

Towards *in situ* determination of sulfur speciation in fluids at high P-T at controlled redox conditions

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Sulfur-bearing fluids play an important role in the degassing of magmas and in the formation of certain types of ore deposits. Since high temperature fluids are often not quenchable, central issue in this study is to investigate sulfur speciation in such fluids *in situ* at high pressure and temperature using Raman spectroscopy. Therefore a new sapphire-based cell is developed which allows abrupt or continuous changes of pressure at constant temperature, operating at pressures up to 200 MPa and temperatures up to 800°C. The concept is based on a flexible gold bag which separates the pressure medium from the fluid inside the cell to avoid any reaction between the sample fluid and steel components. Oxygen fugacity (f_{O_2}) is a key parameter determining the stability of sulfur species in the fluid. In the experiments the redox conditions are either pre-adjusted by the loaded fluid components or controlled by adding a specially designed open buffer capsule filled with Fe/FeO, Co/CoO, Ni/NiO or other redox pairs. Corundum powder on top of the buffer material acts as a getter for transition metal ions. Thus, penetration of these ions to the volume probed by Raman spectroscopy is avoided. First tests with the Fe/FeO buffer demonstrate the efficiency of the buffer assembly. Raman spectra recorded on the post-experimental solution show mainly HS⁻ besides a small amount of sulfate. EDX (energy dispersive X-ray spectroscopy) analyses of the buffer after the experiment indicate formation of Fe-spinel in the reaction zone of the capsule but FeO and metallic iron was also found. These observations give evidence that the buffer assembly has high potential to control redox conditions in the spectroscopic cell.

Ambient aerosol measurements and particle characterization at highly frequented motorways in Germany

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Based on projected future climate scenarios (e.g. heat waves with droughts) in combination with the assumption of no additional reduction in particle emissions, the Intergovernmental Panel on Climate Change (IPCC) predicts a general decrease in air quality in the future. A recent study estimates that in central Europe, the contribution of non-exhaust particulate matter (e.g. brake dust, tire wear, as well as suspension and re-suspension from the road surface) to total traffic emissions will increase to 80 – 90% by the end of this decade [1].

With the competence of BASt and DWD, and in cooperation with the Universities Strasbourg and Freiburg, a long-term monitoring program for coarse and fine particulate matter [2] was started in early 2013. To validate in a first approach the above-mentioned prediction [1], intense field measuring campaigns during different meteorological conditions are being carried out. The aim of this study is to determine size and optical density of individual particles (d_p ; 2.5 - 10 μm) by using computer-controlled single-particle optical microscopy. For selected samples, the chemical composition as well as geometric and morphological characteristics of individual particulates will be analyzed by manual, semi-automated, and fully computer-aided Scanning Electron Microscopy (SEM) combined with energy-dispersive X-ray (EDX) spectroscopy (Genesis, EDAX). Particles will be classified according to their chemical composition and assigned to, e.g., various mineral classes, which provide source information.

[1] Rexeis, M., Hausberger, S. (2009): Atmospheric Environment 43, 4689–4698;

[2] Kaminski, U., Fricker, M., Dietze, V. (2013): Meteorologische Zeitschrift 22, (in press).