Uptake of SO_2, HCl and O_3 on volcanic ash

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Mineral dust linked to soils from arid and semi-arid regions represents a significant fraction of the tropospheric aerosol mass. Many studies suggest that surface reactions involving mineral dust aerosol influence tropospheric chemistry. A largely neglected source of airbone mineral dust is silicate ash produced during explosive volcanic eruptions. The flux of ash into the atmosphere is not well constrained but may be >20 % of the annual mineral soil dust load. However, a single major eruption can inject a mass of fine (100 μm) ash with a total solid surface area on par with that emitted annually to the atmosphere by Saharan desert dust storms. In contrast to mineral dust, surface reactions of trace atmospheric gases on ash have not been studied. As a consequence, we have a limited understanding of the effects of volcanic activity on the chemical composition of the atmosphere.

The heterogeneous reactions of SO_2, HCl and O_3 on representative volcanic ash samples were investigated at room temperatures using a Knudsen cell. Volcanic ash varies in composition and mineralogy depending on source magma conditions. It is expected that natural ash samples will have different reactivities. Our results indicate that the uptake coefficients of SO_2, HCl and O_3 on volcanic ash compare with the values reported for mineral dust. No evidence was found for a significant compositional effect, and measurements performed with synthetic materials suggest that it is the glassy component which primarily drives the ash surface reactivity. Additional experiments are being performed and the new dataset will be integrated to provide a mechanistic description of the heterogeneous reaction of SO_2, HCl and O_3 on volcanic ash.

An inverse modelling approach for assessing CO_2-exposure experiments on Ketzin sandstone

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For 24 months, reservoir sandstone samples from the Stuttgart Formation at the Ketzin pilot CO_2 storage site in Germany were exposed to synthetic brine and pure CO_2 at 55 bar and 40 °C [1]. Only minor mineralogical changes were directly observed after the experiments, making it difficult to discriminate natural variability of the samples from CO_2-induced alterations. During the progress of the experiments fluid samples were taken from the autoclaves in order to track the reactivity of the rock samples as reflected by changes in brine composition. Even these results show high variability and at times qualitatively opposite concentration trends for some dissolved species.

In order to assess the significance and plausibility of the analytical results and to reproduce the experiments numerically we developed and applied a computational two-step inverse modeling approach. Firstly, an extensive set (several thousands) of equilibrium simulations was generated representing all possible combinations from a predetermined pool of minerals supposed to represent all phases in the sandstone samples. These simulations were ranked based on their matching the average brine analysis. Highest ranked simulations were then re-run including kinetics of mineral reactions, with rate laws taken from literature [2]. Secondly, a more fine-grained iterative calibration of selected kinetic models, including a quantitative assessment of reactive surfaces, was built up in conformity to likelihoods estimated from the ensemble of generated simulations. Major uncertainties in the Ketzin sandstone experiments concern reactions involving Fe^{2+}, K^+ and Al^{3+}; the other measured brine data were well matched.

This inverse modeling approach is computationally intensive (the simulations were run using a Pitzer database and generated via the R/PHREEQC interface [3]) but allows setting up models that are consistent to a set of otherwise intricate observations, where it is difficult to discriminate between measurements errors, biased thermodynamic data and erroneous parametrization of the models themselves. The outcome is a set of *possible* models and *ranges* in the parameters, which will then be considered i.e. for long-term predictions of the fate of Ketzin reservoir.

[1] Fischer *et al.*. (accepted), *Envir Earth Sciences* [2] Palandri & Kharaka (2004) *USGS Open File Report* 2004-1068 [3] De Lucia & Kühn (2013), *Geoph Res Abstracts* **15**, EGU2013-9719

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