of Mineralogy* 8, 1081-1096.
- Eadington, P.J., 1983. A fluid inclusion investigation of ore formation in a tin-mineralized granite, New England, New South Wales. *Economic Geology* 78, 1204-1221.
- Eastoe, C.J., 1982. Physics and chemistry of the hydrothermal system at the Panguna porphyry copper deposit, Bougainville, Papua New Guinea. *Economic Geology* 77, 127-153.

Selective copper diffusion into quartz-hosted vapor inclusions: evidence from other host minerals, driving forces, and consequences for Cu-Au ore formation

Elphick, S.C., Graham, C.M., 1988. The effect of hydrogen on oxygen diffusion in quartz - Evidence for fast proton transients. *Nature* 335, 243-245.

Frank, M.R., Simon, A.C., Pettke, T., Candela, P.A., Piccoli, P.M., 2011. Gold and copper partitioning in magmatic-hydrothermal systems at 800°C and 100 MPa. *Geochimica et Cosmochimica Acta* 75, 2470-2482.

Günther, D., Audétat, A., Frischknecht, R., Heinrich, C.A., 1998. Quantitative analysis of major, minor and trace elements in fluid inclusions using laser ablation inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry* 13, 263-270.

Giggenbach, W.F., 1992. SEG distinguished lecture - Magma degassing and mineral deposition in hydrothermal system along convergent plate boundaries. *Economic Geology* 87, 1927-1944.

Guillong, M., Heinrich, C.A., 2007. Sensitivity enhancement in laser ablation ICP-MS using small amounts of hydrogen in the carrier gas. *Journal of Analytical Atomic Spectrometry* 22, 1488-1494.

Guillong, M., Meier, D.L., Allan, M.M., Heinrich, C.A., Yardley, B.W.D., 2008. SILLS: A MATLAB-based program for the reduction of laser ablation ICP-MS data of homogeneous materials and inclusions. *Mineralogical Association of Canada Short Course* 40, 328-333.

Hall, D.L., Sterner, S.M., 1993. Preferential water-loss from synthetic fluid inclusions. *Contributions to Mineralogy and Petrology* 114, 489-500.

Hall, D.L., Sterner, S.M., 1995. Experimental diffusion of hydrogen into synthetic fluid inclusions in quartz. *Journal of Metamorphic Geology* 13, 345-355.

Harris, P.M., Waring, C.E., 1937. Diffusion of lithium ions through quartz in an electric field. *Journal of Physical Chemistry* 41, 1077-1085.

Hedenquist, J.W., Arribas, A., Reynolds, T.J., 1998. Evolution of an intrusion-centered hydrothermal system: Far Southeast-Lepanto porphyry and epithermal Cu-Au deposits, Philippines. *Economic Geology* 93, 373-404.

Heinrich, C.A., Ryan, C.G., Mernagh, T.P., Eadington, P.J., 1992. Segregation of ore metals between magmatic brine and vapor - A fluid inclusion study using PIXE microanalysis. *Economic Geology* 87, 1566-1583.

Heinrich, C.A., Günther, D., Audétat, A., Ulrich, T., Frischknecht, R., 1999. Metal fractionation between magmatic brine and vapor, determined by microanalysis of fluid inclusions. *Geology* 27, 755-758.

Heinrich, C.A., Pettke, T., Halter, W.E., Aigner-Torres, M., Audetat, A., Gunther, D., Hattendorf, B., Bleiner, D., Guillong, M., Horn, I., 2003. Quantitative multi-element analysis of minerals, fluid and

Selective copper diffusion into quartz-hosted vapor inclusions: evidence from other host minerals, driving forces, and consequences for Cu-Au ore formation

melt inclusions by laser-ablation inductively-coupled-plasma mass-spectrometry. *Geochimica et Cosmochimica Acta* 67, 3473-3497.

Heinrich, C.A., 2005. The physical and chemical evolution of low-salinity magmatic fluids at the porphyry to epithermal transition: a thermodynamic study. *Mineralium Deposita* 39, 864-889.

Heinrich, C.A., Erni, M., Von Quadt, A., Márquez - Zavla, F., 2011. Life-times and scales of Cu-Au-mineralizing magmatic-hydrothermal processes: Farallón Negro (Argentina), Proceedings of the 11th Biennial SGA Meeting: Let's Talk Ore Deposits. Society for Geology Applied to Mineral Deposits, Antofagasta, Chile.

Henley, R.W., McNabb, A., 1978. Magmatic vapor plumes and groundwater interaction in porphyry copper emplacement. *Economic Geology* 73, 1-20.

Herzarkhani, A., Williams-Jones, A.E., 1998. Controls of alteration and mineralization in the Sungun porphyry copper deposit, Iran: Evidence from fluid inclusions and stable isotopes. *Economic Geology* 93, 651-670.

Ingrin, J., Blanchard, M., 2006. Diffusion of hydrogen in minerals. *Water in Nominally Anhydrous Minerals* 62, 291-320.

Kamenetsky, V.S., Danyushevsky, L.V., 2005. Metals in quartz-hosted melt inclusions: Natural facts and experimental artifacts. *American Mineralogist* 90, 1674-1678.

Krauskopf, K.B., 1964. The possible role of volatile metal compounds in ore genesis. *Economic Geology* 59, 22-45.

Kronenberg, A.K., Kirby, S.H., 1987. Ionic-conductivity of quartz - DC time - dependence and transition in charge-carriers. *American Mineralogist* 72, 739-747.

Landtwing, M.R., Furrer, C., Redmond, P.B., Pettke, T., Guillong, M., Heinrich, C.A., 2010. The Bingham Canyon Porphyry Cu-Mo-Au Deposit. III. Zoned Copper-Gold Ore Deposition by Magmatic Vapor Expansion. *Economic Geology* 105, 91-118.

Lerchbaumer, L., Audétat, A., 2012. High Cu concentrations in vapor-type fluid inclusions: An artifact? *Geochimica et Cosmochimica Acta* 88, 255-274.

Li, Y., Audétat, A., Lerchbaumer, L., Xiong, X.L., 2009. Rapid Na, Cu exchange between synthetic fluid inclusions and external aqueous solutions: evidence from LA-ICP-MS analysis. *Geofluids* 9, 321-329.

Mavrogenes, J.A., Bodnar, R.J., 1994. Hydrogen movement into and out of fluid inclusions in quartz - Experimental evidence and geological implications. *Geochimica et Cosmochimica Acta* 58, 141-148.

Selective copper diffusion into quartz-hosted vapor inclusions: evidence from other host minerals, driving forces, and consequences for Cu-Au ore formation

- Muntean, J.L., Cline, J.S., Simon, A.C., Longo, A.A., 2011. Magmatic-hydrothermal origin of Nevada's Carlin-type gold deposits. *Nature Geoscience* 4, 122-127.
- Nagaseki, H., Hayashi, K.I., 2008. Experimental study of the behavior of copper and zinc in a boiling hydrothermal system. *Geology* 36, 27-30.
- Palmer, D.A., Simonson, J.M., Jensen, J.P., 2004. Partitioning of electrolytes to steam and their solubilities in steam., in: Palmer, D.A., Fernandez-Prini, R., Harvey, A.H. (Eds.), *Aqueous Systems at Elevated Temperatures and Pressures: Physical Chemistry in Water, Steam and Hydrothermal Solutions*. Elsevier, pp. 407-439.
- Pokrovski, G.S., Roux, J., Harrichoury, J.C., 2005. Fluid density control on vapor-liquid partitioning of metals in hydrothermal systems. *Geology* 33, 657-660.
- Pokrovski, G.S., Borisova, A.Y., Harrichoury, J.C., 2008. The effect of sulfur on vapor-liquid fractionation of metals in hydrothermal systems. *Earth and Planetary Science Letters* 266, 345-362.
- Richards, J.P., 2011. Magmatic to hydrothermal metal fluxes in convergent and collided margins. *Ore Geology Reviews* 40, 1-26.
- Roedder, E., 1984. Fluid inclusions. *Reviews in Mineralogy* 12, 1-&.
- Ryan, C.G., Heinrich, C.A., Mernagh, T.P., 1993. PIXE microanalysis of fluid inclusions and its application to study ore metal segregation between magmatic brine and vapor. *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms* 77, 463-471.
- Sawkins, F.J., Scherkenbach, D.A., 1981. High copper content of fluid inclusions in quartz from Northern Sonora - Implications for ore-genesis theory. *Geology* 9, 37-40.
- Seo, J.H., Guillong, M., Heinrich, C.A., 2009. The role of sulfur in the formation of magmatic-hydrothermal copper-gold deposits. *Earth and Planetary Science Letters* 282, 323-328.
- Seo, J.H., Guillong, M., Aerts, M., Zajacz, Z., Heinrich, C.A., 2011. Microanalysis of S, Cl, and Br in fluid inclusions by LA-ICP-MS. *Chemical Geology* 284, 35-44.
- Seo, J.H., Guillong, M., Heinrich, C.A., 2012. Separation of Molybdenum and Copper in Porphyry Deposits: The Roles of Sulfur, Redox and pH in Ore Mineral Deposition at Bingham Canyon. *Economic Geology* 107, 333-356.
- Seward, T.M., 1984. The formation of lead (II) chloride complexes to 300 °C - A spectrophotometric study. *Geochimica et Cosmochimica Acta* 48, 121-134.
- Shannon, R.D., 1976. Revised effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A* 32, 751-767.

Selective copper diffusion into quartz-hosted vapor inclusions: evidence from other host minerals, driving forces, and consequences for Cu-Au ore formation

- Sillitoe, R.H., 2010. Porphyry Copper Systems. *Economic Geology* 105, 3-41.
- Simon, A.C., Pettke, T., Candela, P.A., Piccoli, P.M., Heinrich, C.A., 2006. Copper partitioning in a melt-vapor-brine-magnetite-pyrrhotite assemblage. *Geochimica et Cosmochimica Acta* 70, 5583-5600.
- Stefansson, A., Seward, T.M., 2004. Gold(I) complexing in aqueous sulphide solutions to 500 degrees C at 500 bar. *Geochimica et Cosmochimica Acta* 68, 4121-4143.
- Turnbull, A.G., Wadsley, M.W., 1986. The CSIRO-SGTE THERMODYNAMIC System (Version V). Commonwealth Scientific and Industrial Research Organisation, Port Melbourne, Division of Mineral Chemistry Communications.
- Ulrich, T., Gunther, D., Heinrich, C.A., 1999. Gold concentrations of magmatic brines and the metal budget of porphyry copper deposits. *Nature* 399, 676-679.
- Verhoogen, J., 1952. Ionic diffusion and electrical conductivity in quartz. *American Mineralogist* 37, 637-655.
- Weis, P., Driesner, T., Heinrich, C.A., 2012. Porphyry-Copper Ore Shells Form at Stable Pressure-Temperature Fronts Within Dynamic Fluid Plumes. *Science*.
- Williams-Jones, A.E., Heinrich, C.A., 2005. 100th Anniversary special paper: Vapor transport of metals and the formation of magmatic-hydrothermal ore deposits. *Economic Geology* 100, 1287-1312.
- Yang, X., Xu, Z., Seo, J.H., Lu, X., Guillong, M., 2009. Fluid properties in porphyry-style to skarn-hosted copper mineralization at Dongguashan, SE China. *Geochimica et Cosmochimica Acta* 73, A1480-A1480.
- Zajacz, Z., Hanley, J.J., Heinrich, C.A., Halter, W.E., Guillong, M., 2009. Diffusive reequilibration of quartz-hosted silicate melt and fluid inclusions: Are all metal concentrations unmodified? *Geochimica et Cosmochimica Acta* 73, 3013-3027.
- Zajacz, Z., Seo, J.H., Candela, P.A., Piccoli, P.M., Heinrich, C.A., Guillong, M., 2010. Alkali metals control the release of gold from volatile-rich magmas. *Earth and Planetary Science Letters* 297, 50-56.
- Zajacz, Z., Seo, J.H., Candela, P.A., Piccoli, P.M., Tossell, J.A., 2011. The solubility of copper in high-temperature magmatic vapors: A quest for the significance of various chloride and sulfide complexes. *Geochimica et Cosmochimica Acta* 75, 2811-2827.