

LETTER

Metals in quartz-hosted melt inclusions: Natural facts and experimental artifacts

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ABSTRACT

Studies of melt inclusions trapped in magmatic phenocrysts can provide a new perspective on several key outstanding problems in the understanding of the genesis of orthomagmatic ore deposits, particularly with respect to the concentration of metals in parental magmas. The published data shows a mismatch between low and high abundances of Cu (and Ag) in unheated and remelted melt inclusions, respectively. This experimental study investigates the possibility that quartz-hosted rhyolitic melt inclusions may change their composition during laboratory heating under different conditions. Exceptional volatility of Cu and Ag and inert behavior of other metals (Zn, Pb, Mo, Sn, W) and lithophile trace elements at high temperature (850 °C) is demonstrated. Heating experiments with melt inclusions require specific conditions that should take the high volatility of Cu and Ag into account. The open system behavior of Cu and Ag can also affect the composition of melt inclusions within the time frame between trapping and eruption

INTRODUCTION

Melt inclusions are small batches (usually <50 µm) of magma incorporated inside crystallizing minerals, and as such they can provide invaluable information about physical parameters and chemical compositions of the magmatic environment (Roedder 1979). Melt temperature and composition, liquidus assemblage and liquid line of descent, pre-eruptive abundances of volatile and metallic elements, and many other variables are more and more constrained from melt inclusions in petrological and geochemical studies.

Reconstruction of originally trapped melt composition, including volatile and trace elements, is invariably hampered because most melt inclusions suffer post-entrapment modifications (Anderson 2003; Roedder 1979; Thomas 1994). Compositional changes to the melt inside inclusions are caused by crystallization on the inclusion walls, diffusion exchange with the host mineral and surrounding magma (Anderson 2003; Cottrell et al. 2002; Danyushevsky et al. 2000; Gaetani and Watson 2000; Qin et al. 1992; Tait 1992; Thomas 1994), and leakage (Anderson 2003; Davidson and Kamenetsky 2001; Frezzotti 2001; Nielsen et al. 1998; Skirius et al. 1990). The melt inside inclusions is rarely quenched to glass, being more often recrystallized, and thus heating of melt inclusions is commonly required to produce glass suitable for analysis (Danyushevsky et al. 2002; Lowenstern 1995; Skirius et al. 1990). Although heating of melt inclusions in the laboratory is often unable to fully reverse post-trapping changes, it aids in obtaining an accurate composition of the melt inside the inclusions.

Melt inclusion studies of magmatic abundances of metallic elements (e.g., Cu, Zn, Pb, Mo, Ag, Au, etc.) are aimed at understanding their behavior during crystallization and degassing, and the role of different silicate magmas in contributing to economic mineralization. The outstanding question in this instance is whether inherently metal-enriched (fertile) magmas exist in

nature and originate metal-bearing fluids, or whether occurrence of mineralization is governed by other factors. The analysis of unheated glass inclusions in quartz from several unmineralized felsic rocks yield low Cu abundances (Lowenstern 1993; Lowenstern et al. 1991), however, several studies of experimentally reheated melt inclusions from mineralized systems have demonstrated exceptionally high metal concentrations (Campos et al. 2002; Dietrich et al. 1999). For example, quartz-hosted homogenized melt inclusions from the Zaldívar porphyry-Cu deposit, Northern Chile, contained ore-grade concentrations of copper (up to 1.5 wt%) (Campos et al. 2002). In another example, significant enrichment in copper (up to 0.7 wt%) and silver (up to 329 ppm) in experimentally reheated and quenched melt inclusions in quartz from the Bolivian tin porphyry system (Dietrich et al. 1999) is in marked contrast with metal-poor compositions of natural glassy inclusions from the same suite.

The existing discrepancy in the results obtained from unheated and reheated inclusions of felsic melts in quartz warranted this study which tests (1) the possibility of metals being introduced into high-Si melt inclusions during experimental heating and (2) the existence of metal-rich magmas in nature.

SAMPLES, EXPERIMENTAL AND ANALYTICAL SETUP

The sample NZL 27b is from a rhyolitic dome within the Maroa Volcanic Center that belongs to the Taupo Volcanic Zone (TVZ), New Zealand. The TVZ is currently the largest active felsic system having produced $\sim 15 \times 10^3$ km³ of volcanic rock over 1.6 Ma (Wilson et al. 1995), dominated by compositionally uniform, metaluminous rhyolites. The rock is composed of phenocrysts of plagioclase, quartz, and minor hornblende and biotite, set in a vesicular glassy groundmass. The groundmass glass is a high-Si rhyolite (in wt%: SiO₂ 75, Al₂O₃ 11.9, Na₂O 3.7, K₂O 4.3) and has major and trace element composition similar to other TVZ rhyolite and orogenic rhyolite worldwide. Unlike many other TVZ samples, this rock has quartz-hosted melt inclusions quenched to glass, and thus, for the purpose of this study, the melt inclusions do not require homogenization and can be analyzed unheated.

The rock was gently crushed in a steel mortar, sieved, and several hundred quartz grains (0.5–1 mm) containing large melt inclusions (>30 µm) were hand-picked under a binocular microscope. The quartz fraction was subdivided onto five sets with roughly equal numbers of grains. The first set (A) was mounted in epoxy resin for analysis, and other sets were heated as described below in a muffle

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furnace in air, and quenched. Sets B and C were heated in ceramic crucibles at 850 °C for 24 and 120 h, respectively. Following heating, about half of the grains from set B were mixed with powdered NaCl, wrapped in 0.05 mm platinum foil and heated again at the same conditions, making a new set E. The grains from set D were wrapped in 0.05 mm platinum foil and placed in a ceramic crucible and heated at 850 °C for 24 h. Set F is represented by quartz grains heated at the same conditions in the mixture with powdered $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$. The chosen temperature of 850 °C was deduced from preliminary experiments with individual melt inclusions in a Linkam TS1500 heating stage in which fluid bubbles, appearing in the melt inclusions at the α - β quartz transition (573 °C), dissolve completely at 820–850 °C (homogenization). After experimental heating, quartz grains were mounted in epoxy mounts, ground, polished with a 0.3 μm alumina powder, thoroughly cleaned in the ultrasonic bath and wiped with a methanol-moistened tissue.

Randomly selected inclusions from sets A and B, exposed at the surface of quartz, were analyzed for major elements using a Cameca SX-100 electron microprobe (University of Tasmania). The major element variations among 22 analyzed inclusions were found to be small (SiO_2 74.0 $\pm$ 1.0 wt%; Al_2O_3 11.0 $\pm$ 0.4 wt%; total 94.3 $\pm$ 1.3 wt%).

Trace element concentrations in melt inclusions were analyzed by LA-ICPMS at the University of Tasmania. This instrumentation comprises a New Wave Research UP213 Nd-YAG (213 nm) laser coupled to an Agilent 4500 quadrupole mass-spectrometer. For this study, analyses were performed in a He atmosphere by ablating 40–110 μm -diameter spots at a rate of 5 shots/s using a laser power of $\sim$ 12 J/cm². The instrument was optimized for sensitivity on mid- to high-mass isotopes (in the range 80–240 a.m.u.) and for minimal molecular oxide species (i.e., $^{232}\text{Th}^{16}\text{O}/^{232}\text{Th} < 0.2\%$) and doubly charged ion species (i.e., $^{140}\text{Ce}^{++}/^{140}\text{Ce}^+ < 0.3\%$) production. The low level of molecular oxide and doubly charged ion production precludes the need to correct any of the analyte signal intensities for interfering species. Each analysis involves sequential peak hopping through the mass spectrum, with the accumulation of $\sim$ 50–150 replicate measurements of $\sim$ 20 milliseconds duration (1–3 seconds total) for each of the 28 analyte isotopes. The analysis time for each sample was 50–90 seconds, comprising a 30 second measurement of background (laser off) and a 20–60 second analysis with laser on. Instrument calibration was performed by ablating the NIST612 glass standard. Data reduction was undertaken according to standard methods (Longerich et al. 1996) using the NIST612 glass as a primary reference material and Al (11 wt% Al_2O_3) as the internal standard. USGS BCR-2g glass was repeatedly analyzed throughout analytical sessions and was used as a secondary reference material. Quartz phenocrysts were analyzed

under similar conditions, using a $\sim$ 110 micrometer beam and the 10 shots/s rate, and Si as the internal standard.

RESULTS

Heating of quartz grains under different conditions had no effect on the appearance of melt inclusions after quenching; they remained clear silicate glass, like in the unheated grains, sometimes with a small shrinkage bubble. Quartz grains from set E developed rounded or spherical shapes following reaction with NaCl added to this charge.

The average compositions of melt inclusions (in ppm) and compositional variability within each experimental set are summarized in Table 1. Melt inclusions from all sets have similar abundances of the analyzed trace elements but Cu and Ag (Table 1). Melt inclusions from a given set display a small range of concentrations of most trace elements (<15 rel%). However, the abundances of Cu and Ag show a large scatter (33–120 and 10–147 rel%, respectively). With the exception of Cu and Ag, the overall composition of the melt inclusions is similar to the matrix glass (Table 1).

Although highly variable within a given set, the concentrations of Cu (2.76 ppm) and Ag (<0.12 ppm) are systematically low in the unheated inclusions (set A), and similar to those in the matrix glass. These low concentrations are in striking contrast with the Cu and Ag enrichment (1–3 orders of magnitude, up to 740 ppm Cu and up to 260 ppm Ag) of the melt inclusions heated in the ceramic crucible (sets B and C), and in the presence of Cu salt (set F). The significant variability in Cu and Ag and Cu/Ag ratios was recorded among the melt inclusions in single quartz grain, and no clear correlation between the concentrations and the inclusions' size and position was found (Fig. 1). In other

TABLE 1. Average compositions (in ppm) of quartz-hosted melt inclusions and matrix glass from the rhyolite NZL27b (Taupo Volcanic Zone, New Zealand)

	matrix glass NZL27b		Set A, unheated		Set B, heated (850 °C, 24 h)		Set C, heated (850 °C, 120 h)		Set D, heated in Pt foil (850 °C, 24 h)		Set E, $\sim$ 1/2 set B mixed with NaCl and heated (850 °C, 24 h)		Set F, mixed with CuSO_4 (850 °C, 24 h)		Detect. limit
		$\delta\%$		$\delta\%$		$\delta\%$		$\delta\%$		$\delta\%$		$\delta\%$		$\delta\%$	
N			26		56		10		6		8		4		
CaO	6400	5200	6		5600	8	n.d.		n.d.		5200	9	5200	4	180
TiO ₂	1250	1020	5		1050	12	n.d.		n.d.		1030	12	1070	8	0
Cu	1.74	2.76	98		172	76	396	42	3.01	33	<0.665	120	294	40	1.28
Zn	42.1	45.3	9		46.0	18	42.0	9	42.7	7	46.8	15	40.3	2	0.427
Rb	153	124	2		122	6	118	3	n.d.		130	4	117	5	0.13
Sr	35.1	27.2	11		28.5	11	30.0	7	n.d.		26.0	22	25.8	6	0.029
Y	31.7	32.5	6		32.2	6	32.0	5	30.2	6	30.7	9	30.5	7	0.017
Zr	88.0	93.8	8		91.9	12	92.3	9	n.d.		87.2	11	86.5	9	0.037
Nb	9.19	8.60	3		8.51	7	8.35	6	n.d.		8.73	5	8.04	4	0.033
Mo	1.88	1.67	22		1.68	25	1.74	12	1.75	10	2.00	30	1.65	29	0.688
Ag	<0.045	<0.123	83		32	147	9.38	52	0.95	70	4.92	84	97.0	10	0.123
Sn	3.16	2.73	10		2.54	9	2.39	13	2.57	8	2.92	14	2.36	6	0.124
Ba	794	681	9		706	5	699	2	n.d.		680	3	634	1	0.156
La	30.3	27.6	8		27.3	5	27.7	3	n.d.		26.8	4	24.9	1	0.016
Ce	64.8	59.5	7		58.7	6	58.5	2	n.d.		57.5	6	53.5	2	0.017
Nd	24.4	25.0	4		24.8	8	24.7	6	n.d.		23.3	9	22.7	7	0.071
Sm	5.42	5.00	6		5.23	13	5.28	8	n.d.		4.90	11	4.49	8	0.087
Eu	0.44	0.475	18		0.443	23	0.455	17	n.d.		0.383	20	0.394	19	0.024
Gd	4.80	4.94	11		4.8	15	4.96	11	n.d.		4.51	13	4.41	8	0.085
Dy	5.18	5.56	8		5.31	11	5.40	7	n.d.		5.13	13	5.04	11	0.047
Er	3.35	3.51	9		3.32	8	3.45	7	n.d.		3.29	9	3.11	5	0.036
Yb	4.20	3.71	9		3.69	10	3.86	7	n.d.		3.71	9	3.45	4	0.049
W	1.91	1.63	7		1.58	16	1.52	5	1.67	9	1.87	12	1.48	16	0.074
Pb	21.9	18.4	8		19.7	26	17.5	5	18.2	4	19.6	13	16.8	6	0.047
Th	15.1	12.3	6		11.8	7	12.4	4	n.d.		12.5	5	11.1	8	0.02
U	3.64	2.92	4		2.88	8	2.87	5	n.d.		3.08	5	2.65	10	0.021

Notes: Compositional variability is shown as $\delta\%$ = standard deviation/average, 100%. Detection limits are given for analyses performed using 55 μm beam. N = number of analyzed inclusions; n.d. = not analyzed.

words, despite similar major and trace element compositions, and sometimes similar Cu/Ag, inclusions display a range of Cu and Ag contents even when they are located <100 μm of each other (Fig. 1). Due to this large scatter, no clear difference in the average Cu and Ag concentrations is observed between inclusions heated for 24 hours (set B) and 120 hours (set C), although it appears that Cu contents are higher in set C.

Quartz-hosted melt inclusions which were isolated from both the ceramic crucible and the furnace environment by a platinum foil (set D) have low Cu abundances (average 3 ppm), comparable with those in the matrix glass and unheated inclusions from set A (Table 1). Unlike Cu, the Ag contents of set D melt inclusions are relatively high (average 1 ppm), but still considerably lower than in the sets B and C inclusions.

The melt inclusions that made up set E were originally in the set B grains, and thus we assume that they had the composi-

tions of the set B inclusions before heating in the presence of NaCl powder. This experiment produced the compositions most depleted in Cu (<0.67 ppm), but still markedly enriched in Ag (4.9 ppm), if compared to the matrix glass and unheated melt inclusions.

The concentration of Ag analyzed in the quartz grains from all sets was always below the detection limit (0.011 ppm). Whereas Cu abundances in quartz from the sets A, D and E were also below the detection limit (0.067 ppm), the sets B and C quartz showed distinctly high concentrations (0.29 and 0.28 ppm, respectively).

DISCUSSION

The compositional similarity between the matrix glass and quartz-hosted melt inclusions (Table 1) implies their close genetic relationships and argues for that the melt inclusions in this study

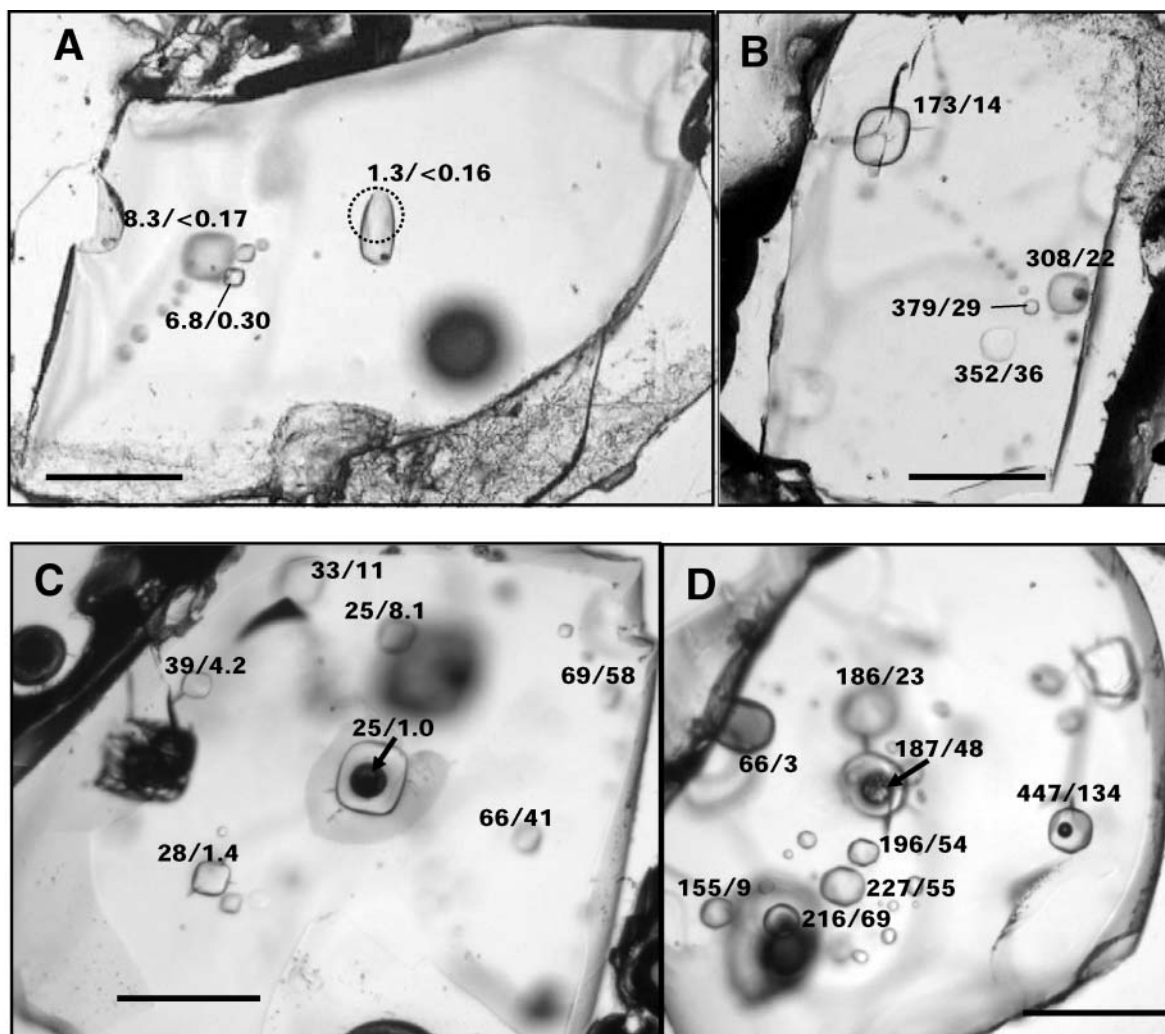


FIGURE 1. Concentrations of copper and silver (labelled as Cu/Ag) in unheated (A) and heated (B-D) melt inclusions. Scale bars 200 μm . Arrows show laser ablation pits. Note that radial cracks around inclusions formed during grinding and polishing.

are representative of the natural magma. Similar contents of most analyzed elements in unheated and heated melt inclusions (Table 1) suggest that host quartz phenocrysts were naturally quenched fast enough to prevent compositional changes related to crystallization on the walls of inclusions.

The main outcome of this study is a different behavior of Cu and Ag from other elements during experimental heating. In the experiments where host quartz was in direct contact with the heating “environment”, we record elevated concentrations of Cu in quartz (0.29 ppm), and abundances of both metals increase in the melt inclusions dramatically (Fig. 1B–D). The results of experiment with quartz grains wrapped in 0.05 mm platinum foil (set D) suggest that optically unidentified Cu–Ag bearing phases (fluid, brine, sulfide, sulfate, etc) in the melt inclusions or host quartz cannot be the source of these metals. Moreover, the experiment in purposefully Cu-rich environment (set F) shows that Cu mobility through the quartz host is the controlling factor of post-heating enrichment.

Diffusion of ions along dislocations, channels, twin boundaries or other structural defects in quartz (Kronenberg 1994 and references therein) can be responsible for the open system behavior of the melt inclusions, and in particular, for observed variability in the absolute abundances of Cu and Ag, and often Cu/Ag ratios, among melt inclusions in a single quartz grain (Fig. 1). However, diffusion into melt inclusions is noted for only two elements (Cu and Ag) among >30 chemical elements measured (sets B and C), whereas diffusion out of melt inclusions is confidently recorded for Cu only (set E). This means that the diffusion is determined by specific properties of the Cu and Ag ions rather than a control from structural characteristics of quartz. Thus, the phenomenal volatility of Cu and Ag can be accounted for when interpreting the results of other melt inclusion studies that showed metal enrichment in heated (remelted) melt inclusions compared to unheated inclusions from the same samples (Dietrich et al. 1999; Lowenstern et al. 1991).

Although Na behaved “inert” in our experiments, the heating-related gain of Na₂O (from 4 to 7.7 wt%) by quartz-hosted melt inclusions in the rhyodacitic pumices from Guadeloupe (Métrich 1988) implies that the uptake and/or loss of certain elements for each particular sample and/or experimental setup can be a problem. For example, in our experiments the “isolating” effect of the platinum foil, while strong for Cu, is clearly diminished for Ag (set D), if the source of Ag enrichment in the melt inclusions was outside their host quartz. Thus, the geochemical applications

of the melt inclusion data cannot be made without accessing all possible, naturally and experimentally induced, changes to the originally trapped compositions.

The process of Cu loss from melt inclusions (studied here and in other TVZ samples, our unpublished data), occurring in nature, is suggested by (1) exceptionally low Cu abundances in the unheated melt inclusions, (2) the results of the set E experiments. The latter clearly demonstrated that melt inclusions that are artificially enriched in Cu, can be almost completely deprived of their Cu enrichment by a chloride-rich medium outside the host quartz.

Low Cu contents in the unheated melt inclusions (2.8 ppm) are unusual if compared with the concentrations of similar incompatible elements, for example Yb (3.7 ppm) or Zn (45.3 ppm). The Cu/Zn (0.06) of the TVZ unheated melt inclusion is almost an order of magnitude lower than in a model depleted mantle (Salters and Stracke 2004) or the silicate Earth, “pyrolite” (McDonough and Sun 1995), but comparable with that in the matrix glass (0.04).

The presence of Cu (Fig. 2A) and Cu and Ag (Fig. 2B) in the shrinkage bubbles in the melt inclusions belonging to sets A and B is consistent with our record of their exceptional volatility. Strong Cu partitioning in the degassing fluid (Lowenstern 1993; Lowenstern et al. 1991) can account for Cu loss from the TVZ rhyolitic magma during eruption, and thus low Cu content in the matrix glass (Table 1). On the other hand, the melt trapped as melt inclusions appears to be undegassed (up to 7–8 wt% H₂O according the microprobe totals and direct measurements of H₂O in other TVZ melt inclusions; our unpublished data and Dunbar and Kyle 1993). Thus the assumption of Cu loss from the melt via degassing prior to entrapment of the inclusions is not justified. The alternative explanation for unusually low Cu in the set A melt inclusions is that they lost their original Cu (at least 25 ppm according a model Cu/Zn ratio of 0.55 (McDonough and Sun 1995; Salters and Stracke 2004) to the levels in the matrix glass during magma decompression and related degassing. In other words, the phenomenon of Cu diffusion out of melt inclusions, similar to that recorded in the set E experiments, suggests the possibility of re-equilibration of quartz-hosted melt inclusion with continuously Cu-degassing magma during its ascent and eruption.

Our study demonstrates that (1) experiments that are not designed carefully can result in the open system behavior of quartz-hosted rhyolitic melt inclusions, and (2) natural processes

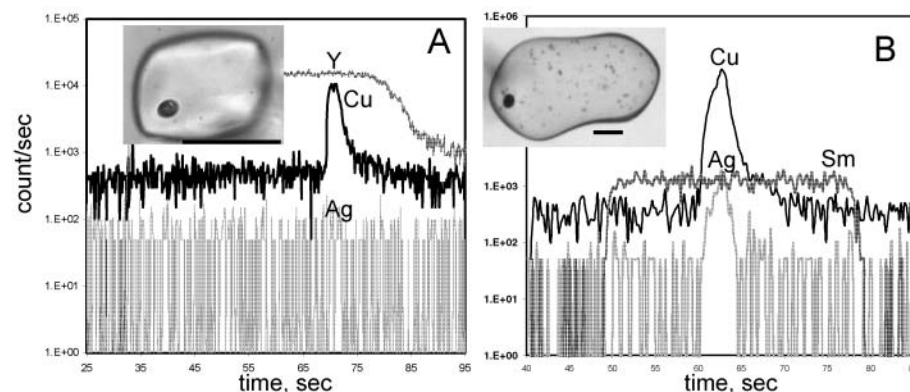


FIGURE 2. Signal intensities with time for copper and silver and selected lithophile elements recorded on the mass-spectrometer during analysis of unheated melt inclusions (set A, photos shown). Note increase in abundances of Cu (A) and Cu and Ag (B) that corresponds in time to the ablation of the shrinkage bubble. Scale bars 50 μm.

(magma contamination, mixing and degassing) can change the composition of originally trapped melt by diffusion of certain elements in and out, to maintain equilibrium. Although we have recorded diffusion of Cu and Ag only, similar behavior of other elements in different samples cannot be excluded.

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