

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.


Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Elemental partitioning in liquid-vapour fluid inclusion assemblages during sub-critical phase separation	Experiment number: CH-1936
Beamline: ID22F	Date of experiment: from: 9.6.2005 to: 14.6.2005	Date of report: 27.2.2006
Shifts: 15	Local contact(s): Ph.D. Pierre Bleuet	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr. Karen Rickers, HASYLAB at DESY, Notkestrasse 85, D-22603 Hamburg Dr. Volker Lüders, GFZ, Telegrafenberg, D-14473 Potsdam Miriam Haack, Institute of Mineralogy, University of Hannover, D-30167 Hannover* Mathias Hahn, Institute of Mineralogy, University of Hannover, D-30167 Hannover*		

Report:

Fluid phase separation (boiling) can be the primary cause of major variations in fluid composition in many land-based and marine hydrothermal systems. Such major variations commonly lead to extreme enrichments of important metals and to the formation of ore deposits. As fluids rise from their reservoirs they often undergo boiling due to changes in pressure and temperatures. Subcritical phase separation produces a vapour phase and a brine that can be chemically very different from each other and from their parent fluid.

When boiling occurs, the chemical species in a fluid are distributed according to their physical and chemical properties. For example, gaseous species such as CO₂, CH₄, H₂S or He have a strong affinity to the vapour phase, whereas dissolved ionic species is enriched in the liquid phase. Consequently, changes in salinity and gas content of vent fluids are mostly the product of phase separation of deeply circulating seawater in modern submarine hydrothermal systems. However, boiling is not only related to marine hydrothermal or geothermal systems but also occurs in modern and fossil magmatic systems. During the past decades, fluid inclusions hosted in quartz and other minerals from fossil magmatic systems have been studied in great detail and these studies have yielded important data on the probable source(s) and paths of ore fluids, and almost all of the known data on the temperature, compositions, densities, and pressures of hydrothermal ore fluids.

Most examples studied so far are related to porphyry copper systems where boiling processes generate significant amounts of metal-enriched highly saline brines besides huge amounts of vapour trapped as fluid inclusions in quartz. Under the best circumstances, fluid inclusions can provide a direct link between hydrothermal minerals and the fluids that formed them.

The fluids studied here are hosted in quartz in miarolitic cavities of the barren Torres del Paine complex (Chile). The granite intruded into sediments about 12 Ma ago. Due to low formation pressures, the magma intruded into the sedimentary host rocks and formed apophyses and cavities. The formation temperatures of hydrothermal quartz in vugs range between 280 – 340°C. Fluid inclusion boiling assemblages are preserved in hydrothermal quartz (Fig. 1).

Scanning and single point X-ray fluorescence analysis were performed on fluid inclusions in doubly polished quartz chips of a maximum thickness of 120 µm. First experiments were performed at Beamline L at HASYLAB using polychromatic excitation conditions and a collimating capillary yielding a beam diameter of 11 µm impinging on the sample surface. Polychromatic excitation allows simultaneous detection of trace elements with Z between 20 and 92 via K-shell excitation. However, the beam diameter is not suitable for the detection of daughter crystals hosted in fluid inclusions. For a better spatial resolution and lower limits

of detection additional experiments were performed at ID22 allowing in-situ microscopic multi-element analysis down to ppm/ppb concentration levels. The He chamber developed at ID 22 which enables



Fig. 1: Fluid inclusion assemblages preserved in hydrothermal quartz. Homogenisation temperatures and salinities were determined using micro-thermometry.

measurements in He atmosphere was used for the measurements. This set-up has the advantage of reducing the absorption of fluorescence radiation between sample and detector thus optimizing the detection of light elements like Cl. Kirkpatrick-Baez mirrors were used to achieve vertical and horizontal beam sizes of $3 \mu\text{m}$ (V) * $4 \mu\text{m}$ (H) which are well suited for the analysis of fluid inclusion of diameters between 5 to $70 \mu\text{m}$ and minimum daughter crystal sizes of several micrometer. Step sizes for area scan measurements were $2 \mu\text{m}$. Monochromatic Si_{111} excitation conditions at energies of 31 keV were chosen for first experiments at ID22 in order to detect important trace metals such as Sn and Sb. Higher-Z elements at the chosen conditions are in principal detectable by their L-lines. However, for inclusion analysis, the emission lines in the low energy region are strongly attenuated by the host matrix (quartz), significantly increasing detection limits. Due to the low photon flux at 31 keV at the desired spot size (5×10^8 ph/sec), the energy was reduced to 23 keV (3×10^{10} ph/sec) for most measurements. Acquisition times per point ranged between 25 sec and 1 to 2 sec for brine-type inclusions and 60 sec and 5 to 7 sec for vapour-rich inclusions for 31 and 23 keV, respectively. An energy-dispersive Si(Li) detector in 90° geometry was used to acquire the XRF spectra.

SR XRF analysis of four different types of inclusions (Fig. 1) revealed strongly different trace element compositions. Due to their low density (and low salinity?) no SR XRF signal was obtained for carbonic inclusions of type I at optimized measurement conditions at ID22. In type II high-salinity brines Cu, Mn, Fe, Zn, Ge, Br, Rb, Sr, As, Mo, Yb, Pb, Sn, Sb and Cs were detected at ID22. Elemental distribution maps show a correlation of Sn, Sb, Ag and Ge with Cu. Boiling results in an extreme elemental partitioning: type III brines contain Mn, Fe, Ni, Zn, Br, Rb, Sr, Mo, Nb, Ag, Cd, Sn, Sb, Cs, W and Pb and type III vapour-rich inclusions Mn, Fe, Ni, Cu, Zn, Rb, Sn, Sb and Pb. Copper is always strongly enriched in the vapour phase. In some inclusions As, Fe, Mn, Zn and additionally Pb partition into the vapour phase. All other elements get enriched in the liquid phase during phase separation (Fig. 2). Elemental distribution maps using a spatial resolution of $3 \mu\text{m}$ allows to distinguish between different daughter crystals within individual inclusions, thus contributing to the identification of daughter phases (Fig. 2).

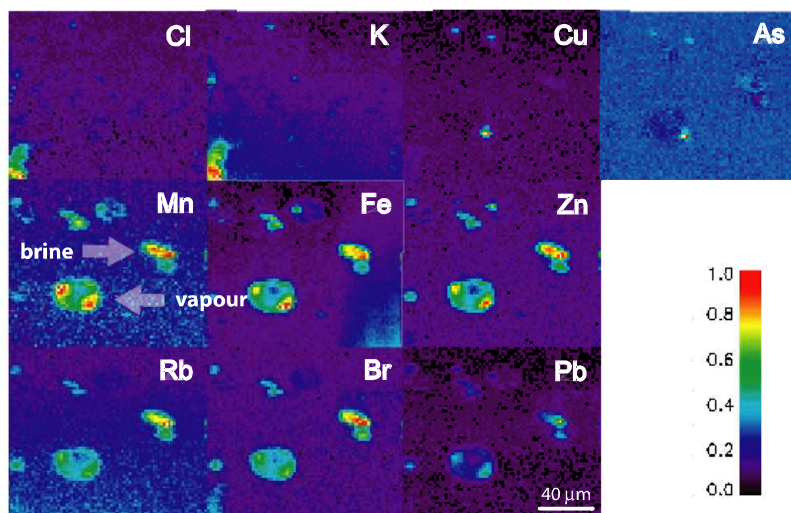


Fig. 2: Elemental distribution map of coexisting brine and vapour. Measurements were performed at 23 keV.