

## Polysilicic acid and the dissolution of silicates

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In the natural environment the mobilization and transport of silica is closely related to the dissolution of silicates. Concentration and composition of silicic acid depend on the chemical composition of the solid, the solution, and on reaction time.

In several experiments albite, orthoclase, diopside, muscovite, sepiolite, magadiite,  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$ ,  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$ ,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  and amorphous silica were dissolved in aqueous solutions at a pH of about 3.0. The pH was controlled by the addition of dilute sulphuric acid. The continuously stirred suspension was kept at 20°C. The concentration and the polymerization degree of the silicic acid were analysed after various time periods of the reaction via the  $\beta$ -silico-molybdate-method (e.g. Iler, 1979).

The experimental results show that most of the solutions contain silicic acid as both polymeric and monomeric species (Table 1). Polysilicic acid was measured as high and as low molecular weight silica. The polymers may amount to about 40 mol% of the total dissolved silica. At the pH of 3.0 decomposition of polysilicic acid is very slow, and a neoformation of polysilicic acid by polymerization of monosilicic

acid is not possible. The relative content of polymers varies with the reaction time of the dissolution experiment. The transfer of polysilicic acid into the solution represents a transition stage during the dissolution of silicates. As a function of reaction time polymers decompose into monomeric species, which are the stable silica species at experimental conditions.

Therefore, as a matter of fact, polysilicic acid may be an important component in acid solutions at the initial time period of the dissolution of  $\text{SiO}_2$  containing minerals. Silica molecules, disorderly linked by siloxan bonds, not only exist at the mineral surfaces of silicates (Casey *et al.*, 1993) but also in the solutions. The stability of such polysilicic acids depends on the geochemical environment.

The polymer stability or depolymerization capacity was studied between 5 and 40°C by the addition of polymeric silica to solutions of various compositions (Dietzel and Usdowski, 1995; Dietzel *et al.*, 1997). Hydroxyl ions catalyse the depolymerization rather than hydrogen ions. A maximum stability of polymers was obtained at a pH of about 2.5. Bivalent cations stabilise polysilicic acid, especially  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$

TABLE 1. Content of silicic acid on the dissolution of silicates (20°C; pH = 3.0)

	hp-s	op-s/m	[T]
hp-s: high molecular weight silica in mol %			
op-s/m: low molecular weight and monomeric silica in mol %			
[T]: total dissolved $\text{SiO}_2$ in mg/l			
albite	—	100	2.1
orthoclase	6	94	5.1
diopside	11	89	8.2
muscovite	12	88	12.2
sepiolite	39	61	2.0
magadiite	—	100	3.7
$\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$	38	62	10.9
$\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$	23	77	5.2
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	24	76	9.8
$\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$	11	89	12
amorphous $\text{SiO}_2$	—	100	1.2

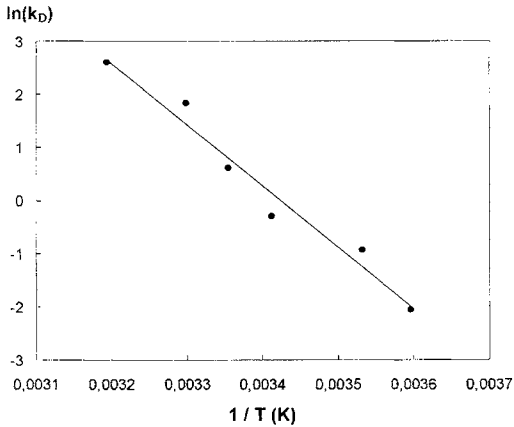


FIG. 1. Arrhenius plot of the reaction rate constant of depolymerization,  $k_D$  (l/mol s).

ions, whereas monovalent cations had no considerable effect. The depolymerization capacity depends also strongly on temperature. An activation energy of about 96 KJ/mol was measured for the reaction rate constant

of the depolymerization (Fig. 1).

The pH, the temperature and the kind of the dissolved components of most waters in natural systems provide high depolymerization capacities. Polysilicic acid decomposes to monomers within a few hours or days in mean river water and seawater. Therefore, it is not amazing that in most natural waters silicic acid consists of monomeric species. However, in natural environment with acid solutions abundant in bivalent cations polysilicic acid may exist as a metastable component over several months.

## References

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