ESRF	**Experiment title:** Differentiation between sulphate sorption and precipitation in S-impacted volcanic soils by S K-edge micropectroscopy	**Experiment number:** EC 151
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Report:

Soils in the vicinity of active volcanoes are subject to high atmospheric SO_2 deposition of volcanogenic origin (Delfosse et al., 2005) resulting in large sulphur and H^+ inputs into these soils. Sulphur is at least partially retained by adsorption to pedogenic minerals such as Al and Fe oxyhydroxides or allophane (Rajan, 1979). Due to a large specific surface area and a point of zero charge around pH 7, allophanes have a large sulphate sorption capacity under the natural pH conditions between pH 4 and pH 5 in these soils. On the other hand, the high proton input at sites subject to volcanogenic acid deposition results in strong protolysis of Al-bearing soil minerals like volcanic glass or plagioclase phenocrysts, and thus in an elevated Al^{3+} concentration in the soil solution (Herre et al., 2007). In such environments, sulphate may also be retained by precipitation of Al hydroxy sulphate minerals (e.g. jurbanite, basaluminite, alunite).

Recent studies on sulphate sorption in volcanic soils infer the presence of Al and Fe hydroxy sulphate minerals from the ionic composition of the soil solution, from thermodynamic considerations or by comparing the amount of SO_4^{2-} that can be mobilized from the soil with different extractants which had been tested for their ability to dissolve Al hydroxy sulphate minerals (Delfosse et al., 2005, Herre et al., 2007). However, all these methods do not allow an unambiguos proof of Al hydroxy sulphate phases. Contrastingly, S K-XANES is a powerful tool to distinguish between adsorbed and precipitated sulphate in soils as has been shown very recently by Prietzel et al. (2008). The height ratios of the white line (WL) at 2482.5 eV to the post-edge feature (PEF) at 2499 eV are lower for precipitated sulfate (WL/PEF 3.9 to 5.7) than for adsorbed sulphate (WL/PEF 8.1 to 11.9). Thus the calculation of the WL/PEF ratio of samples allows the estimation of the fractions of adsorbed and precipitated sulphate. Additionally, precipitated sulphates of the main cations present in soil solution can be distinguished from each other due to differences in additional post-edge features (Prietzel et al, 2008).

We hypothesized that sulphate is adsorbed to allophane surfaces and that there is a shift from S adsorption to precipitation on allophane with an increasing S load. We studied S K-XANES spectra of (i) synthetic allophane from sulphate sorption isotherms conducted at different pH values in the laboratory, (ii) synthetic allophane which has been exposed for 18 months during a field experiment close to Masaya and Poás Volcanoes (Central America) and (iii) natural soil samples collected close to Masaya Volcano.

Sulphate sorption on allophane at pH 5 results in S K-XANES spectra and a WL/PEF ratio comparable to sulphate sorbed to other mineral compounds as Al-hydroxide and goethite. Contrastingly, sulphate sorption at pH 4.5 and at pH 4 results in lower WL/PEF ratios. In sorption experiments at pH 4.5 the WL/PEF ratios are independent of the sulphate load meanwhile they decrease with increasing sulphate load for samples of experiments at pH 4.0 (Fig. 1 and Fig. 2). These results are in agreement with thermodynamic equilibrium calculations. Based on the procedure described in Prietzel et al. (2008) we calculated the portions of precipitated and adsorbed sulphate in the analyzed samples. Therefore the WL/PEF ratio of 10.6 - corresponding to sulphate sorbed to allophane at pH 5 - was taken as 100% adsorbed sulphate and the mean WL/PEF ratio of 5.0 for standard mineral compounds was taken as 100% precipitated sulphate. In allophane samples approximatly 22-30% and 7-32% of the total sulphate were in precipitated form after sorption experiments at pH 4.5 and pH 4, respectively. Sulphur K-XANES spectra of synthetic allophane which has been exposed in S-impacted volcanic soils during the 18 months´ field experiment, and XANES spectra of soil samples of a study site close to Masaya Volcano show WL/PEF ratios from 8.7 to 9.9 and 7.6 to 8.3, respectively. These ratios correspond to 13 – 54% of precipitated sulphate. The comparison of the post-edge features of S K-XANES spectra of all analyzed samples with spectra of standard mineral compounds as described in Prietzel et al. (2008) reveals the presence of a basaluminite like Al hydroxy sulphate phase.

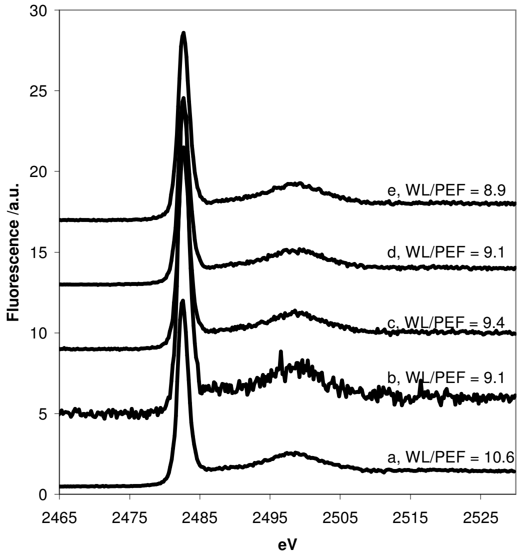

Fig. 1: S K-XANES spectra of a) sulphate sorbed to allophane at pH 5, b-e) sulphate sorbed to allophane at pH 4.5 with increasing sulphate load from b-e (sulphate concentration in added solution 0.5-3–9-15mM)

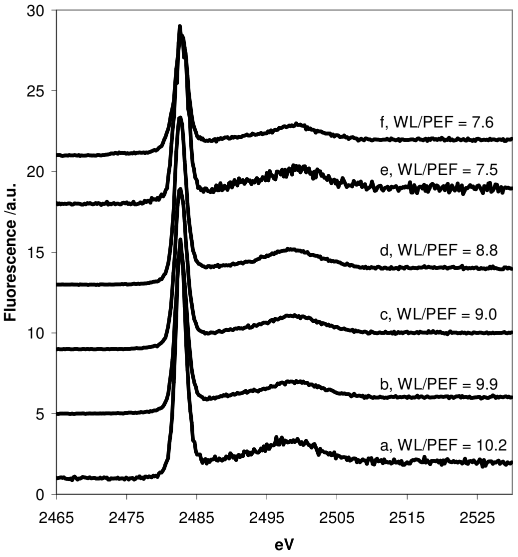

Fig. 2: S K-XANES spectra of a-d) sulphate sorbed to allophane at pH 4 with increasing sulphate load from a-d (sulphate concentration in added solution 0.5–3–9-15mM), e) synthetic allophane from the field experiment at Masaya and f) soil sample from Masaya

Spatially resolved S K-XANES spectra of allophane which has been exposed in S-impacted volcanic soils during the field experiment demonstrate that sample regions with the largest sulphur concentration (sulphur “hot-spots”) present larger WL/PEF ratios than the bulk samples indicating that under field conditions the relevance of precipitated sulphate increases with locally increasing sulphate load.

References:
Delfosse T., Delmelle P., Givron C. & Delvaux B. 2005. European Journal of Soil Science, 56, 127-133.
Herre A., Lang F., Siebe C., Dohrmann R. & Kaupenjohann M. 2007. European Journal of Soil Science, 58, 431-444.
Prietzel J., Thieme J., Herre A., Salomé M. & Eichert D. 2008 European Journal of Soil Science (accepted).
Rajan S.S.S. 1979. Soil Science Society of America Journal, 43, 65-69.