# The controls of post-entrapment diffusion on the solubility of chalcopyrite daughter crystals in natural quartz-hosted fluid inclusions

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## ABSTRACT

The presence of chalcopyrite daughter crystals in natural quartz-hosted fluid inclusions that do not dissolve when heated to trapping conditions suggests that inclusions are subject to post-entrapment modifications that affect chalcopyrite solubility. Previous double capsule experiments conducted by Mavrogenes and Bodnar (1994) concluded that the post-entrapment outward diffusion of $H_2$ is responsible for the presence of non-dissolvable chalcopyrite crystals in natural, quartz-hosted brine inclusions. However, recent studies have shown that quartz-hosted inclusions can also be modified by diffusional $H^+$ loss and $Cu^+$ gain. This means that multiple factors may influence chalcopyrite solubility in different fluid inclusion types. In this study, the experimental procedure of Mavrogenes and Bodnar (1994) was recreated in order to rehydrogenate quartz-hosted, chalcopyrite-bearing fluid inclusions from the El Teniente Cu–Mo porphyry deposit, Chile. These inclusions had a range of salinities and densities. Results show that the experimental technique is successful for fluid inclusions that contain relatively small chalcopyrite daughter crystals and have moderate salinities ($>5$ wt.% $NaCl_{eq}$). In contrast, chalcopyrite crystals do not dissolve in low density vapor inclusions even after rehydrogenation. The failure of chalcopyrite crystals to dissolve in these inclusions is attributed to their lower initial pH and higher sulfide concentrations, which led to greater post-entrapment $H^+$ loss and $Cu^+$ gain. This considered, Cu concentrations in moderate to high salinity inclusions are likely to reflect those present at trapping, suggesting that $H_2$ loss is the primary control on the failed dissolution of chalcopyrite. By contrast, Cu concentrations in S-rich vapor inclusions can increase considerably via inward $Cu^+$ diffusion in the presence of an external Cu-bearing fluid and a pH gradient between the inclusion and this fluid (Lerchbaumer and Audétat, 2012; Seo and Heinrich, 2013). In accordance with these studies, the post-entrapment modification of Cu concentrations in vapor inclusions may undermine the apparent importance of phase separated vapors as a key agent of Cu transport and deposition in porphyry systems.

## 1. Introduction

Fluid inclusion analysis is a fundamental technique for determining the physical and chemical characteristics of fluids that were once present in geological environments. One of the assumptions of this approach is that the concentration of elements within a fluid inclusion remains unchanged following entrapment in a host mineral such as quartz. Despite this, it has been suggested that hydrogen diffusion ($H_2$) through quartz can occur, resulting in significant changes in inclusion redox potentials (e.g. Roedder, 1984). This is supported by spectrophotometric diffusion tests in the temperature range 400–900 °C, which showed that over time hydrogen can migrate through quartz via bulk diffusion (Kats et al., 1962). Changes in inclusion $fH_2$ have subsequently been used to explain the presence of anomalous daughter phases, volatile species and isotopic ratios in natural quartz-hosted fluid inclusions (Hall, 1989; Hall and Bodnar, 1990; Hall et al., 1991; Morgan et al., 1993; Mavrogenes and Bodnar, 1994).

The effect of hydrogen diffusion on metal-sulfide solubility, in particular the impact on sulfide daughter minerals, was studied previously using small, chalcopyrite-bearing, high salinity (~55 wt.% $NaCl_{eq}$) fluid inclusions from the Red Mountain porphyry Cu deposit, Arizona (Mavrogenes and Bodnar, 1994). Here, the occurrence of large numbers of coeval, chalcopyrite-bearing fluid inclusions with broadly uniform vapor fractions, number of phases and volumetric proportions provided strong evidence that the chalcopyrite crystals were daughter crystals and not accidentally incorporated grains. The high Cu concentrations of these inclusions were interpreted to be typical of the high solubility of Cu in saline magmatic-hydrothermal fluids and were in accordance with solubility data obtained from synthetic fluid inclusion studies (Mavrogenes et al., 1992). However, these apparent daughter crystals

did not dissolve, as they should do, when heated above the inferred trapping temperatures but did dissolve once the samples had been equilibrated in double-capsule experiments designed to diffuse hydrogen into the trapped fluids. These results are consistent with post-entrapment loss of hydrogen as $H_2$ from the fluid inclusions by diffusion through quartz and imply that $fH_2$ is a key control on the solubility of chalcopyrite in porphyry brines.

Chalcopyrite daughter crystals have also been reported in a wide range of other fluid inclusion types from porphyry systems, including low salinity liquid, intermediate density and vapor inclusions (e.g. Vry, 2010). The high Cu concentrations in these inclusions are inconsistent with experimental data (e.g. Candela and Holland, 1984, 1986; Hemley et al., 1992; Bai and Koster van Groos, 1999; Archibald et al., 2002; Hack and Mavrogenes, 2006; Simon et al., 2006) and it has recently been shown that these high concentrations may be due to a different post-entrapment modification involving diffusion through quartz of small, univalent ions such as $H^+$, $Cu^+$, $Na^+$, $Li^+$ and $Ag^+$ in the presence of an external fluid (Li et al., 2009; Zajacz and Halter, 2009; Lerchbaumer and Audétat, 2012).

Reequilibration experiments of synthesized coexisting vapor and brine inclusions in quartz showed that $Cu^+$ diffusion can significantly modify the Cu concentrations of fluid inclusions (Lerchbaumer and Audétat, 2012). Sulfur is interpreted to enhance the inward migration of Cu via the precipitation of Cu-sulfide crystals such as $CuFeS_2$ by the reaction of incoming $Cu^+$ with trapped $H_2S$ and/or $SO_2$. Substantial Cu-gain only occurred when the external fluids were less acidic than the inclusion fluid suggesting that outward diffusion of $H^+$ was responsible for maintaining charge balance. This process was interpreted to continue until the system reached chemical equilibrium, explaining why S-rich vapor inclusions appear to be particularly prone to Cu gain (Lerchbaumer and Audétat, 2012) and why quartz-hosted inclusions commonly record 1:2 molar ratios of Cu and S (i.e. buffered to chalcopyrite stoichiometry by adding Cu until the S content of the inclusion was exhausted; Seo et al., 2009). A study of coeval fluid inclusions hosted by topaz and quartz showed that the average Cu concentrations in S-rich vapor inclusions tended to be lower in topaz than in the same fluid populations hosted in quartz (Seo and Heinrich, 2013). This was attributed to the smaller diffusion channels in topaz, which prevented $Cu^+$ diffusion into the vapor inclusions. By contrast, Cu concentrations in coeval brine inclusions were similar in both host minerals, leading to the conclusion that brine inclusions are subject to much lower degrees of $H^+$ loss and $Cu^+$ gain, presumably due to a lower reduced S content (Seo and Heinrich, 2013).

Given these results, it is now unclear whether outward $H_2$ diffusion affecting $fO_2$, inward Cu diffusion, or changes in pH via $H^+$ diffusion is the main control on the non-dissolution of chalcopyrite daughter minerals in porphyry-related fluid inclusions. We might predict that chalcopyrite daughters in brine inclusions may dissolve on heating after rehydrogenation if it is only diffusive $H_2$ loss that has occurred. By contrast, low salinity inclusions may have undergone significant diffusive Cu gain meaning that rehydrogenation alone would not be expected to lead to chalcopyrite redissolution.

The present study uses the experimental technique of Mavrogenes and Bodnar (1994) to rehydrogenate quartz-hosted fluid inclusions with variable salinities from the El Teniente Cu–Mo porphyry deposit, Chile. This deposit was selected due to the abundance of chalcopyrite daughter crystals hosted in both intermediate density aqueous and low salinity vapor inclusions. In addition, fluid inclusion compositions from this deposit have been studied previously using LA–ICP–MS (Klemm et al., 2007; Vry, 2010) so that there is extensive knowledge of fluid inclusion compositions that was not available in the study of Mavrogenes and Bodnar (1994). This allows for a more quantitative assessment of the reactions that govern chalcopyrite solubility before and after rehydrogenation. Unlike in the study of Mavrogenes and Bodnar (1994), the same inclusions were measured before and after each experiment to confirm that chalcopyrite dissolution (if it occurred) was a function of increased $fH_2$ and that the inclusions studied were not subject to leakage or volume changes during the experiments. In addition, this allowed inclusions at variable depths in the sample to be examined in order to test for any limits of $H_2$ diffusion into the samples.

## 2. Samples

The El Teniente supergiant Cu–Mo porphyry deposit is located on the western margin of the Andean Cordillera, within the confines of the central Chilean porphyry copper belt. The deposit is one of the world's largest repositories of Cu with a current and mined resource total in excess of 94.4 Mt (Cannell et al., 2005). Main mineralization type quartz ± anhydrite veins (type 6a, type 6b and type 8 veins; Vry et al., 2010) usually contain multiple generations of fluids trapped in inclusions with typical diameters of 5–40 μm. Previous microthermometric and LA–ICP–MS analyses revealed that they have highly variable densities (0.25–1.5 g/cm³), salinities (0.1–60 wt.% $NaCl_{eq}$) and Cu concentrations (100–25,000 ppm) (Vry, 2010). Chalcopyrite daughter minerals are common in the more Cu-rich inclusions and pyrite and molybdenite have also been observed (Klemm et al., 2007; Vry, 2010).

Fluid inclusion types at El Teniente are subdivided into salt-undersaturated (type A) inclusions and salt-oversaturated (type B) inclusions based on the presence or absence of a halite daughter crystal at room temperature (Vry, 2010). A total of nine fluid inclusion types have been recognized (Fig. 1), five of which contain opaque daughter phases. The most abundant of these are 1–3 μm, triangular, chalcopyrite daughter crystals, particularly in intermediate salinity $A_{IDO}$ and $A_{LO}$ inclusions and high salinity $B_{HO}$ brine inclusions. The presence of opaque-bearing inclusions in assemblages that have consistent microthermometric properties, compositions and number of phases supports the interpretation that these opaques are daughter phases and not accidentally trapped crystals. Chalcopyrite daughters are also reported in rare, multiphase $B_M$ inclusions and $A_{VO}$ inclusions (Vry, 2010).

As with the inclusions from Red Mountain, Arizona (Mavrogenes and Bodnar, 1994), the chalcopyrite daughter crystals in all inclusion types from El Teniente failed to dissolve when heated. This contrasts with the successful dissolution of chalcopyrite daughter crystals in synthetic fluid inclusions (e.g. Sterner and Bodnar, 1984) that have similar compositions and microthermometric properties to those encountered in porphyry Cu systems. One possible explanation for this is that the opaque-bearing, quartz-hosted inclusions at El Teniente have been subject to post-entrapment modification.

## 3. Methodology

### 3.1. Fluid inclusion microthermometry

Two quartz vein samples were selected for analysis (08-2452-577 and 07-2406-07) based on their coarse textures, lack of anhydrite and abundance of chalcopyrite-bearing fluid inclusions with a range of densities and salinities. Both samples were associated with deep zones of Cu–Mo mineralization related to separate diorite finger porphyries on the eastern side of the deposit. These were prepared as double-polished sections with thicknesses of ~600 μm and broken into several pieces of 1–3 mm length and 2 mm width so that they could fit inside the 3 mm internal diameter (ID) Pt capsules used in the rehydrogenation experiments.

Microthermometry was carried out using a Linkam MDS600 heating–freezing stage with operating temperatures between −190 °C and 600 °C and heating/cooling rates of 0.1–99 °C/min. Quartz wafers were optically imaged using a motorized stage to produce a grid of high-resolution images. This allowed the position of each chalcopyrite-bearing inclusion to be recorded so that they could be relocated after rehydrogenation experiments. Each inclusion was classified in accordance with Vry (2010), (Fig. 1), and the inclusion dimensions and vapor fractions ($Vf$)