

Supplementary material

Silicon incorporation reduces the reactivity of short-range ordered aluminosilicates toward organic acids

Katharina R. Lenhardt^{a*}, Mathias Stein^{a,b}, Thilo Rennert^a

^a Department of Soil Chemistry and Pedology, Institute of Soil Science and Land Evaluation, University of Hohenheim, Emil-Wolff-Str. 27, 70599 Stuttgart, Germany

^b Present address: Working Group Silicon Biogeochemistry, Leibniz Centre for Agricultural Landscape Research (ZALF), 15374 Müncheberg, Germany

*Corresponding author: katharina.lenhardt@uni-hohenheim.de

Contact information:

M. Stein: mathias.stein@zalf.de

T. Rennert: t.rennert@uni-hohenheim.de

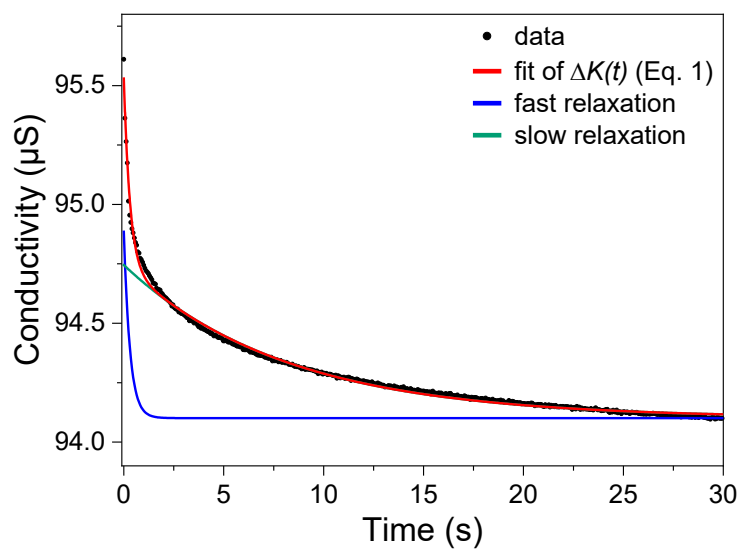


Fig. S1 Exemplary data analysis of stopped-flow conductivity measurements. The red curve results from fitting a bi-exponential function (Eq. 1) to data obtained at 25 °C from experiments with a short-range ordered aluminosilicate (Al:Si = 1.4; 1 g L⁻¹) and oxalic acid (0.5 mmol L⁻¹) at initial pH 5. The red curve is the sum of the two exponential functions representing a fast (blue) and a slow process (green)

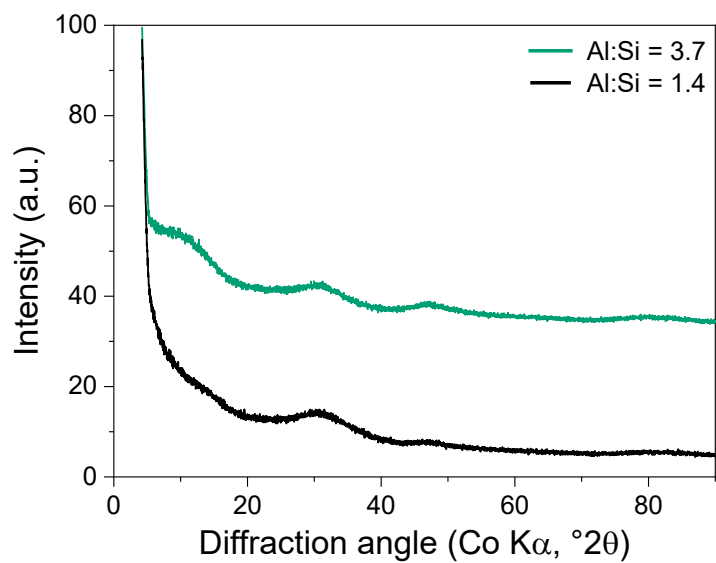


Fig. S2 X-ray diffractograms of short-range ordered aluminosilicates used as adsorbents. Data are shifted along the y-axis for clarity

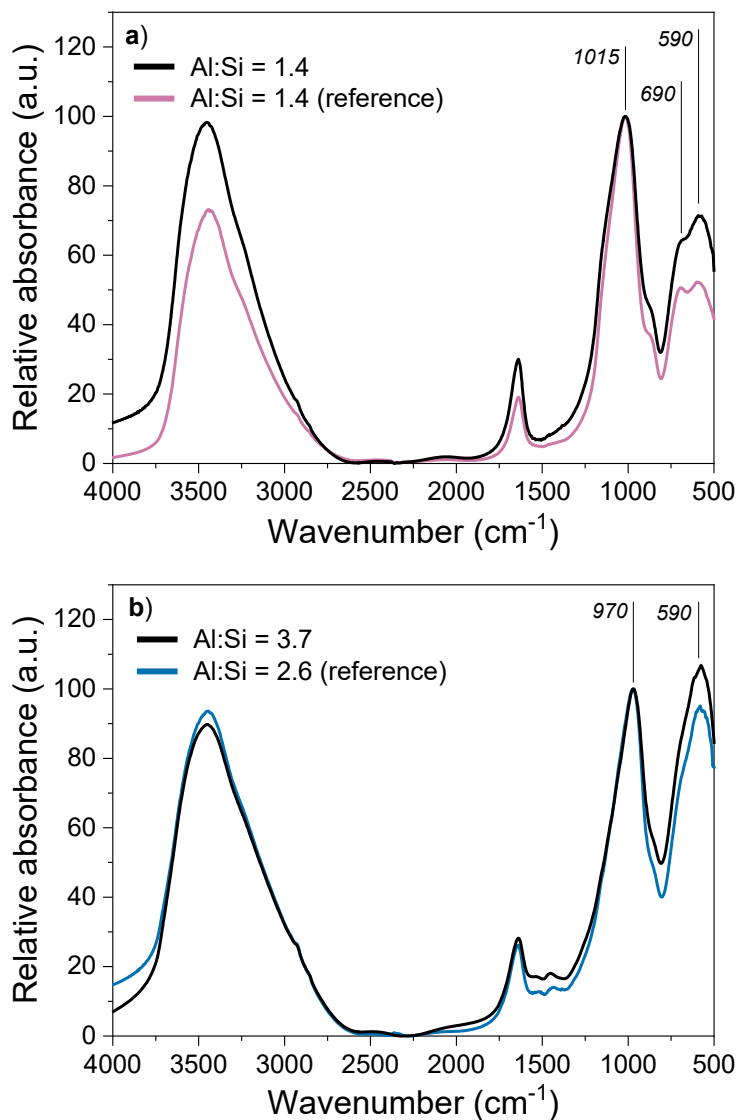


Fig. S3 Transmission Fourier-transform infrared spectra of short-range ordered aluminosilicates (SROAS) with an Al:Si ratio of 1.4 (a) and 3.7 (b) used as adsorbents. Spectra of SROAS previously characterized by ²⁷Al and ²⁹Si nuclear magnetic resonance spectroscopy (Lenhardt et al., 2021) are given as reference. Data were normalized to absorption maxima at 1015-970 cm⁻¹

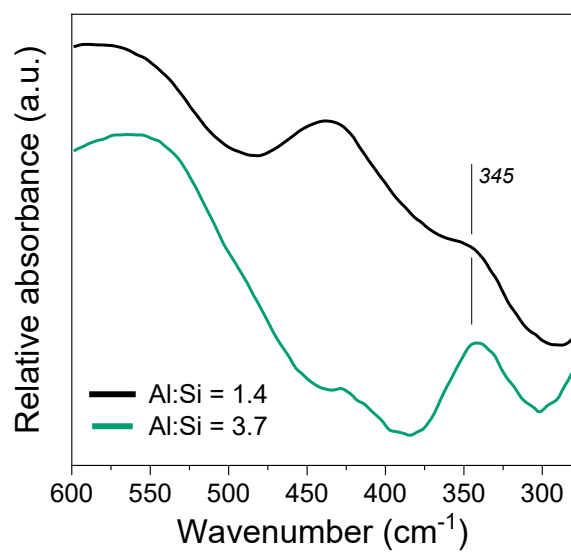


Fig. S4 Transmission Fourier-transform infrared spectra of short-range ordered aluminosilicates used as adsorbents. Data were normalized to absorption maxima at 590-565 cm⁻¹ and shifted along the y-axis for clarity

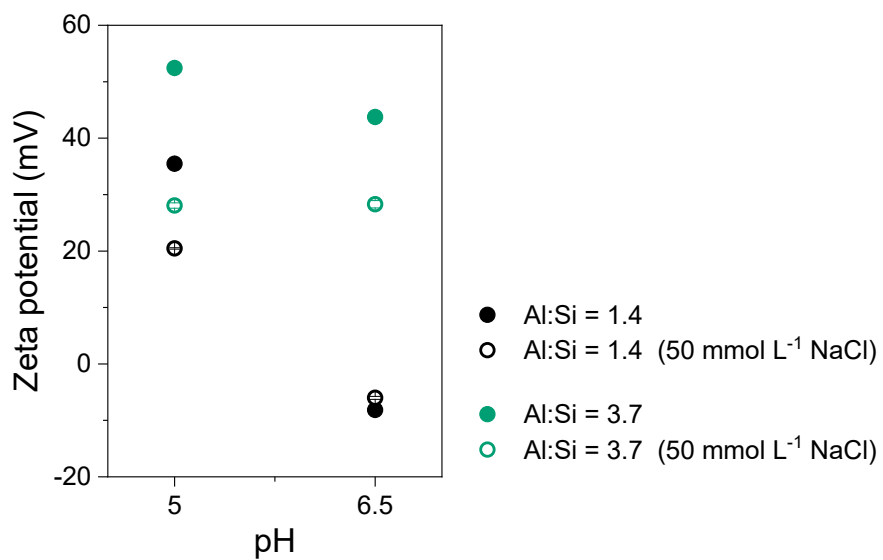


Fig. S5 Zeta potential of short-range ordered aluminosilicate particles measured in water and 50 mmol L⁻¹ NaCl solution at pH 5 and 6.5

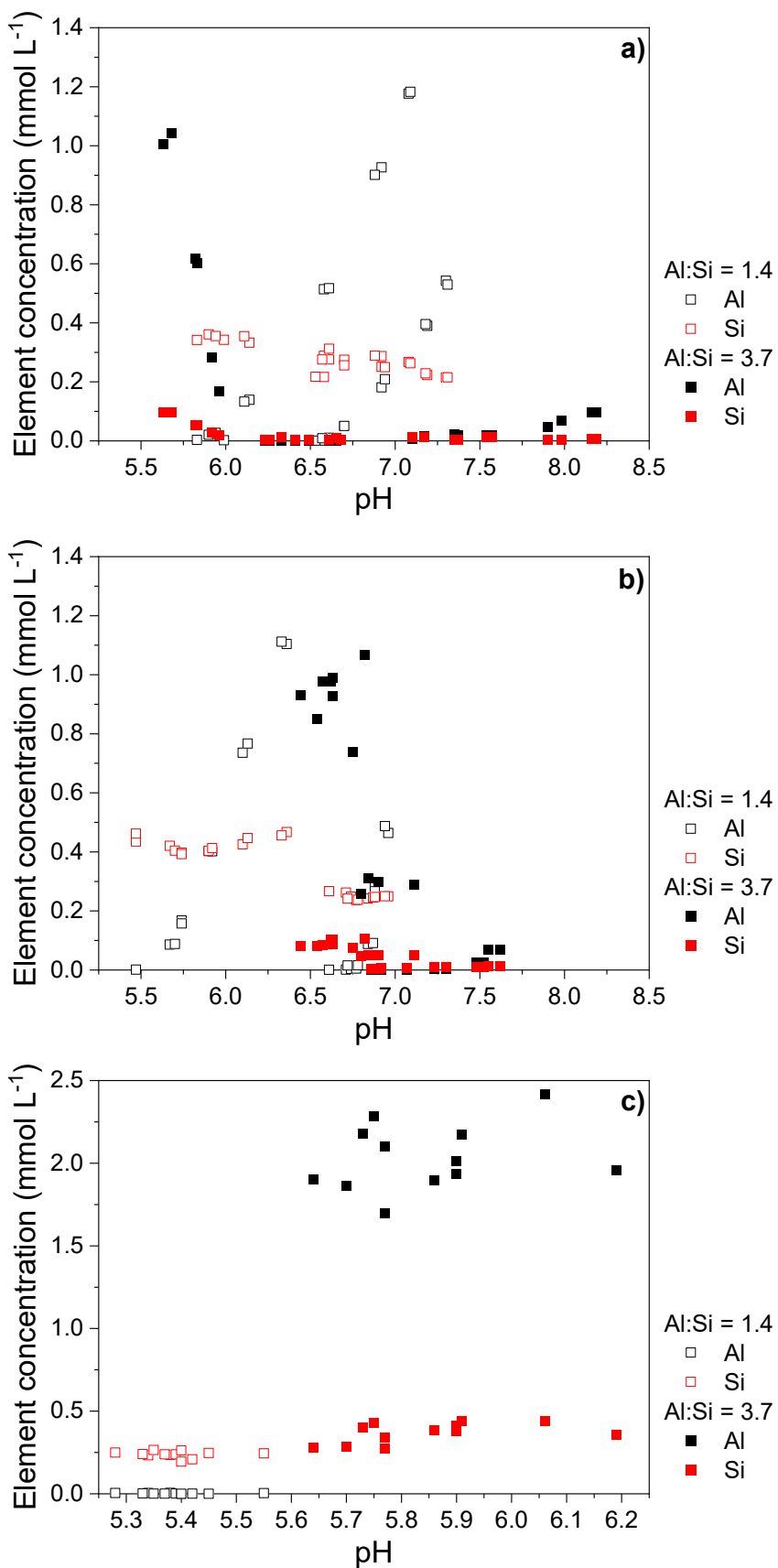


Fig. S6 Aluminum and silicon concentrations in filtrates of batch-adsorption experiments with short-range ordered aluminosilicates (molar Al:Si ratio 1.4 and 3.7) and oxalic acid (a), salicylic acid (b), and octanoic acid (c) plotted against pH

Release of Al and Si from SROAS during batch-adsorption experiments

Figure S6 gives Al and Si concentrations in filtrates of batch-adsorption experiments with organic acids after 5 h reaction time. Maximal relative amounts of Al and Si released were 4.3% and 2%, respectively. Therefore, the processes discussed in the following do not affect the conclusions in the main article on adsorption phenomena.

We plotted the concentrations against pH, since dissolution of SROAS and the processes that may have led to incomplete phase separation depend on pH. However, since adsorption of organic acids caused OH⁻ release as a function of their concentration, the final pH was proportional to organic-acid concentration, particularly for oxalic and salicylic acid.

The pH of the filtrates ranged from 5.2 to 8.2. The presence of Al and Si in filtrates with pH <7 from experiments with Al-rich SROAS cannot be explained by dissolution, since the concentrations surpassed the solubility of proto-imogolite (Lumsdon & Farmer, 1995; 1997). Hence, especially at lower pH, net positive surface charge likely favored disaggregation and thus incomplete phase separation. Molar Al:Si ratios in filtrates were slightly higher than those of the adsorbent (4.9-6.8; adsorbent: 3.7). A slight increase in Al concentrations at pH >7 that was reached only in the presence of oxalic and salicylic acid, may be caused by dissolution of Al-rich SROAS or mobilization of Al by organic acids.

Incomplete phase separation was negligible in batches with Si-rich SROAS. In filtrates from experiments with octanoic acid (Fig. S6c) and from variants without organic-acid addition (lowest pH, Fig. S6), Al concentrations were very low. A lower point of zero charge of Si-rich SROAS likely thwarted disaggregation (Su et al., 1992). With increasing concentrations of oxalic and salicylic acid, Al concentrations increased (Figs. S6a, b), while Si concentrations were unaffected. This indicates that organic acids formed soluble complexes with Al. Surprisingly, this process was negligible in batches with Al-rich SROAS, although oxalic and salicylic acid had a much higher affinity for Al-rich SROAS (see main article). Concentrations of Si markedly surpassed Al concentrations in most samples and were generally independent of final pH. This indicates preferential release of Si by depolymerization of ill-defined SROAS (Farmer et al., 1991; Strekopytov et al., 2006). Particularly Si-rich SROAS contain ill-defined and thus less stable Si species (Farmer et al., 1991; Strekopytov et al., 2006; Lenhardt et al., 2021).

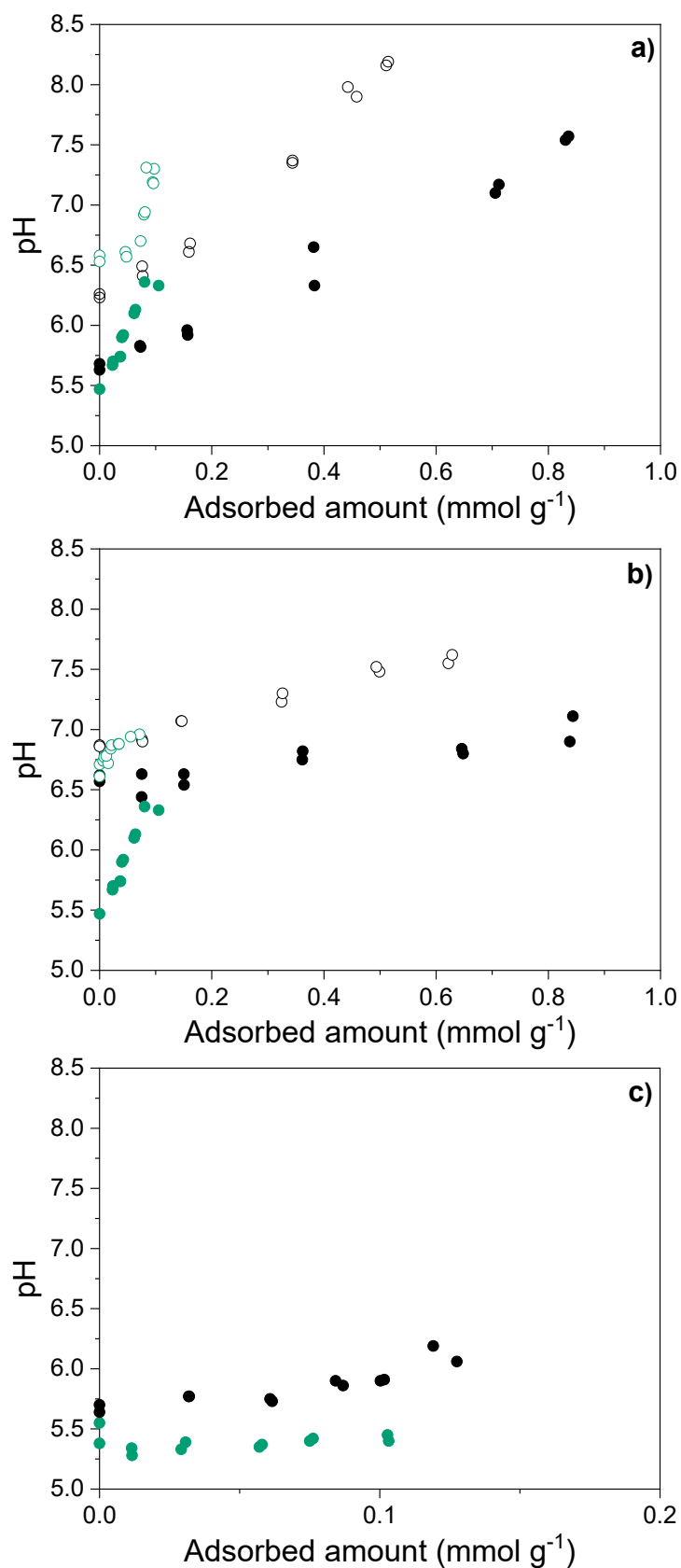


Fig. S7 Filtrate pH as a function of oxalic-acid (a), salicylic-acid (b) and octanoic-acid (c) adsorption on two short-range ordered aluminosilicates ($\text{Al}:\text{Si} = 1.4$ and 3.7 , green and black symbols, respectively) after a contact time of 5 h. Initial pH was adjusted to 5 and 6.5 (full and open symbols, respectively) in mineral suspensions and adsorptive solutions. There was no adsorption of octanoic acid at initial pH 6.5

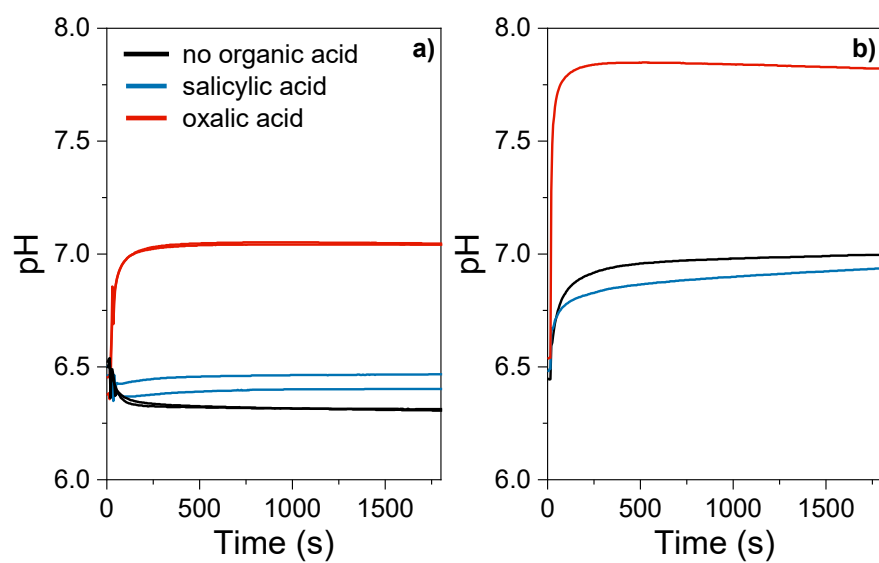


Fig. S8 Time-dependent pH change during adsorption of salicylic and oxalic acid (1.2 mmol L⁻¹) on short-range ordered aluminosilicates with molar Al:Si ratio of 1.4 (a) and 3.7 (b) at initial pH 6.5

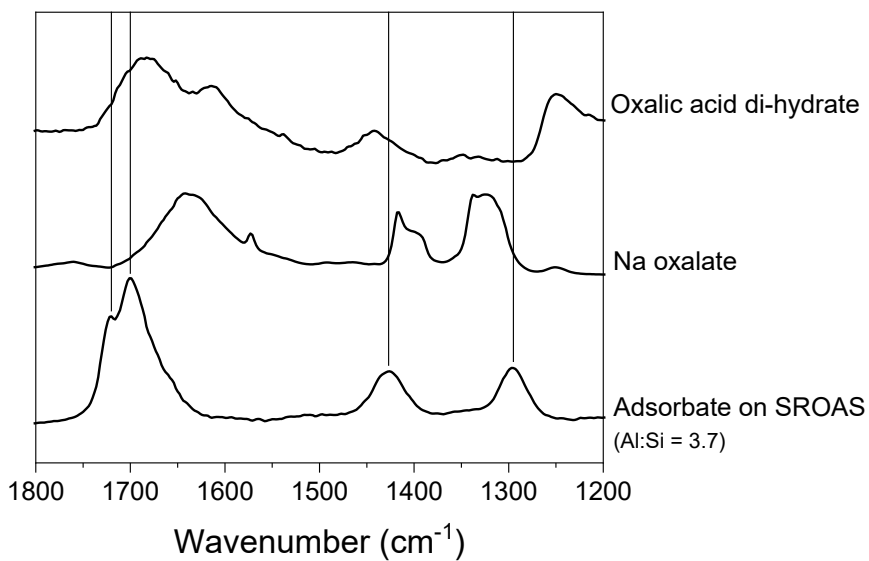


Fig. S9 DRIFT spectra of reference compounds and difference spectra of adsorption complexes formed by interaction of oxalic acid and a short-range ordered aluminosilicate (SROAS; Al:Si = 3.7) at initial pH 5. Bands of C-O stretching in adsorption complexes are marked by vertical lines

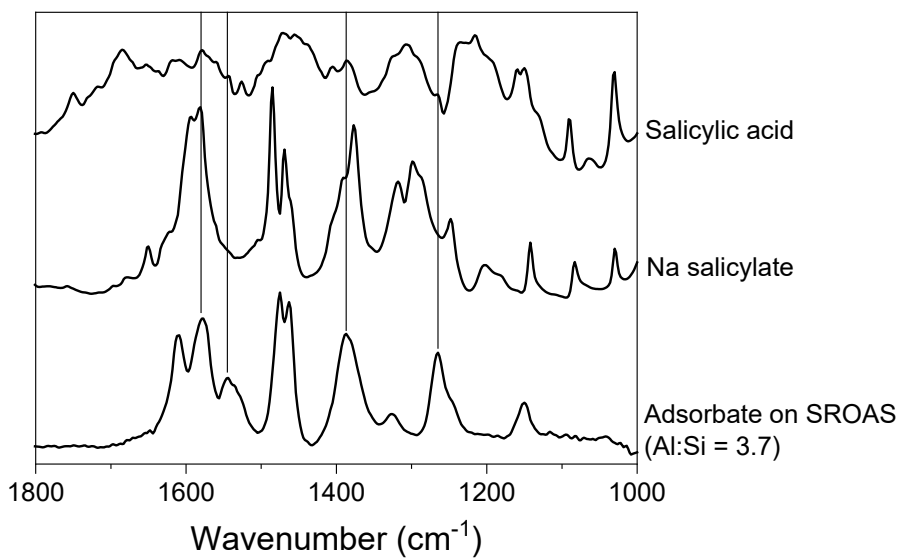


Fig. S10 DRIFT spectra of reference compounds and difference spectra of adsorption complexes formed by interaction of salicylic acid and a short-range ordered aluminosilicate (SROAS; Al:Si = 3.7) at initial pH 5. Bands of C-O stretching in adsorption complexes are marked by vertical lines

Table S1 Limiting molar conductivities ($\text{S cm}^2 \text{mol}^{-1}$) of ions used in stopped-flow experiments. At low adsorptive concentration (0.5 mmol L^{-1}), the limiting molar conductivity is an appropriate indicator for the contribution of the various ions to specific conductivity.

Ion	10 °C	15 °C	20 °C	25 °C	Reference
H_3O^+	314	344	375	404	Kinart (2019)
Octanoate	15.6	18.8	21.9	25.0	Kinart (2017)
Oxalate	51.0	58.7	66.4	74.9	Kinart (2021)
Salicylate		26.9	30.4	34.2	Stańczyk et al. (2019)

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