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Fluid salinities obtained by infrared microthermometry of opaque minerals: Implications for ore deposit modeling — A note of caution

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Abstract

Infrared microthermometry of opaque minerals has revealed that temperatures of phase changes vary with the infrared light source intensity, resulting in an overestimate of fluid salinities and an underestimate of homogenization temperatures. Failing to recognize this analytical artifact during infrared microthermometry may result in meaningless geological models. A fluid inclusion investigation on enargite from a high-sulfidation epithermal deposit is used as an example to document this. Fluid salinities obtained during an early investigation ranged between 6.3 and 20.4 wt.% NaCl, which were interpreted as intense boiling or as evidence for the involvement of a magmatic brine during ore formation. Fluid inclusion salinities obtained with improved analytical settings, i.e. low light intensities, fall between 1.1 and 1.7 wt.% NaCl and are in better agreement with fluid salinities obtained in quartz from similar deposits, and recent modeling suggesting vapor transport of Au and Cu from deep porphyry-Cu environments to shallower high-sulfidation epithermal deposits.

Keywords: Infrared microthermometry; Opaque minerals; Ore deposits

1. Introduction

Fluid inclusion salinities and homogenization temperatures obtained by microthermometry of fluid inclusions trapped in minerals are fundamental pieces of information providing constraints about the source or the pathways of fluids and about different processes during the evolution of crustal fluids, such as boiling and fluid-mixing. Accurate microthermometric fluid inclusion data are a prerequisite for such interpretations. Infrared fluid inclusion microthermometry has been used in recent years to collect directly data from fluid inclusions trapped in opaque minerals, which proves useful in deposits with no appropriate visible-light-transparent minerals, and when the temporal relationship of coexisting transparent and ore minerals is questioned, and doubts are raised whether fluid inclusions studied in transparent minerals adequately reflect conditions during ore mineral deposition.

During recent infrared microthermometric studies of various opaque minerals, it was noticed that temperatures of phase changes vary with infrared light source intensity. This analytical artifact has profound implications about the interpretation and the geological meaning of such fluid inclusion data, in particular salinity. In order to document this, microthermometric data gathered with different light intensities during recent infrared fluid inclusion investigations of enargite from a high-sulfidation Cu–Au epithermal deposit will be presented. The

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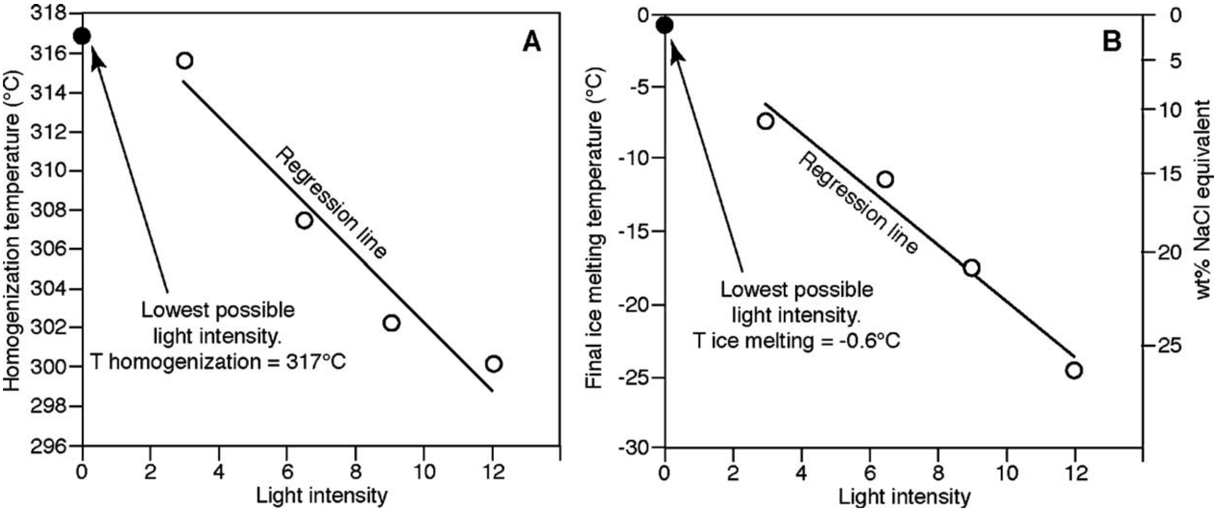

Fig. 1. Effect of light intensity on homogenization temperatures (A) and final ice melting temperatures (B) during infrared microthermometry of a fluid inclusion hosted by enargite. Note the decreasing temperature of the phase changes as the light intensity is increased. Open dots: measured temperature of the phase changes with variable light intensities. Black dot: measured temperature of the phase changes with the lowest light intensity and all diaphragms nearly closed.

implications of erroneous and nearly accurate salinity estimates will be discussed in the case of modeling metal transport from deep porphyry-Cu environments to shallow epithermal systems, as well as interpreting physicochemical processes during epithermal ore formation.

2. Infrared microthermometry and standard analytical procedures

Fluid inclusions were studied in about 100 μm-thick, double polished single minerals, using a U.S.G.S heating-freezing stage mounted on an Olympus-BHMS infrared microscope equipped with long working distance, high magnification infrared objectives, and an infrared-sensitive Hamamatsu type C2400-03D camera, allowing the observation of phase changes on a TV monitor. Calibrations of the heating-freezing stage were carried out with quartz-hosted synthetic fluid inclusions. Final ice melting and bulk homogenization in two-phase fluid inclusions trapped in sphalerite occurred at nearly identical temperatures under both visible and infrared light, therefore giving an apparent confidence about the accuracy of the infrared technique. The later test is typically carried out with a low light intensity to avoid oversaturation of the infrared-sensitive camera.

3. Effect of light intensity on the temperature of phase changes during infrared microthermometry

The observation of phase changes in fluid inclusions hosted by opaque minerals during infrared microthermometry requires a high image quality. One of the principal controls for improving the image of inclusions in opaque minerals is light intensity, in particular for weakly infrared transparent minerals. The effect of light intensity on measured temperatures of phase changes has not been addressed in previous studies. Therefore, microthermometric measurements have been carried out in a series of opaque minerals with various intensities of the infrared light source, with all other analytical settings remaining unchanged (e.g. gas flow, diaphragm opening, camera gain and sensitivity, sample position, etc.). The thermocouple holding the sample and measuring the temperature within the sample cell was carefully placed out of the way of the infrared light beam. The tests included measurements of final ice melting, bulk homogenization and freezing temperatures of two-phase inclusions in enargite (Fig. 1), pyrite, wolframite and sphalerite. The results show a nearly linear correlation with a negative slope, and that temperatures of all three phase changes decrease dramatically as the light intensity is increased (Fig. 1).

4. Analytical implications

The tests indicate that microthermometric measurements under high infrared light intensity overestimate fluid salinities and underestimate homogenization temperatures. The degree of the analytical error is a direct function of the opacity of the ore mineral with respect to infrared light, i.e. a more opaque mineral requires a higher light intensity, therefore resulting in a more serious overestimate or underestimate of fluid salinity or homogenization temperature, respectively. The salinity overestimate can be fairly significant and may reach 10 to 20 wt.% NaCl equivalent in certain cases. The covariation of light intensity and measured temperatures of phase changes is likely due to local absorbance of infrared light by the host mineral, which results in local heating of the inclusion under study, while at the same time the thermocouple holding the sample measures the ambient temperature of the sample cell, therefore yielding an apparent temperature reading that is lower than the real internal temperature of the fluid inclusion. It can be predicted that other phase changes, such as temperatures of salt and clathrate melting, and CO_2 homogenization are most certainly also affected, thus resulting in errors of salinity and CO_2 density estimates during microthermometry with a high infrared light intensity.

In order to minimize this analytical artifact, it is recommended to work with the lowest possible light intensity and with all possible diaphragms nearly closed (see black dots in Fig. 1). This approach certainly decreases the number of suitable inclusions for infrared microthermometry. The infrared transparency of minerals maybe improved by reducing the sample thickness, therefore requiring a lower light intensity during analysis. Using a CCD chip-type camera, which requires lower light intensities than a tube-type camera such as the Hamamatsu C2400 of this study, may also reduce the described problem. Preliminary tests were undertaken on an enargite sample with a Hitachi-KP 161 CCD camera on which the infrared filter was removed. The co-variation between light intensity and temperature of phase changes still remains, although the analytical artifact is reduced due to the higher light sensitivity of the CCD-type camera, and nearly closing all diaphragms. Unfortunately, this approach significantly reduces the number of opaque minerals that can be analyzed by infrared microthermometry, because the CCD-camera used in this study has only a sensitivity up to 1.2 μm, compared to 2.2 μm for the Hamamatsu tube-type camera.

5. Geological implications and conclusions

Failing to recognize the effect of light intensity on measured temperatures of phase changes during infrared microthermometry will produce erroneous data and meaningless geological models. A recent fluid inclusion investigation on enargite from the Chelopech high-sulfidation epithermal deposit in Bulgaria (Moritz et al., 2004) is used as an example to document this. Such deposit types are renown to contain little or no transparent mineral phases that are coeval with gold, enargite and the other ore minerals, because of the highly corrosive nature of the ore fluids. Therefore, an opaque mineral like enargite remains the only available mineral phase to obtain information about the fluid from the main ore stage.

High-sulfidation epithermal deposits are fundamental objects to understand processes during the magmatic to hydrothermal transition. Indeed, a genetic link is suggested between porphyry-Cu deposits forming at depth and shallower high-sulfidation epithermal Cu–Au deposits (Hedenquist and Lowenstern, 1994). The metal transport from the deep magmatic setting to the shallow epithermal environment is still debated. Recent LA-ICP-MS fluid inclusion analyses from porphyry-Cu deposits, and thermodynamic modeling, suggest that Au, Cu and As are transported in the vapor phase from the deep porphyry environment to the site of epithermal ore formation at shallower crustal levels (Heinrich, 2005). The magmatic brine produced during vapor–liquid separation in the porphyry environment is too dense a phase to migrate from depth to the shallow epithermal environment (Fournier, 1999), and therefore it cannot be considered as a major metal-transporting phase.

Initial results gathered from enargite of the Cu–Au stage at the Chelopech deposit yielded salinities between 6.3 and 20.4 wt.% NaCl equivalent correlating with homogenization temperatures ranging between 175 and 221 °C. It was concluded that either intense boiling of the ore fluid occurred during Au and Cu deposition, or that a high-temperature magmatic brine was involved during ore formation that mixed with a superficial, low-temperature and dilute fluid. The latter conclusion is at variance with respect to the LA-ICP-MS results, the thermodynamic calculations and predicted brine behavior described above. Once the effect of light intensity on measured temperatures of phase changes was noticed, the most transparent enargite samples were analyzed again with the lowermost light intensity and nearly closed diaphragms. The few suitable inclusions under such analytical conditions yielded significantly lower salinities between 1.1 and 1.7 wt.% NaCl equivalent. Homogenization temperatures were shifted to higher temperatures by 15 to 25 °C. The difference in salinity significantly changes the interpretation of the fluids and physico-chemical processes during high-sulfidation ore formation. Indeed, the low fluid inclusion salinities obtained with the more recent and improved analytical settings are in line with the low salinity of contracted vapors (Heinrich, 2005), therefore with a metal transport by a vapor phase, and speak against the involvement of any magmatic brine or intense boiling during high-sulfidation epithermal ore formation. This interpretation is more coherent with recent LA-ICP-MS results, thermodynamic modeling (Heinrich, 2005) and predicted brine behavior (Fournier, 1999).

A recent review on ore-fluid compositions in epithermal precious metal deposits (Sillitoe and Hedenquist, 2003) shows that, based on infrared microthermometric investigations in various high-sulfidation epithermal deposits, the fluid during enargite precipitation has apparently salinities between 2 and 20 wt.% NaCl equivalent, which contrasts with low salinities (mostly below 2 wt.% NaCl equivalent) reported for quartz associated with gold deposition in identical deposits (Hedenquist et al., 1994; Jannas et al., 1999). Thus, except the study by Mancano and Campbell (1995) quoting low salinities of 1 to 3 wt.% NaCl equivalent for fluid inclusions trapped in enargite from the Lepanto deposit, it is questioned whether the high salinities reported so far for many enargites are truly representative of the fluids involved during high-sulfidation epithermal ore formation or if they are mainly analytical artifacts.

As a conclusion, one should remain very cautious with the interpretation of fluid inclusions in cases where intimately intergrown transparent and opaque minerals yield contrasting data, in particular when significantly higher salinities, or trends of highly variable salinities for a restricted range of homogenization temperatures are reported for opaque minerals which are absent in coexisting transparent minerals. Despite these limitations, infrared microscopy is a powerful tool for revealing growth textures in opaque minerals, and for comparing petrographic characteristics of fluid inclusion populations in coexisting transparent and opaque minerals. Moreover, if microthermometric analyses are carried out carefully with opaque minerals that are highly transparent with respect to infrared light and with a light intensity that is kept to a minimum, measured temperatures of phase changes are likely to be close estimates of the real temperatures of phase changes in the studied fluid inclusions. Using CCD-type cameras requiring lower light intensities may minimize the analytical artifact, but at the same time reduces the number of opaque minerals for infrared microthermometry.

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