## QUANTITATIVE ANALYSIS OF MAJOR AND TRACE ELEMENTS IN FLUID INCLUSIONS IN QUARTZ USING A ICP-MS LINKED WITH A MERCHANTEK 266 NM ND:YAG LASER

GRAUPNER, T.1, BRAETZ, H.1, KLEMD, R.1

<sup>1</sup> Institute of Mineralogy, Universitate Wuerzburg, Am Hubland, 97074 Wuerzburg, Germany.

E-mail: torsten.graupner@mail.uni-wuerzburg.de

There have been many problems reported for the laser ablation – inductively coupled plasma – mass spectrometric microanalysis (LA-ICP-MS) of individual fluid inclusions in so-called "difficult" minerals such as quartz when using the 266 nm laser developed by Cetac Technologies (Guenther, Heinrich, 1999; Heijlen, Muchez, 2001). The results of this pilot study show that using an commercial Merchantek 266 nm Nd:YAG laser system, LA-ICP-MS analysis of fluid inclusions in quartz is possible. The laser system used is a New Wave Merchantek LUV 266x which contains a frequency-quadrupled Nd:YAG laser capable of delivering an energy of 4 mJ to the sample site. A proprietary beam delivery system generates a Flat-Top beam profile which can be controlled to generate spot sizes < 10 up to 400  $\mu$ m in diameter.

The quartz samples used for the experiments are from the Zinnwald ore field of the Zinnwald-Cinovec tin deposit (Ore Mountains, Germany and Czech Republic). The fluid inclusion wafers contained large (30 to 80  $\mu$ m) two- and multiphase primary/pseudosecondary aqueous inclusions as well as sometimes very large (> 100  $\mu$ m) secondary aqueous inclusions with salinities ranging from 0.4 to ~ 32.0 wt. % NaCl equivalent and homogenization temperatures (Th) from ~ 390 ° to ~ 120 °C (n > 25).

A set of artificial fluid inclusion standards was prepared by injecting different concentrations of multi-element standard solutions as well as pure deionised water into thin walled (0.01 mm) capillaries with closed tips. The volumes of the produced "fluid inclusions" were about 0.20 to 0.48  $\mu$ l. Ablation of the artificial "inclusions" frequently resulted in the formation of gas bubbles close to the ablation pit.

Internal standardization to transform the relative abundances into absolute concentrations in the trapped hydrothermal fluids is based on Na. The microthermometrically determined wt. % NaCl equivalent values were corrected for other major cations and the absolute concentration of Na calculated using the procedures of Heinrich et al. (1992) and Audetat et al. (2000).

Altogether, about 60 fluid inclusions located at depth between  $\sim 10$  and  $< 50~\mu m$  below the sample surface were opened during our experiments. With one exception, the quartz could always be ablated controllably and the inclusions opened subsequently. However, there was generally some evidence of spalling of fragments at the borders of the ablation pits.

Thirty-five fluid inclusion having sizes in the range from 25 to 100  $\mu$ m were opened and analyzed in this pilot study. The length of the transient signals from the fluid inclusions varied from ~ 5 to ~ 95 seconds depending on the sizes, shapes and phase compositions of the investigated inclusions.

Sixteen elements (Li, Na, K, Mg, Fe, As, Rb, Sr, Sn, Ba, Mo, U, W, Mn, Cu, and Pb) were determined for aqueous fluid inclusions from the Zinnwald Sn deposit. The concentrations of the measured major and trace elements are in good agreement with literature data for the same location (Heinrich et al., 1999). However, the data in this study are somewhat lower for certain elements like, for instance, K and Pb.

A first evaluation of the data for the Zinnwald ore veins shows that the high temperature fluid inclusions (Th:  $400^{\circ} - 370^{\circ}$ C) contain high Fe and Na concentrations as well as Sn contents typical of tin-bearing fluids. Furthermore, they contained high As concentrations (~ 0.4 to ~ 0.1 wt. %), and mostly significant Cu ( $\leq$  3400 ppm), Pb ( $\leq$  4300 ppm), Mn ( $\leq$  2200 ppm) and W contents ( $\leq$  128 ppm). A decrease in salinity from the high temperature fluid inclusions to low temperature secondary inclusions probably reflects a dilution trend of the magmatic fluid by external fluids.

## Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (KL 692/13-1 and 2). The authors are grateful to D. Wolf and U. Kempe (Institute of Mineralogy, TU Bergakademie Freiberg) for providing samples from the Zinnwald Sn deposit and for useful discussions.

## References

AUDETAT, A., GUENTHER, D., HEINRICH, C. A. (2000): Economic Geology, 95, 1563-1581.

GUENTHER, D., HEINRICH, C. A. (1999): Journal of Analytical Atomic Spectrometry, 14, 1369-1374.

HEIJLEN, W., MUCHEZ, P. (2001): ECROFI abstracts (F. Noronha et al., eds). Universidade do porto, Porto, 213-216.

HEINRICH, C. A., RYAN, C. G., MERNAGH, T. P., EADINGTON, P. J. (1992): Economic Geology, 87, 1566-1583.

HEINRICH, C. A., GÜNTHER, D., AUDETAT, A., ULRICH, T., FRISCHKNECHT, R. (1999): Geology, 27, 755-758.