

# Tracing element enrichment processes in nature using fluid inclusions and micro-XRF

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Natural fluid inclusions may conserve the composition of fluids present during mineral formation and thus may allow to study element enrichment processes in the upper crust. Synchrotron radiation induced micro-XRF has been proven to be a useful analytical tool to obtain the chemical composition of fluid inclusions e.g. [1, 2]. In this study, we focus on samples from the Ehrenfriedersdorf complex, Germany which are in close relation to important W and Sn ore deposits. While W and Sn were shown to be deposited from early fluids with formation temperatures above 500°C, in the present study we focus on fluids enriched in other precious metals such as Zn. One halite-rich inclusion trapped in quartz was studied exemplary using synchrotron radiation induced XRF. At room temperature, the inclusion is composed of a liquid and a vapor phase as well as several daughter crystals. Raman spectroscopy was applied to identify the daughter crystals within the inclusion. However, not all phases could be identified. Thus, synchrotron radiation induced micro X-ray fluorescence analysis was applied in order to identify the missing daughter crystals. In addition, the chemical composition of the fluid trapped as inclusion was determined as it allows to deduce on the ore forming process.

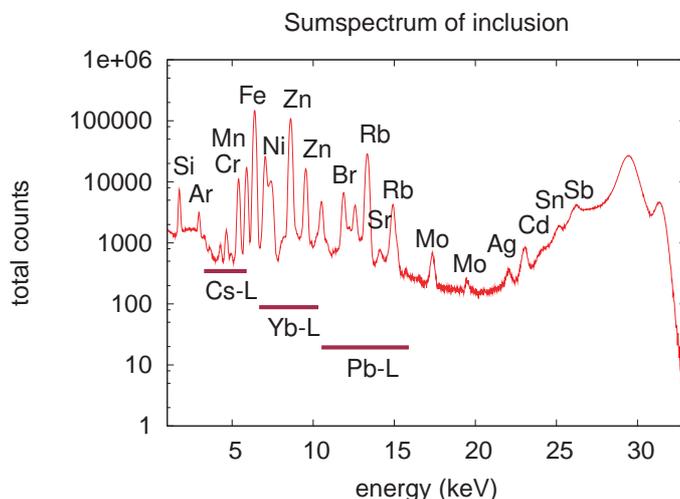


Figure 1: Sumspectrum of 342 single point spectra on inclusion taken during a larger mapping.

Micro-fluorescence analysis was performed at beamline L at HASYLAB. The multilayer monochromator was chosen to achieve maximum photon flux at the sample. The energy was set to 31.5keV in order to detect the important element Sb via K-shell excitation. Due to the high energies a 400 $\mu$ m Al absorber was chosen to protect the multilayer from radiation damage. Measurements were performed using the high energy polycapillary to achieve the best spatial resolution available at beamline L, i.e. 5 $\mu$ m. Fluorescence spectra were recorded with a Vortex SDD detector oriented at 90° to the incoming beam. For energies above 20keV this detector is not very sensitive but was

used nevertheless as measurements were compared to the confocal set-up later in the beamtime. The inclusion was scanned step-by-step covering the complete inclusion with step sizes of  $3\mu\text{m}$  in vertical and  $5\mu\text{m}$  in horizontal direction. Sample times per point were 30sec. The scanned area was a factor of 2 -3 larger than the inclusion. Peak areas were detected for each point with the software packages microxrf2 and Linux-AXIL [3].

Silicon, Ar, K, Cr, Mn, Fe, Ni, Zn, Br, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Cs, Yb and Pb were detected in the spectra (Figure 1). Elemental distribution maps show that K, Mn, Fe, Zn, Br, Rb, Sr, Ag, Cd, Cs, Yb and Pb are present in the inclusion (Figure 2). Concentrations are always highest in the daughter phases of the inclusion. Iron, Zn, Br, Pb and Ag were shown to be present in several daughter phases. Identification of the daughter minerals in the inclusion and correlation to Raman spectroscopy investigations turned out to be difficult as the daughter minerals were rearranged after exposure to the photon beam. As a main phase we could identify  $(\text{K,Rb})_2\text{Zn}(\text{Cl,Br})_4$ .

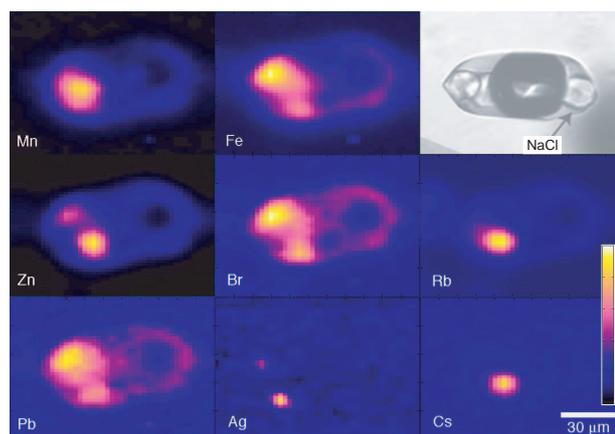


Figure 2: Elemental distribution map of selected elements for the mapped inclusion.

For quantification of the inclusion composition, the spectra taken on the inclusion were summed after normalization to intensity of the beam and detector live time (Figure 2). The sum spectrum was simulated with a Monte Carlo simulation [4] in the standardless mode based on the method described by [1]. The reliability of the quantification procedure was checked with the standard reference materials NIST612 and NIST610 measured during the same analytical session. Results will also be cross-checked with laser-ablation ICP MS analysis of the same inclusion.

## References

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