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NMR evidence for formation of octahedral and tetrahedral Al and repolymerization of the Si network during dissolution of aluminosilicate glass and crystal

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ABSTRACT

Five sodium aluminosilicate glasses in the series Na_2O: xAl_2O_3:(3–x) SiO_2 and Na_2O:Al_2O_3:$ySiO_2$ were prepared and subjected to leaching at pH 2 under ambient conditions for up to 1000 h. Solid-state nuclear magnetic resonance (NMR) spectroscopy revealed the identity of aluminate and silicate environments in the leached surface layers of these glasses as well as a sample of albite crystal subjected to the same aqueous leaching. While ^{29}Si and ^{27}Al magic-angle spinning (MAS) NMR experiments report on the bulk structures of the samples, cross-polarization from hydrogen atoms that are present only in the surface layers provides structural information from the regions of the sample transformed during treatment. Aluminum in octahedral coordination by O atoms (Al^{VI}) is confirmed for the first time on the near-surface region of an albite crystal under the treatment conditions of this study. A quantification of the change in the amount of six-coordinate aluminum as a function of bulk Al/Si ratio is made possible by comparing the relative amounts of $^{1}H \rightarrow {}^{27}Al$ CPMAS signals from Al^{IV} and Al^{VI} obtained from different samples under reproducible experimental conditions. The relative contribution of Al^{VI} to total Al in the hydrated layers increases with the Al/Si ratio of the glasses studied. The leached albite crystal sample has an anomalously high concentration of Al^{VI} given its Al/Si ratio. This anomaly is probably related to the relatively low thickness of the leached layer developed on this phase: little hydrogen penetrates the crystal surface and almost all of the Al in the thin leached layer is octahedrally coordinated, similar to Al in solution. These data suggest that hydrolysis of bridging O atoms around Al atoms in the glass or crystal hydrated layer is accompanied by a change in the coordination number of the Al atom. Aging of surfaces documents no formation of Al^{VI} during storage after leaching. The MAS data, coupled with $^{27}Al \rightarrow {}^{29}Si$ CPMAS experiments, describe the bulk network structure and provide further insight into the surface structures, including documentation of repolymerization of the silicon network in the surface layer of a nepheline glass via formation of condensed Q^4 units. Further triple-resonance experiments correlate ^{1}H, ^{29}Si, and ^{27}Al environments in the glasses, and indicate that the repolymerized structures in nepheline glass are not phase-separated from aluminum-containing network structures. These data for acid dissolution under ambient conditions yield the first picture of the complicated series of reactions relating connectivity and coordination number of Al and Si at the altered surfaces of geologically interesting aluminosilicates.