Changes in Fe Speciation during Early Soil Formation in an Alpine Glacier Forefield

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In this project, we investigate the transformation of Fe during granite weathering and early soil development in the forefield of a retreating glacier (Damma glacier, Central Aare massive, Switzerland). This work is integrated in a multidisciplinary project on the links between climate change, rock weathering, soil formation, and ecosystem evolution (BigLink; http://www.cces.ethz.ch/projects/BigLink). Fe is an essential nutrient and its release from weathering rock is a key factor in initial soil development [1]. To study Fe transformation during early weathering and soil formation, we combine two comparatively new geochemical tools, namely stable Fe isotope studies and X-ray-absorption spectroscopy (XAS). While stable Fe isotope studies provide insight into different physical and chemical weathering mechanisms, XAS allows following the changes in Fe speciation and redox state, as shown in our earlier feasibility study [2].

In order to assess the variability of Fe speciation in the parent rock, we analyzed unweathered granite specimens from different locations in the glacier forefield and their biotite fractions by Fe K-edge XANES and EXAFS spectroscopy at the beamline A1. To study the changes in Fe speciation during rock weathering and initial soil formation, we investigated a series of soil materials spanning a period from 1 to 100 years of soil development from granite. In addition, different Fe reference compounds were analyzed. Depending on Fe content, either fluorescence or transmission setup was used. While XANES spectra were recorded in high resolution (4-crystal) mode, EXAFS data were collected in standard mode. Sample spectra were analyzed by linear combination fitting (LCF) using spectra of known reference compounds (error of fitted fractions: ±5%).

The two granite specimens A and B differed in total Fe content (A: 1.3 wt% Fe; B: 3.0 wt% Fe) and geological metamorphosis (A: no metamorphosis; B: early metamorphosis towards gneiss). LCF showed that the amounts of Fe bound in biotite (A: 64%; B: 73%) and magnetite (A: 26%; B: 17%) was similar within experimental error and also compared with the results from a previously analyzed specimen [2]. About 10% of the Fe in the granites are contained in Fe-oxides, epidots, or feldspars.

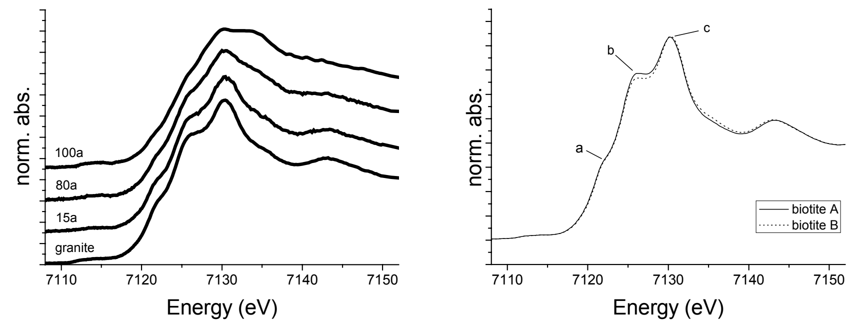

Figure 1: XANES of the bulk granite and the bulk soils sampled along the chronosequence (time since deglaciation is given in years) (left); XANES of the biotite fraction separated from two different granite specimen (cf. text for details) (right).

The XANES (Fig. 1) and EXAFS spectra of the biotite fraction (the most important Fe source) separated from the respective rock show identical features with differing intensities indicating only subtle variations in the molecular environment of Fe. The assignment of the single XANES peaks (labelled by a, b, c in Fig. 1) is still a matter of research. Recent data [3] suggest however that the relative intensities of peaks b and c are determined by the Fe(II)/Fe(III) ratio and by the distribution of Fe upon the two different crystallographic sites (denoted M1 and M2) in the octahedral sheet of the biotite. Since the pre-edge feature (being very sensitive to the oxidation state) of both samples does not show any significant variations we suggest that the differences in the XANES are brought about by the locations of Fe in the octahedral sheet. This conclusion is further confirmed by the higher Fe content of biotite A (biotite A: 16.47wt% Fe; biotite B: 12.87wt% Fe) and the EXAFS analysis (data not shown), both indicating a higher number of Fe in the first metal shell in biotite A in comparison to biotite B.

EXAFS shell fitting, XANES modelling and the inclusion of additional reference samples will further constrain the interpretation of the structural data.

The comparison of the XANES spectra (Fig.1) of three soils (most likely developed from granite of type A) from the chronosequence with the spectra of the bulk granite shows a clear dependence of Fe speciation on soil age. Predominant is the rapid initial loss of the characteristic biotite peak at 7125 eV. Dyar et al. (2001) [3] proposed that the relative intensity of this peak could be associated with the Fe(II)/Fe(III) ratio in the biotite structure (cf. above). Hence, our results suggest a significant oxidation of structural Fe in biotite already before the site was deglaciated and in the first years after deglaciation. Subsequently, the proportion of Fe(II) decreases from approximately 60% to 40% in the next roughly 100 years of soil development.

		Linear Combination Fit:					
age	Fe tot	Bio	Mag	Clay-ox	Clay-red	Fe oxides	Fe(II)
[a]	[%]	----------------------		% -	----------------------		[%]
granite	1.34	64	26	-	-	10	73
15	2.27	60	10	10	-	20	63
80	1.31	30	-	30	25	15	55
100	0.84	4	1	30	35	31	40

Table 1: Total soil Fe content and parameters of linear combination fits for three soil samples of the chronosequence (Bio: biotite; Mag: magnetite; Fe oxides: Ferrihydrite and Goethite; Clay: source clay SWa-1 either oxidized or reduced; age: years since deglaciation)

In the older soils an increase of the shoulder at 7133eV is the most characteristic feature. Increased intensity in this spectral region is indicative for octahedrally coordinated Fe(III) in clay minerals and (to a lesser extent) in Fe hydroxides. The indicated change in the dominant Fe bearing mineral phases is corroborated by preliminary LCF of the soil spectra (Tab. 1) showing that within the first 100 years of soil formation nearly all Fe initially bound in biotite is transformed into Fe in clay minerals and Fe oxides. However some references are still missing. In particular, references for Fe(III) bound to organic matter and a more complete selection of Fe bearing silicates (e.g. allanite, illite and vermiculite) need to be recorded and included in the reference database to further enhance the quality of the LCF in the ongoing work.

The preliminary conclusions clearly show, that XAS is a powerful tool to detect and characterise changes in Fe speciation during the initial stages of soil formation. By complementing our reference database and by extending the linear combination fitting approach to the EXAFS region we will further strengthen the conclusions regarding the dominating Fe transformations and reduce remaining ambiguities in the assignment of spectral features to particular mineral phases. Additional work will moreover include further soil samples from the chronosequence (comprising also different soil horizons). Ultimately, the statistical analysis (including PCA) of the final dataset will lead to a more complete understanding of the Fe dynamics during the early soil formation.

Acknowledgements:

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References:

[1] J. G. Wiederhold, N. Teutsch, S. M. Kraemer, A. N. Halliday and R. Kretzschmar, SSSAJ, 71, 1840 (2007)

[2] J. Frommer, M. Kiczka, A. Voegelin and R. Kretzschmar, HASYLAB Annual Report 2006, 1083

[3] M. D. Dyar, J. S. Delaney and S. R. Sutton, Eur. J. Mineral., 13, 1079 (2001)