

## Fluid evolution along a cross section through the Central Alps, Switzerland

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The classical Alpine fissure veins, large cavities lined by occasionally giant quartz crystals, occur in regionally metamorphosed rocks in the Central Alps. They record important information about the composition and evolution of metamorphic fluids, and fluid sources and mass transfer during fluid-rock interaction. The fluid composition shows a distinct evolution with increasing metamorphic grade, where consecutive zones are dominated by (1) heavier hydrocarbons, (2) methane, (3) aqueous fluids, and (4) aqueous-carbonic fluids [1]. This study addresses the chemical evolution of fluids in Alpine fissure veins in the Central Swiss Alps by integrating field work, fluid inclusion studies (microthermometry and LA-ICPMS microanalysis of individual fluid inclusions), and geochemical modeling.

The field locations were selected along a cross section through the Central Alps that covers different lithologies and metamorphic conditions. This includes vein systems in the Aar massif (Gauli glacier, Gerstenegg vein, Tiefen glacier), the Bedretto valley, and the Cavagnoli and Faido region. The fluid inclusions from the Aar massif are low-salinity aqueous two-phase, whereas the Cavagnoli and Faido samples dominantly contain aqueous-carbonic fluid inclusions. The salinity increases from the Gauli samples with 4.5-5.0 wt% equivalent (eqv.) NaCl to those from the Gerstenegg and Tiefen glacier with salinities of around 10-11 wt% eqv. NaCl. The aqueous-carbonic fluids of the Faido and Cavagnoli region have very low salinities of around 3.4 and 0.4 wt% NaCl, respectively. This differences in salinity are also reflected in their major and trace element concentrations, as determined with LA-ICPMS. Higher salinities do systematically correlate with higher concentrations of elements that are largely complexed by chlorine such as the alkali and earth alkaline metals, and divalent transition metals [2]. The concentrations of base metals such as Pb, Zn and Ag are consistently higher in the fluid inclusions from the Gerstenegg and Tiefen glacier than in the Gauli samples. The Cavagnoli and Faido samples contain even higher concentrations of ore metals (up to several tens of ppm) and sulfur, reflecting their higher metamorphic grade. The measured fluid compositions will be compared with results from multicomponent-multiphase fluid-mineral equilibria modeling to evaluate the status of fluid-rock equilibrium along the metamorphic gradient.

[1] Mullis, J., Dubessy, J., Poty, B., O'Neil, J. (1994) *Geochim. Cosmochim. Acta* **58**, 2239-2267. [2] Yardley, B.W.D. (2005) *Econ. Geol.* **100**, 613-632.

## Evidence for the accumulation of heterocyclic N compounds in temperate forest soils as a function of depth

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Leaching of dissolved organic nitrogen (DON) from forest (organic-rich) surface soils is likely the primary vehicle for the observed movement of N into underlying mineral soils. Our goal is to understand the accumulation and storage of nitrogen in soils. The overarching hypothesis that drives this research is that heterocyclic N compounds derived from the decomposition of litter are transported and accumulate in the soil column. The analytical approaches typically used to study N-containing compounds are not sensitive to the presence of heterocyclic N. This has resulted in the general belief that amide-N (as in proteins/peptides) is the only N form important in N accumulation and storage in soils. Still, biomolecules such as DNA are composed of heterocyclic N containing subunits and these molecules, although in lower concentrations than amide-N in proteins/peptides, are chemically recalcitrant, sorb onto soil solids, and are thus expected to accumulate and persist in natural soil environments. In this investigation, we used an innovative technique, nitrogen X-ray absorption near edge structure (N-XANES) spectroscopy, to determine the N chemical forms in temperate forest soils as a function of depth and varying mineralogy.

Soil columns (down to approx. 1 meter) were collected from two forest locations in Pennsylvania. These include an Inceptisol soil with mineralogy dominated by illite and chlorite, and a Spodosol soil with mineralogy dominated by Fe oxides, illite and kaolinite, but that also contains organic matter accumulations at depths of about 25-50 cm. The N K-edge (409.9 eV) XANES spectra was collected at the National Synchrotron Light Source, BNL.

The N-XANES spectra of these forest soils can be divided into two regions:  $\pi^*$  resonances at 398-404 eV and  $\sigma^*$  resonances at 404-420 eV. Furthermore, the spectra reveal two well-resolved  $\pi^*$  resonances, one (lower energy  $\pi^*$ ) corresponding to spectral features present in biomolecules such as DNA/RNA and their constituent nucleic acids, and a second resonance (higher energy  $\pi^*$ ) which is present in proteins and their constituent amino acids and polypeptides. We observed an increase in the lower energy  $\pi^*$  resonance with soil depth that was mirrored by a decrease in the higher energy  $\pi^*$  resonance. This trend is consistent for all soil columns, except when an accumulation of organic matter occurs in deep soil layers. The lower energy  $\pi^*$  resonance originates from molecular structures with extended  $\pi$ -electron systems and indicate the presence of heterocyclic N compounds. Thus, our results indicate N long-term leaching processes result in the selective accumulation of heterocyclic N compounds at soil depths. The accumulation of heterocyclic N at soil depths might be a consequence of its presumed recalcitrance and/or bonding to mineral surfaces.