

Association of aluminum with silica: Connecting molecular structure to surface reactivity using NMR

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Characterizing the structural form of Al associated with silicate solids is critical towards understanding the solubility of complex mineral phases. The motivation behind our study is to explain silicate surface reactivity in terms of molecular structure using NMR spectroscopy. We use both bulk and surface-selective solid-state NMR techniques (^{27}Al MAS NMR, $^{27}\text{Al}\{^1\text{H}\}$ cross-polarization (CP) MAS NMR and $^{29}\text{Si}\{^1\text{H}\}$ CP-MAS NMR) to identify the structural form of Al associated with amorphous silica over a pH range similar to that of natural waters. The speciation information we obtain from NMR combined with the water chemistry data allow us to identify three reaction mechanisms that describe the solubility of Al and surface reactivity of amorphous silica (Fig. 1).

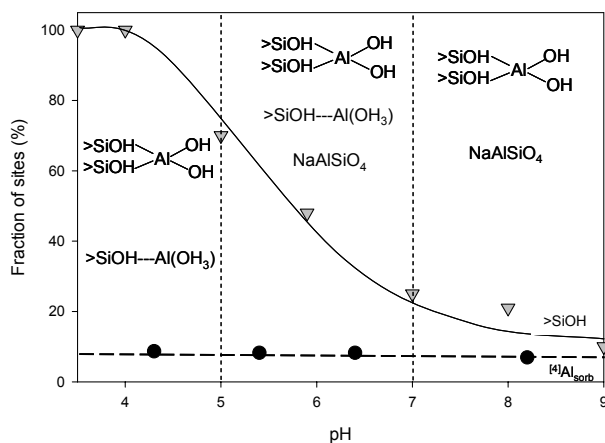


Figure 1: Schematic depicting sorption, surface precipitation and bulk precipitation of Al. The fraction of sorbed ^{41}Al (black circles) relative to the number of silanol surface sites ($>\text{SiOH}$, grey triangles) is $\sim 8\%$ and is independent of pH.

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The significant effect of alkali-site occupancy on phase equilibria and thermodynamic behavior of nepheline - kalsilite crystalline solutions

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We have investigated three Na-K ion-exchange series in the nepheline-kalsilite system $(\text{K},\text{Na})_{1-x}[\text{Al}_x\text{Si}_{1+x}\text{O}_4]$ containing excess $[\text{Si}]$ contents that range up to 12.5 mole % ($x = 0.125$; $[\text{Si}] = \text{vacancies}$). The nepheline structure has a 3:1 ratio of smaller oval to larger hexagonal alkali sites, which results in compositions for natural specimens that are less K-rich than $\text{K}_{0.25}\text{Na}_{0.75}\text{AlSiO}_4$. Our recent research on synthetic high- $[\text{Si}]$ specimens demonstrates that at the transition to more K-rich nepheline all smaller oval sites are occupied by $\text{Na} \pm \text{vacancies}$ and all hexagonal sites by $\text{K} \pm \text{vacancies}$. Vacancies thus act as the "swing occupant" that nepheline needs for as much Na as possible to occupy the smaller alkali site. K occupancy of the smaller site creates strain in the structure, which accounts for the fact that the sodic limb of the nepheline-kalsilite solvus involves compositional pairs in which one of the quenched phases is relatively K-rich nepheline. This also explains enthalpies of solution (20.1 wt % HF, 50 °C, isoperibolic conditions) that show linear trends with composition so long as K is replacing Na in the larger hexagonal site of nepheline; these switch to curved relationships once K initiates occupancy of the smaller alkali site. The resulting positive enthalpies of mixing (H_{ex}) correlate with the presence of a solvus. Reversed phase equilibria from solvus experiments produce critical temperatures (T_c) for the three series that range from 961 °C to 1265 °C, reflecting behavior that is affected dramatically by (K,Na)Al = $[\text{Si}]$ substitution. As one would expect, higher T_c is accompanied by higher H_{ex} . T_c for the most silicic specimens is lowest among the three series, perhaps explained by the shortened compositional space over which Na-K substitution can operate in that series. Below 900 °C the potassic limbs of all three solvi are superimposed upon one another and depend solely on the Na (not vacancy) content of the (one and only) ditrigonal alkali site of kalsilite.