

Trends in Solute fluxes across a 3.8 km elevation transect from Narayani river system in central Himalaya

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Chemical weathering is an integral part of the rock and carbon cycles and rates vary largely. To study the variability of chemical weathering rates and controls within a mountainous system, the hydrochemistry along the Narayani basin in central Himalaya region has been sampled including glacial meltwater samples of the upstream Langtang glacier.

Cation composition of the water was dominated by carbonate and silicate dissolution. Preliminary results based on samples of the first months show that concentration of measured chemical parameters such as the sum of base cations, dissolved silica and alkalinity decreased exponentially with elevation (from 169 m to 3989 m). Contribution of sea-salt appeared negligible to the total mass of solute along the drainage network except for the lowermost elevation site. The export of sea-salt corrected sulfate at the outlet point of the Narayani river suggests pyrite dissolution as its main source. Thus the oxidation of sulfide minerals might regulate significantly the dissolution of minerals within the basin. Export of nitrate from the Narayani basin appeared many fold higher than observed fluxes in the Langtang sub-basin, located upstream in the upper Himalaya.

First results suggest that area specific cationic and silica weathering fluxes were comparable with previous reports from the region but appeared to be increased at lower latitudes if compared to the upper Himalayan section of the basin and the world average. Human influence, primarily agricultural activities, may have increased the rate to some extent. Preliminary results of the weathering advance rate of the basin, at the terminus of the Himalaya, also appeared increased compared to large river systems of the world [1, 2, 3]. Influence of controlling factors like relief, physical erosion rates, temperature and precipitation will be discussed.

[1] Navarre-Sitchler & Brantley (2007) *EPSL* **261**, 321-334.

[2] Meybeck and Ragu (1997) *UNEP*, 245p.

[3] Gaillardet et al. (1999) *CG* **159**, 3-30.

Monitoring of Oxidation-Reduction Reactions between redox active Fe and Cysteine : Spectroscopic studies and Multiplet Calculations

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Section Heading

Introduction This study aims to monitor the electron exchange interactions between the Fe(II,III) center and the different functional groups of cysteine (carboxylic, amine and thiol) with time using X-ray absorption spectroscopy. We present the XANES spectra of Fe(II,III)-cysteine complexes at all relevant absorption edges (Fe L-edge and C, N,O and S K-edges) collected at different times (0,2,10 and 12 months) after the initial synthesis of the complexes as well as the Fe K-edge EXAFS of Fe(II,III)-cysteine complexes, also as a function of time. The experimental results are compared with multiplet and quantum mechanical simulations, providing a detailed picture of the iron-ligand structure, coordination, and electron shuttling capabilities of the complex.

Results and Conclusion

The Fe L-edge XANES of Fe(III)-cysteine indicates an initial reduction of Fe(III) caused by an internal electron transfer reaction either from N of -NH₂ or S of -SH, both of which show oxidation in their respective spectral features. The N K-edge of Fe(II) cysteine at all time scales did not show much variation and is identical to the N spectrum of cysteine. The N of Fe(III) cysteine showed oxidation of N (to nitrate, a +5 oxidation state of N) at time scales 0, 10 and 12 months; however, at time=2 months the N spectral features resemble that of N in cysteine. The O K-edge spectra for Fe(II) cysteine shows a change in spectral pattern with passage of time whereas that for Fe(III) cysteine does not change much after the time of initial synthesis and had characteristics similar to that of O in cysteine. Oxidation of Fe(II) in Fe(II)-cysteine with time was accompanied by a simultaneous reduction of the C as revealed by the C K-edge features of Fe(II) cysteine. This is reflected in a reduction of the C which involves an electron exchange of the C within the unsaturated -COOH of cysteine. In contrast, the C K-edge features for Fe(III) cysteine show no variation with time. The S K-edge of Fe(II) cysteine show S oxidation states intermediate between sulfoxide and sulfate. Overall, spectral characteristics of Fe(II,III)-cysteine complexes suggest thiol/disulfide exchange, H-atom transfer, or electron transfer between Fe and cysteine. Our studies of the Fe(II,III)-cysteine system provide a mechanistic understanding of the electron shuttling that occurs between a redox active metal and a redox active ligand. In this particular case, cysteine represents an organic molecule with functionalities (O-, S-, N- functional groups) and a C backbone that may mimic the functional groups present in organic matter from terrestrial and aquatic environments.