Analysis of Trace Metals in Fluid Inclusions: The Porgera Gold Deposit, Papua New Guinea

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Introduction

Fluid inclusions are minute (typically 10 to 20 µm long) samples of hydrothermal fluid trapped inside crystals during their growth from that fluid. As such, they can provide a wealth of information about the fluid, including its temperature, pressure, and chemical and isotopic compositions. Direct chemical analysis of such inclusions can provide constraints on hydrothermal processes, including the transport and deposition of ore-forming metals such as gold. Gold in particular, however, is present in such low concentrations (typically parts per million or less) in ore forming fluids, that its detection in the small sample volumes that fluid inclusions represent is extremely difficult. Laser inductively coupled mass spectrometer analytical techniques have been used to extract the contents of single-fluid inclusions and analyze them as a plasma, but even with this technique, elements present in trace concentrations in fluid inclusions are difficult to detect. The synchrotron x-ray fluorescence technique offers an alternative microbeam method for fluid inclusion analysis, with complementary strengths and weaknesses to the laser ablation inductively coupled mass spectrometer approach. In particular, x-ray methods should be particularly sensitive for heavier elements, such as metals.

Previous investigations using synchrotron x-ray fluorescence (SXRF) have attempted to analyze single fluid inclusions *in situ*, by focusing the x-ray beam on inclusions preserved within the host mineral (typically quartz). This method has the major advantage of being nondestructive. However, a problem arises from the absorption of both incident and fluorescence x-rays by the host mineral, an effect that is dependent on the depth of the inclusion beneath the mineral surface. The complexity of this effect also means that the geometry and volume of the inclusion must be accurately known if quantification is to be achieved.

A simpler but destructive method of exposing fluid inclusion solute contents to microbeam analysis is thermal decrepitation, whereby the inclusion is ruptured by overheating (at temperatures between 400 and 600° C). The inclusion contents leak to the surface of the sample wafer, where they evaporate to leave a residue of nonvolatile salts and other solutes. The salt pile may then be exposed directly to the incident beam, thereby minimizing absorption effects. This technique has been developed semi-quantitatively for major solute components using electron microprobes, and the objective of this study was to explore the potential of this technique using SXRF.

Methods and Materials

The experiment was designed in two main stages:

(1) Sensitivity test analyses of standard sample solutions containing a wide range of metals and solutes of interest. Two ICP-MS calibration standards, containing 10 ppm each of [Al, Ag, As, Ba, Be, Bi, Cd, Ca, Cs, Cr, Co, Cu, Ga, Na, In, Fe, Pb, Li, Mg, Mn, Ni, K, Rb, Sr, Se, Th, U, V, Zn] in 5% HNO_3 (ICP-MS 2), and 10 ppm each of [Au, Hf, Ir, Pd, Pt, Sb, Se, Rh, Ru, Te] in 10% HCl + 1% HNO_3 (ICP-MS 3), were drawn into silica-glass capillary tubes (i.d.=100 µm). The liquid-filled tubes were then exposed to the x-ray beam.

(2) Test analyses of natural fluid inclusion decrepitates. Samples of vein quartz from the Porgera gold mine, Papua New Guinea, were used for this work. Fluid inclusions were mapped and microthermometrically characterized in ~100-µm-thick doubly polished fluid inclusion sections of quartz. Fragments of the wafers were then heated to ~600° C using a Linkam Scientific Instruments TS1500 heating stage, causing decrepitation of several inclusions. The resultant salt residue piles, measuring 10-20 micrometers in diameter, were then exposed to the x-ray beam.

In order to attempt quantification of the resulting data, analyses were made of the thin-film Standard Reference Materials standards 1832 and 1833 (containing 10 $\mu g/cm^2$ each of [Al, Si, Ca, V, Mn, Co, Cu] and [Si, K, Ti, Fe, Zn, Pb], respectively). These standards were used to calibrate count rate per mass of each element within the beam circumference.

Results

Analysis of the standard solutions in the capillary tubes produced good fluorescence signals from all of the elements in the visible range of the instrumental setup. Peak heights were similar for each element, suggesting little differential absorption of x-rays from different elements. However, the volumes of fluid analyzed by this method were several times larger, and the concentrations of elements several orders of magnitude greater, than those expected in natural samples.

Analysis of fluid-inclusion decrepitates proved practicable, and the beam could be focused clearly onto the small salt residue piles on the surface of the sample wafers. Within the range of fluorescence x-rays visible under the incident beam energy configuration, strong signals were observed for the elements Fe, Zn, and As, whereas Ti, V, and Cr were variably detected. Cu, Ga, and Au, if present, were masked by large backgrounds from Fe, Zn, and Ge (the latter primarily from the natural quartz substrate).

By selecting decrepitation residues of approximately the same size as the beam diameter, the thin-film calibration could be assumed to apply directly to the mass of elements in the residue pile. By then assuming an original fluid inclusion volume, a rough estimate of original element concentration in the fluid inclusion could be calculated.

Future Development

Better quantification might be achieved if the detector response could be calibrated against the known concentration of an element within the inclusion, such as chlorine (estimated from microthermometry). However, sensitivity tests indicated that atmospheric Ar seriously interfered with Cl, except at high concentrations. Analysis in vacuum or helium would reduce this background and is a possible direction for future technique development.

The Ge background from natural quartz might be reduced by analyzing the decrepitate residues on pure silica glass wafers. An attempt was made to do this by sandwiching the quartz wafer between silica glass coverslips, but decrepitations in these samples were apparently not explosive enough to produce fountains that stuck to the overlying glass. This procedure has worked for other samples, however, and might be tried in the future.

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