

NEW ASPECTS ON THE MECHANISM OF SILICATE WEATHERING –
IMPACT OF POLYSILICIC ACIDS AND HYDROXYALUMINOSILICATE COLLOIDS

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The availability of both silica and aluminium in natural systems is mainly controlled by the dissolution and neoformation silicates. At a primary stage dissolved silica and aluminium are liberated into the solution by weathering of minerals and rocks. The concentration of free Al^{3+} and $Si(OH)_4^0$ may be reduced by precipitation of new solid phases as well as by adsorption at solid surfaces or by the formation of dissolved complexes and colloids. Although, dissolved polysilicic acids as well as hydroxyaluminosilicates complexes and colloids (HAS) may affect the mechanisms of silicate weathering [1] and are assumed to be a precursor of aluminosilicates in natural environments [2, 3], the boundary conditions of their formation as well as the stability and the occurrence in nature are still a matter of debate [4, 5].

In analogy to the structures of silicates various linked Al- and Si-components occur in aqueous solutions as dissolved molecules, complexes, and colloids (e.g. polysilicic acids, HAS, Al₁₃). Dissolution experiments by [6] confirmed that upon dissolution of silicate minerals monosilicic as well as polysilicic acids are liberated into the solution. Such polysilicic acids are thermodynamically stable only in alkaline solutions, but can survive up to several months in acid solutions. Considering this new aspect the occurrence and formation of polymeric silica complexes and colloids are experimentally studied and their occurrence is verified in natural environments. Experiments were carried out at 20°C and at constant pH values between 3.5 and 4.5 by the interaction of dissolved aluminium ions with monosilicic and polysilicic acid. As the experiments proceed various fractions of the solution were separated by ultrafiltration (0.5 to 300 kDalton). The concentrations of Si and Al as well as the polymerisation degrees of Si were analysed in the filtrated and unfiltrated solutions by ICP-OES and β -silicomolybdate reaction rate method, respectively [see 6]. Precipitates and colloids were characterized by photon correlation spectroscopy, atomic force microscopy, X-ray diffraction, infrared, and ²⁷Al-NMR spectroscopy.

The results show that the reaction of $Al(H_2O)_6^{3+}$ with polysilicic acid can lead to the formation of a significant amount of HAS at rather low pH even in solutions which are undersaturated with respect to amorphous $Al(OH)_3$ and proto-imogolite ($Al_2O_3SiOH(OH)_3$), potential precipitates with respective high solubility products.

This implies a decrease of “free” dissolved Si and Al of 50 up to 80 mol%. Colloidal HAS ($0.5 < \text{Si/Al} < 2$) appear as spherical particles with typical size dimensions of 0.1 or 0.8 μm and survive several months. The destruction of polymeric silica molecules is inhibited within the HAS structure and polymerized silica reduces the substitution of Al within the Si-O-tetrahedron. Following the experimental results, linked silica tetrahedrons released by the dissolution of silicates can be fixed within dissolved polymers and HAS. Nevertheless, the occurrence of polysilicic acid and colloidal HAS have to be verified in natural systems. For this purpose soil samples from acidic soils were collected in France and Austria which are suitable for the existence of polysilicic acids and HAS. The respective soil solutions were separated by drainage centrifugation and 0.45 μm filtration and were subsequently analysed by the above methods.

The soil solutions comprise pH values between 3 and 5. Several solutions contain significant concentrations of dissolved polymeric silica. The proportion of silica fixed within such polymeric structures versus total dissolved silica reaches 30 mol% of Si. Subsequent ultrafiltration of the 0.45 μm filtrated soil solutions reduces the concentration of the dissolved aluminium and silica. Thus, linked silica molecules occur within such acidic solutions.

It is verified from experiments and analyses of soil solutions that dissolved and colloidal polymeric silica appear at high proportions of total dissolved silica in acidic waters. Such components are thermodynamically not stable but can survive for several months, especially in the presence of aluminium ions. The polymeric silica is primarily liberated from silicates by weathering. Nevertheless, the polymerisation degree of the liberated silica mostly does not represent the structure of the solids. This is caused by incongruent dissolution behaviours and low dissolution rates of silicates which provide a formation of a boundary layer at solid-liquid interface. The chemical composition and structure of such layers are different from that of the primary crystalline silicate and significantly affect the solid-liquid interaction. Thus, aspect of dissolved and colloidal polymeric silica has to be carefully considered for analyses and geochemical modelling in acidic soil and interstitial solutions with respect to both the mechanisms of the silicate weathering and the aluminium and silica speciation.

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