Bromine detection in Fe-rich geological samples using SR XRF

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Bromine is an element that becomes transported from the continental crust into the stratosphere during volcanic activity. It has a major input on compositional changes in the stratosphere and as it has a destructive behavior for ozone, also on climate change. In order to evaluate the amounts of bromine input in the geologic past and to get better data for climate modeling, the input of bromine to the stratosphere related to volcanic eruptions is part of a major study (see also [1]). The input Br content into the stratosphere can be estimated from Br contents in melts which formed during several stages of the volcanic eruption cycle and the amounts of erupted melts. Fragments of the melts are preserved either as glass or as inclusions in volcanic minerals. Bromine concentrations in the melts can thus be measured by analyzing the melts and inclusions. Bromine concentration in such materials is generally below 10 ppm and often below the lower limit of detection. The detection of bromine is affected as Fe is often a major constituent of the volcanic glasses (around 10 % wt), the inclusion hosts and the inclusions. During the course of this study, we aimed at improving the lower limits of detection in Fe-rich volcanic material.

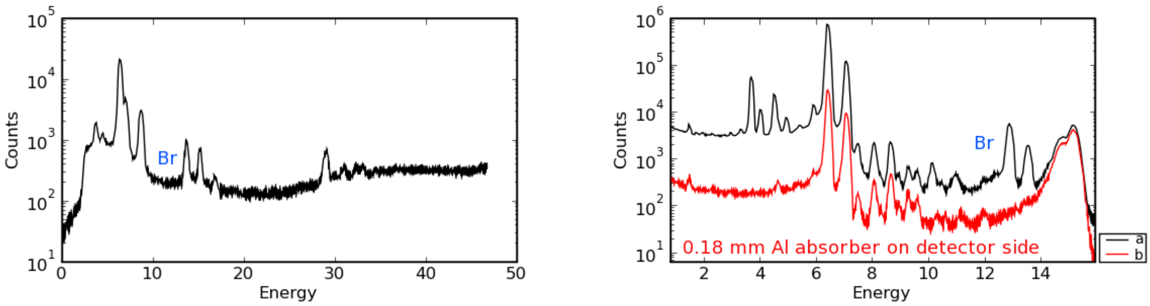

Figure 1: Fluorescence spectra of reference material MPI-DING ML3B-G with different excitation and detection conditions: polychromatic excitation (left) and monochromatic excitation at an energy slightly above the binding energy for Br (right). The concentration of Br in the glass is 3 ppm. The introduction of a 0.18 mm thick Al absorber between sample and absorber (red curve) turned out to be crucial for the detection of Br in the Fe-rich sample.

Measurements were performed at the microfluorescence beamline L at DORIS III. During the first part of the study, polychromatic excitation conditions were chosen also with the objective to measure in parallel rare earth elements (REE), iodine and bromine via K-shell excitation. Copper absorbers of thicknesses between 0.1 and 0.5 mm were introduced in the primary beam in order to optimise the sensitivity of bromine. The beam was collimated to a diameter of 10 μm using a glass capillary. Fluorescence was detected at 90° from the incoming beam. Both, a Ge and a Si(Li) detector were tested to achieve optimum sensitivity. However, with the chosen set-up, iodine was never detected and in most cases, bromine was found to be below the lower limit of detection. Therefore, in a next approach, excitation conditions of 15 keV were set with the double multilayer monochromator, in order to enhance the sensitivity of bromine and reduce the Compton scatter (Figure 1). The beam was focussed to a spot size of 15 μm using an XOS polycapillary half-lens and the fluorescence signal was recorded at the same geometry with a Vortex silicon drift detector. Peak to background ratios could be improved significantly, but the high Fe contents in the samples turned out to be problematic as Fe pile-up peaks formed. In order to suppress Fe fluorescence, a 180 μm thick Al absorber was introduced between sample and detector (Figure 1). This resulted in an improvement of the sensitivity for Br by a factor of 2. With the optimised conditions, measurements on standard reference materials displayed lower limits of detection of 0.18 ppm in an Fe-poor glass (MPI-DING ATHO-G) and 0.3 in an Fe-rich sample (MPI-DING ML3-G). Quantification was achieved with external calibration with a standard set of 6 different standard reference materials (Br contents between 1.2 and 18 ppm). With the optimised set-up the most important samples were re-measured and Br could now be detected and quantified in most samples. Elemental maps have been performed in addition in order to check the Br distribution between host material and inclusion. As displayed in Figure 2 Br is only present in the inclusion. This behaviour is generally related to an enrichment of Fe and Rb. With the improved lower limits of detection, an extensive data set could be established. Those results can now be used for reconstruction of the Br input related to volcanic eruptions into the stratosphere ([2]).

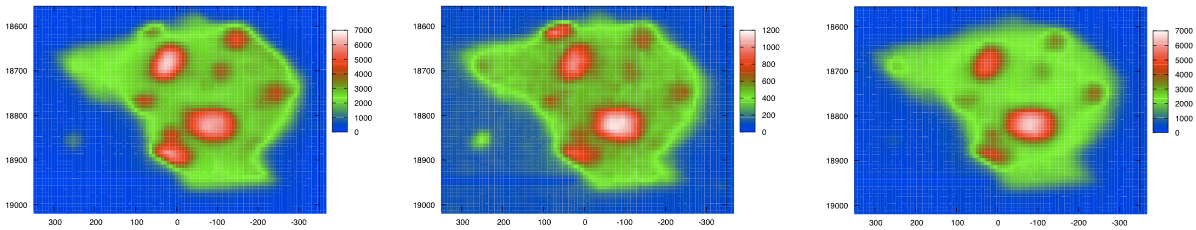

Figure 2: Normalised peak areas of Fe, Br and Rb (normalised to 100 mA). Length scales in μm.

References

[1] S. Kutterolf, T. Hansteen, K. Rickers-Appel, A. Freundt, W. Perz, Wehrmann, H., Frische, M., HASYLAB annual report (2009), 2009892.pdf.

[2] T. Hansteen, S. Kutterolf, K. Appel, A. Freundt, W. Perz-Fernandez, Wehrmann, H. (2010) AGU, V14B-05.