Sugars have also been found to inhibit the corrosion of metal surfaces by forming thin adsorbed layers that prevent heterogeneous reactions in the presence of water (6). In aluminosilicate zeolite and lower molecular weight alkenes at aluminosilicate zeolite surfaces play crucial roles in a variety of natural and synthetic processes, including biomineralization, biomolecule synthesis, bone resorption, heterogeneous catalysis, corrosion inhibition, and cement hydration. For example, mono- and oligosaccharides are thought to control the morphologies and structures of carbonate skeletons in marine organisms through site-specific binding to the mineral phases (1, 2). Interactions of saccharides to form a mixture of aluminate hydration products, such as tricalcium aluminate (C₃A, abbreviated as “C₃A” in cement chemistry). As shown in the scanning electron microscopy (SEM) images of Fig. 1, very different crystal morphologies are observed for the aluminate components following hydration for 4 h at 95 °C in the absence or presence of 1% glucose or sucrose, saccharides which have closely related molecular structures (Fig. 1). Initially, anhydrous C₃A (Fig. L1) consists of crystalline particles ranging in size from 1–20 μm that rapidly hydrate in the presence of CaSO₄·2H₂O without saccharides to form a mixture of aluminate hydration products, primarily as 1–10 μm acicular crystallites (Fig. 1B). Such needle-like crystal morphologies are consistent with the formation of ettringite (Ca₆Al₂O₇(SO₄)₂·3H₂O) and calcium aluminate monosulfate (Ca₄Al₂O₆(SO₄)·12H₂O, referred to as “monosulfate”), both of which form hexagonal crystals that are the expected products of C₃A hydration with calcium sulfate dihydrate (9). By comparison, Fig. 1C shows an SEM image of C₃A


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hydrated with 1% sucrose, which results in a notable decrease in the quantity of aluminohydrate-crystals and with numerous anhydrous C₃A particles still present. Some acicular hydrates are observed, but the crystals are generally much fewer and smaller than those formed in the absence of saccharides (Fig. 1B). In contrast, the crystal morphologies of C₃A hydrated with 1% glucose (Fig. 1D) are very similar to those obtained without saccharides (Fig. 1B), indicating that glucose has much less influence than sucrose on the hydration of C₃A.

**Quantitative analyses of tricalcium aluminohydrate hydration.** The extent of C₃A hydration and the quantities of different aluminohydrate hydration products can be established in detail by solid-state 1D and 2D ²⁷Al NMR measurements. At very high magnetic fields (18.8 T), single-pulse 1D ²⁷Al magic angle spinning (MAS) NMR spectra of C₃A hydrated without and with saccharides (Fig. S1) show signals from ²⁷Al⁴⁺ moieties in anhydrous C₃A and ²⁷Al⁶⁺ species into which the ²⁷Al⁴⁺ moieties are converted during hydration. By comparing the relative integrated intensities of these signals, the extents of hydration can be estimated. In the absence of saccharides, 74% of anhydrous ²⁷Al⁴⁺ moieties in C₃A are converted into hydrated ²⁷Al⁶⁺ species (Table 1 and Fig. S1A). In combination, solid-state single-pulse ²⁷Al MAS and 2D ²⁷Al(¹H) heteronuclear correlation (HETCOR) NMR spectra (Fig. S2) allow different resolved ²⁷Al⁶⁺ species to be assigned and quantified in hydrated C₃A. The ²⁷Al peak assignments are based on previous studies (10, 11), and the 2D ²⁷Al(¹H) HETCOR measurements are consistent with the formation of six-coordinate Al(OH)₆ species, including ettringite (Fig. 2A), monosulfate, tricalcium aluminohexahydrate (Ca₃Al₂O₆·6H₂O), and dicalcium aluminohexahydrate (Ca₂Al₂O₆·8H₂O). Without saccharides, ettringite (24%), monosulfate (19%), and Ca₂Al₂O₆·8H₂O (22%) are the dominant species, along with a minor fraction (9%) of Ca₃Al₂O₆·6H₂O (Table 1). These analyses allow the extents of hydration and relative quantities of aluminohydrate hydration products to be compared with systems containing glucose, maltodextrin, and sucrose.

Notably, in the presence of small amounts of the different saccharides, the hydration of tricalcium aluminohydrate is reduced by dramatically different extents under otherwise identical conditions. These differences are reflected in quantitative solid-state single-pulse ²⁷Al NMR analyses (Fig. S1B–D) of C₃A hydrated with 1% glucose, maltodextrin, or sucrose. As measured by the conversion of anhydrous ²⁷Al⁴⁺ to hydrated ²⁷Al⁶⁺ species (Table 1), sucrose most effectively inhibits overall C₃A hydration with only 28% conversion, followed by maltodextrin (53%) and glucose (60%). These results are consistent with the distinct product morphologies observed in Fig. 1, manifesting the significantly different influences that these saccharides have on C₃A hydration. The relative quantities of the different aluminohydrate hydration products are estimated from single-pulse 1D ²⁷Al MAS spectra (Fig. S3) and are shown in Table 1. All of the saccharides examined inhibit the formation of monosulfate, whereas only sucrose delays the formation of all aluminohydrates to significant extents. All aluminohydrates form directly from the hydration of C₃A, whereas monosulfate can also form from the subsequent conversion of ettringite. This suggests that sucrose adsorbs onto C₃A surfaces, thereby passivating hydration sites and inhibiting the formation of other C₃A hydration products.

**Saccharide–aluminohydrate interactions.** The different aluminohydrate behaviors in the presence of sucrose and glucose can be correlated to their significantly different adsorption properties on C₃A and its hydration products. Specific saccharide–aluminohydrate interactions in hydrated C₃A can be probed by solid-state 2D ¹³C(¹H) HETCOR NMR measurements that are sensitive to dipole–dipole couplings between ¹³C and ¹H nuclei. For example, Fig. 3A shows the 2D ¹³C(¹H) HETCOR spectrum acquired for C₃A hydrated in the presence of 1% ¹³C-labeled glucose, in which correlated 2D signal intensity reveals interactions between ¹³C and ¹H moieties that are in molecular proximity (<1 nm). Compared to the 1D single-pulse ¹³C MAS NMR spectrum of crystalline glucose (Fig. 3A, Top), the absence of ¹³C intensity correlations at 92 and 95 ppm from C1α and C1β moieties, along with the appearance of ¹³C signals from carboxylate moieties (-COO⁻, 185 ppm), alkyl groups (-CH₂, 40 ppm; -CH₃, 20 ppm), and carbonyl species (-CHOH, -COH, 55–85 ppm), establish that the cyclic form of glucose has completely degraded. Such signals are consistent with the formation of saccharinic or other short-chained carboxylic acids, which have previously been reported for glucose degradation in aqueous alkaline solutions (12).

Analysis of the intensity correlations in the 2D ¹³C(¹H) HETCOR spectrum (Fig. 3A) of C₃A hydrated in the presence of glucose reveals specific interactions between glucose degradation species and aluminohydrate hydration products. Strong intensity correlations are observed between the ¹³C carbonyl signal centered at 75 ppm and ¹H signals at 3.6 and 1.5 ppm (Fig. 3A, right red dashed box) associated with the carbonyl protons and hydroxyl groups from aluminohydrate (²⁷Al⁶⁺) hydration products (Fig. S2).

**Table 1.** Relative populations of NMR-visible ²⁷Al species and overall conversion of Al⁴⁺ species in tricalcium aluminohydrate to Al⁶⁺ products during hydration in the presence of saccharides

<table>
<thead>
<tr>
<th>Saccharide</th>
<th>Al⁴⁺ Ca₃Al₂O₆ (C₃A) 50–80 ppm, %</th>
<th>Al⁴⁺ Ca₃Al₂O₆·6H₂O 11.0 ppm, %</th>
<th>ettringite 10.0 ppm, %</th>
<th>monosulfate 9.3 ppm, %</th>
<th>Ca₂Al₂O₆·8H₂O 8.6 ppm, %</th>
<th>% ²⁷Al conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>26</td>
<td>9</td>
<td>24</td>
<td>19</td>
<td>22</td>
<td>74</td>
</tr>
<tr>
<td>1% glucose</td>
<td>40</td>
<td>12</td>
<td>19</td>
<td>6</td>
<td>23</td>
<td>60</td>
</tr>
<tr>
<td>1% maltodextrin</td>
<td>47</td>
<td>12</td>
<td>15</td>
<td>4</td>
<td>22</td>
<td>53</td>
</tr>
<tr>
<td>1% sucrose</td>
<td>72</td>
<td>6</td>
<td>8</td>
<td>4</td>
<td>10</td>
<td>28</td>
</tr>
</tbody>
</table>

From quantitative line-fitting of 1D ²⁷Al MAS NMR spectra in Figs. 51 and 53. Percent values are estimated to be accurate within ±2%.
Fig. 2. Schematic diagrams of (A) hydroxylated Al\(^{13}\) species in ettringite, and (B) the different four-coordinate $Q^2$, $Q^3$, and $Q^4$ silicate moieties in CSH.

respectively. This establishes that carbinol-containing glucose degradation products adsorb strongly on aluminate-hydrate surfaces, although the broadened $^1\text{H}$ signal does not allow interactions with specific hydrates to be distinguished. Intensity correlations observed between the $^{13}\text{C}$ signal at 185 ppm and $^1\text{H}$ protons at 1.5 ppm (Fig. 3A, left red dashed box) show additional molecular interactions between -COO\(^-\) moieties and aluminate-hydrate surfaces. Carboxylate groups in organic molecules likely bind to aluminate surfaces in aqueous environments through electrostatic interactions (Fig. 3A, Inset i), whereas carbinol moieties form hydrogen bonds (Fig. 3A, Inset ii). Intensity correlations between $^{13}\text{C}$ signals at 20 and 40 ppm associated with alkyl species and the $^1\text{H}$ signal at 1.5 ppm may result from intramolecular (i.e., directly bonded -CH\(_2\) or -CH\(_3\) protons) or intermolecular (i.e., -AIOH) interactions. Both types of interactions are expected to yield correlated signal intensity in similar regions of the 2D $^{13}\text{C}[^1\text{H}]$ HETCOR spectrum and are not resolved in Fig. 3A. Intramolecular interactions account for intensity correlations between $^{13}\text{C}$ signals at 185 and 40 ppm and the $^1\text{H}$ signal at 3.6 ppm associated with adjacent carbinol species. Using $^{13}\text{C}$-labeled glucose, molecular interactions are thus observed between carboxylate and carbinol moieties found in glucose degradation products, providing direct evidence that these species adsorb onto, or are intercalated within, aluminate hydration products.

In contrast, similar measurements under identical alkaline conditions show that sucrose does not degrade and does not adsorb on aluminate hydration products. Fig. 3B shows the solid-state 2D $^{13}\text{C}[^1\text{H}]$ HETCOR spectrum of hydrated C\(_3\)A in the presence of 1% $^{13}\text{C}$-labeled sucrose that exhibits intensity correlations corresponding to dipole-dipole–coupled moieties associated with adsorbed sucrose molecules. All of the $^{13}\text{C}$ signals appear at similar chemical shifts, but are broadened, compared to those observed in the 1D single-pulse $^{13}\text{C}$ MAS NMR spectrum of crystalline sucrose (Fig. 3B, Top), consistent with intact adsorption of sucrose on C\(_3\)A. Intramolecular 2D intensity correlations are observed between multiple $^{13}\text{C}$ signals and $^1\text{H}$ signals centered at 3.6 ppm that also are present in the solid-state 2D $^{13}\text{C}[^1\text{H}]$ HETCOR spectrum of crystalline sucrose (Fig. S4). Importantly, no intensity correlations are observed between the $^{13}\text{C}$ signals and the $^1\text{H}$ signal centered at 1.5 ppm (Fig. 3B, red dashed box) that are associated with -AIOH moieties, indicating that the $^{13}\text{C}$ species are not in molecular proximity to aluminate-hydrate species. Unlike hydrating C\(_3\)A systems containing glucose, the 2D $^{13}\text{C}[^1\text{H}]$ intensity correlations establish that sucrose does not bind to aluminate-hydrate surfaces, the formation of which sucrose is notably most effective at inhibiting (Table 1).

Based on these results, we hypothesize that sucrose adsorbs intact selectively at C\(_3\)A surfaces, thereby inhibiting C\(_3\)A hydration. In contrast, the degradation species associated with glucose and maltodextrin adsorb nonselectively to aluminate hydration products, resulting in the delayed formation of monosulfate, as depicted schematically in Fig. 4. In alkaline solutions, the glucose ring structure opens at the carbon 1–5 oxygen linkage (Fig. 3A), to form a linear structure with a carboxyl endgroup, before degrading further (12). By comparison, sucrose is composed of glucose and fructose monomer units that are conjoined such that similar ring opening does not occur because the carbon 1–7 oxygen linkage prevents formation of a carboxyl moiety. This suggests that sucrose is a more effective hydration inhibitor because it selectively adsorbs at C\(_3\)A surfaces, with its ring structure intact, resulting in higher local surface coverages, compared to glucose or maltodextrin degradation species that also adsorb on diverse degradation products, e.g., ettringite (white hexagons) under alkaline conditions. Whereas the glucose degradation species adsorb nonselectively, sucrose molecules are selective for the anhydrous aluminate moieties.

Fig. 3. Solid-state 2D $^{13}\text{C}[^1\text{H}]$ HETCOR NMR spectra acquired at 18.8 T, 298 K, 10 kHz MAS for hydrated tricalcium aluminate (4 h, 95 °C) in the presence of CaSO\(_4\)·2H\(_2\)O and with 1% (A) glucose or (B) sucrose by weight of C\(_3\)A. The Insets in (A) show glucose degradation moieties binding to aluminate surfaces through (i) -COO\(^-\) interactions and (ii) -COH hydrogen bonds.

Fig. 4. Schematic diagrams depicting the different adsorption properties of (A) glucose degradation products (carboxylic acids, red) versus (B) sucrose (green) on tricalcium aluminate particles (gray) or aluminate hydration products, e.g., ettringite (white hexagons) under alkaline conditions. Whereas the glucose degradation species adsorb nonselectively, sucrose molecules are selective for the anhydrous aluminate moieties.

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aluminate hydration products. The less-selective interactions of carboxylic acid species with aluminate hydration moieties are likely a consequence of their much higher dissociation constants (e.g., saccharinic acids, \(pK_a < 4.0\) versus sucrose, \(pK_a = 12.6\)), which promote electrostatic interactions with cationic surface sites. The combination of 1D and 2D NMR techniques provides important insights on saccharide-dependent aluminate hydration and the molecular mechanisms that account for the distinctly different saccharide behaviors.

**Saccharide-Mediated Silicate Hydration.** Quantitative analyses of tricalcium silicate hydration. Similarly, the solution behaviors and/or structural transformations of saccharides under alkaline conditions also lead to different binding configurations and coverages at silicate surfaces that result in significantly different silicate hydration behaviors. As a technologically important example, the hydration of silicates such as tricalcium silicate (C\(_3\)S\(_2\)O\(_5\), often abbreviated as “C\(_3\)S”), are primarily responsible for setting and strength development of cements (9), which are often modified by saccharides that significantly affect bulk rheological or mechanical properties. The extent of C\(_3\)S hydration and formation of calcium-silicate-hydrate (“CSH,” Fig. 2B) products are elucidated by quantitative single-pulse 1D \(^{29}\)Si MAS NMR measurements, which show that certain saccharides more effectively suppress the formation of CSH during the early stages of hydration than others. For example, the single-pulse 1D \(^{29}\)Si MAS spectra of C\(_3\)S hydrated for 4 h at 95 °C without and with saccharides (Fig. S5) show \(^{29}\)Si signals from \(^{29}\)Q\(_n\) species (“\(^{29}\)Q\(_n\)” refers to \(^{29}\)Si atoms that are covalently bonded via bridging oxygen atoms to \(n \leq 4\) other Si atoms) in anhydrous C\(_3\)S that are converted upon hydration to cross-linked \(^{29}\)Q\(_2\), \(^{29}\)Q\(_4\), and \(^{29}\)Q\(_6\) silicate species associated with CSH. Fig. 2B shows a postulated structure of CSH that is consistent with previous \(^{29}\)Si NMR measurements (10), recent molecular modeling analyses (13, 14), small-angle neutron and X-ray scattering data (15, 16), and transmission electron microscopy studies (17). In the absence of saccharides, the extent of hydration can be established by comparing the relative integrated \(^{29}\)Si NMR signal intensities from \(^{29}\)Q\(_n\) (54%), \(^{29}\)Q\(_2\) (22%), \(^{29}\)Q\(_4\) (4%), and \(^{29}\)Q\(_6\) (20%) \(^{29}\)Si species, where hydration is measured as the conversion of anhydrous \(^{29}\)Si \(^{29}\)Q\(_n\) to hydrated \(^{29}\)Q\(_1\), \(^{29}\)Q\(_2\), and \(^{29}\)Q\(_4\) \(^{29}\)Si species (Table 2 and Fig. S5A). Thus, under these conditions, approximately 46% of the \(^{29}\)Si species have hydrated to form CSH. Similar analyses on C\(_3\)S under otherwise identical conditions, except containing 1% glucose, maltodextrin, or sucrose (Fig. S5 B–D), show that the conversion of \(^{29}\)Q\(_2\) species during hydration is reduced for all saccharides to 24, 8, and 3%, for glucose, maltodextrin, and sucrose, respectively. These measurements establish the significantly different influences of these saccharides on C\(_3\)S hydration, which follow the same sequence as observed for the aluminates, but with greater effect.

**Saccharide–silicate interactions.** The molecular origins of the different tricalcium silicate hydration properties in the presence of the saccharides are due to differences in their adsorption interactions at specific silicate surface sites. Two-dimensional NMR measurements resolve interactions between water, organic moieties, and silicate species that account for the suppression of cross-linked \(^{29}\)Si species in hydrated C\(_3\)S. For example, molecular interactions between different silicate moieties and organic species are observed in the 2D \(^{13}\)C\(^{1}\)H HETCOR spectrum of C\(_3\)S hydrated in the presence of 1% \(^{13}\)C-labeled glucose (Fig. S4). As with the aluminates, the absence of \(^{13}\)C and \(^{13}\)C\(^{1}\) \(^{13}\)C signals at 92 and 95 ppm indicates that the cyclic form of glucose has completely degraded, with the appearance of \(^{13}\)C signals at 182, 40, and 20 ppm being consistent with the formation of saccharinic or short-chained carboxylic acids. Intensity correlations are clearly observed between the carboxylate \(^{13}\)C signals at 172 and 182 ppm and the \(^{1}\)H signal at 1.3 ppm (Fig. S4, left red dashed box) that is associated with the hydrated \(^{29}\)Si \(^{29}\)Q\(_1\) and \(^{29}\)Q\(_2\) species (Fig. S6), along with the carbinol protons (3.6 ppm). Likewise, the carbinol \(^{13}\)C signals centered at 75 ppm are correlated with the \(^{29}\)Q\(_1\) and \(^{29}\)Q\(_2\) silanol \(^{1}\)H signals at 1.3 ppm (Fig. S4, right red dashed box) and the carbinol \(^{1}\)H signal at 3.6 ppm. These observations provide strong evidence that the glucose degradation products adsorb strongly on CSH surfaces and that both the -COO" and -COH moieties are in close proximities to the surface -SiOH species. Carboxylate groups are expected to bind to silicate surfaces in aqueous environments through electrostatic interactions (Fig. S4, Inset 1), with carbinol moieties adsorbing via hydrogen bonds.

<table>
<thead>
<tr>
<th>Saccharide</th>
<th>(^{29})Q(_1), %</th>
<th>(^{29})Q(_2), %</th>
<th>(^{29})Q(_4), %</th>
<th>(^{29})Q(_6), %</th>
<th>(^{29})Si conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>54</td>
<td>22</td>
<td>4</td>
<td>20</td>
<td>46 (±3)</td>
</tr>
<tr>
<td>1% glucose</td>
<td>76</td>
<td>12</td>
<td>2</td>
<td>10</td>
<td>24 (±3)</td>
</tr>
<tr>
<td>maltodextrin</td>
<td>92</td>
<td>4</td>
<td>1</td>
<td>3</td>
<td>8 (±1)</td>
</tr>
<tr>
<td>sucrose</td>
<td>97</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>3 (±1)</td>
</tr>
</tbody>
</table>

From quantitative line-fitting of 1D \(^{29}\)Si MAS NMR spectra in Fig. S5.

![Fig. 5. Solid-state 2D \(^{13}\)C\(^{1}\)H HETCOR NMR spectra acquired at 11.7 T, 298 K, 10 kHz MAS for hydrated tricalcium silicate (4 h, 95 °C) with 1% (A) glucose or (B) sucrose by weight of C\(_3\)S. The Insets in (A) show glucose degradation moieties binding to CSH surfaces through (i) -COO" interactions and (ii) -COH hydrogen bonds. The Inset in (B) shows sucrose binding to CSH surfaces through hydrogen bonds.](image-url)
(Fig. 5A, Inset ii). Weaker intensity correlations observed between the $^{13}$C signals at 172, 182, and 75 ppm and the $^1$H signal at 4.7 ppm indicate adsorbed water in close proximity to the -COO$^-$ and -COH moieties. Weak intensity correlations between these $^{13}$C signals and the $^1$H signal at 6.3 ppm result from nearby hydrogen-bonded -OH moieties. Intramolecular interactions account for the correlated intensity between $^{13}$C signals at 20 ppm and the $^1$H signal at 0.9 ppm associated with alkyl species (i.e., $-CH_3$, $-CH_2$). The molecular interactions between CSH moieties and both -COH and -COO$^-$ groups establish that adsorbed glucose degradation products, as opposed to glucose itself, are responsible for inhibiting C-S hydrogen.

Similar 2D NMR analyses of C$_3$S hydrated in the presence of sucrose manifest site-specific interactions between sucrose and silicate hydration products. Fig. 5B shows 2D $^{13}$C($^1$H) HETCOR spectra of crystalline sucrose (red) and C$_3$S hydrated with 1% $^{13}$C-labeled sucrose (black), which are superimposed to emphasize similarities and differences in their correlated signals. Comparison of the $^{13}$C signals in the 1D projections of crystalline sucrose and hydrated C$_3$S establish that sucrose molecules adsorb intact with no degradation products observed (within the sensitivity limits of the measurements). Furthermore, strong intensity correlations are observed between all sucrose $^{13}$C signals and the $^1$H signal at 1.3 ppm (Fig. 5B, black) associated with the hydrated $Q^1$ $Q^2$ silanol species. This indicates that sucrose molecules are adsorbed strongly at CSH surface sites in configurations where all of the carbon atoms can be in close ($< 1$ nm) proximity to the hydrate surfaces. Intramolecular intensity correlations are observed between multiple $^{13}$C signals and the $^1$H signal centered at 3.6 ppm, which are also observed in the solid-state 2D $^{13}$C($^1$H) HETCOR spectrum of crystalline sucrose (Fig. 5B, red). Weaker intensity correlations observed between the $^{13}$C signals at 67 and 75 ppm and the $^1$H signal at 4.7 ppm indicate that some adsorbed water is also in close proximity to the sucrose molecules. However, compared to the 2D $^{13}$C($^1$H) HETCOR spectrum of C$_3$S hydrated with 1% glucose (Fig. 5A), these intensity correlations with water are significantly weaker, establishing that sucrose more effectively excludes water from CSH surface sites.

Additionally, comparison of the $^{13}$C chemical shifts between crystalline sucrose (Fig. 5B, red) and sucrose adsorbed on CSH (Fig. 5B, black) allow specific $^{13}$C moieties that interact most strongly with the hydrated silicate species to be identified. When an organic molecule binds to an inorganic ion or surface, the local $^{13}$C electronic environments can be altered, leading to changes in the $^{13}$C isotropic chemical shifts. For example, the isotropic $^{13}$C chemical shifts of carbon atoms 7, 2, and 4 are each displaced by 2–3 ppm for the adsorbed species, compared to crystalline sucrose, whereas all other $^{13}$C shifts are nearly the same ($|\Delta \delta| < 1$ ppm). Importantly, this suggests that sucrose molecules interact via several carbon moieties with multiple CSH surface sites (Fig. 5B, Inset) leading to stronger adsorption. Multiple interaction sites are expected similarly to promote sucrose adsorption on C$_3$S where -SiOH moieties are present under aqueous conditions, though in relatively low fractions that are challenging to observe. These measurements establish that, compared to glucose, sucrose more effectively inhibits C$_3$S hydration, because of the presence of multiple interaction sites on (nondegraded) disaccharide molecules, which lead to strong sucrose adsorption that competitively excludes water at CSH sites.

**Saccharide–Aluminosilicate Interaction Forces.** The different molecular interactions of saccharides at aluminolate and silicate surfaces observed by 2D NMR similarly result in distinct adsorption and hydration behaviors at aluminosilicate surfaces. Surface forces measurements, employing molecularly smooth aluminosilicate mica sheets, corroborate the molecular (<1 nm) NMR analyses and quantify longer-range (1–100 nm) forces between aluminosilicate surfaces hydrated in the presence of the different saccharides and/or their degradation products. For example, Fig. 6 shows normal forces measured as functions of the distance separating two aluminosilicate surfaces immersed in otherwise identical alkaline solutions (pH 12.7, 25 °C) initially containing none or 0.2 wt%, of the different saccharides. In the absence of saccharides, the forces between the aluminosilicate surfaces are consistent with Derjaguin–Landau–Verwey–Overbeek (DLVO) theory (18), which describes the combination of attractive van der Waals and repulsive electric double-layer forces that exist between two surfaces in aqueous solutions. The characteristic decay length of the interaction, or Debye length ($\kappa^{-1}$), measured to be 1.5 nm (Fig. 6, Inset), is close to the value of 1.1 nm calculated from DLVO theory (19). A so-called “hard wall,” where the repulsive force increases rapidly at very short separation distances, is observed at approximately 1 nm, due to “steric-hydration” forces caused by water and cations solvated at the mica surfaces. The surface forces apparatus (SFA) measurements permit quantitative comparisons to be made among different alkaline solutions, including those containing saccharides that may be adsorbed onto the hydrated aluminosilicate mica surfaces.

Similar surface force measurements between mica surfaces in contact with alkaline solutions containing 0.2 wt% glucose or sucrose establish very different behaviors for the different saccharides. As for the alkaline solution alone, the force-distance profiles for glucose and sucrose (Fig. 6) exhibit similar hard walls, though at significantly different separation distances of approximately 1 nm for glucose and 7 nm for sucrose. For glucose, the hard wall at 1 nm is the same as that observed in the aqueous solution without saccharides, indicating that most of the organic species have been removed from the mica. The hard-wall repulsion at 1 nm provides quantitative evidence that the alkaline glucose degradation products adsorb relatively weakly on the aluminosilicate mica surfaces and can be “squeezed out” by fluid convection as the mica surfaces approach molecular contact.

In contrast, for sucrose the 7-nm hard wall is significantly larger than observed for glucose or the alkaline solution alone. This is due to steric forces between strongly adsorbed multilayers of sucrose molecules on the mica surfaces, which remain bound as the surfaces are brought together, thereby presenting an addi-
tional strong repulsive contribution. The binding of sucrose on silicates established by solid-state NMR (Fig. 5B) suggests that the sucrose molecules adsorb in a planar fashion on the mica surfaces. This is similar to the stacking configuration of sucrose molecules in its monoclinic crystal, which are separated by approximately 0.8 nm (20). The 7-nm hard wall corresponds to multiple layers (approximately 4-5) of strongly adsorbed sucrose molecules on each mica surface (Fig. 6, Top), which remain intact even at relatively high local pressures (≥10 atm). This establishes that sucrose forms multilayers on the aluminosilicate surfaces, possibly through complexation with cations near the negatively charged mica or by precipitation from the aqueous solution.

Quantitative analyses of the force-distance profiles for glucose and sucrose indicate that complexation with cations occurs near the aluminosilicate surface and confirms strong sucrose adsorption at the mica surfaces. Comparison of the force-distance curves for glucose and sucrose (Fig. 6, Inset) reveals repulsive interactions with significantly different decay lengths as the mica surfaces approach, which reflect their different adsorption properties on hydrated aluminosilicate mica, as similarly observed and discussed for the aluminates and silicates above. Longer-range interactions observed at separation distances of about 40–100 nm are due to electrostatic interactions associated with the double layers near the surfaces of organic species adsorbed on the mica. The Debye lengths (1/k), determined directly from the slopes of the linesfits in this region (Fig. 6, Inset), are approximately 10 nm in the presence of sucrose or glucose. The longer Debye lengths, in comparison to alkaline solutions without saccharide (1/k ~ 1.5 nm), are consistent with cation-saccharide complexation near the anionic mica surfaces, which is expected to result in decreased overall concentrations of cations in the bulk solutions (e.g., k ~ Na⁺/bulk) (21). The SFA results establish that sucrose adsorbs more strongly than glucose (or the latter’s associated degradation products) and in multilayers (for a sufficiently high concentration) on the aluminosilicate mica surfaces in aqueous alkaline media. Such strong adsorption appears to be enhanced by cation complexation and the multiple interaction sites established by the molecular-level NMR analyses.

Conclusions

The very different hydration behaviors of aluminates, silicates, and aluminosilicates in the presence of the closely related saccharides glucose, sucrose, and maltodextrin are shown to be due to their different alkaline stabilities, adsorption selectivities at oxide surfaces, and binding strengths. Such different hydration and adsorption properties are shown to be directly related to subtle but important differences in the molecular structures of the saccharides. Solid-state NMR spectroscopy and surface forces measurements establish over complementary length scales (<1 nm and 1–100 nm, respectively) the transformations and interactions of the respective mono- and disaccharide species at silicate, aluminate, and aluminosilicate surfaces. Two-dimensional 13C(1H) HETCOR NMR spectra of hydrated tricalcium aluminate and silicate establish that glucose degradation species interact nonselectively with aluminile and silicate hydration products and suggest selective adsorption of sucrose at C₃A surface sites and multiple interactions with silicate hydrates. Quantitative surface force measurements furthermore establish the formation of strongly adsorbed sucrose multilayers on hydrated aluminosilicate surfaces that are stable at relatively high local pressures, compared to weak binding of glucose degradation species.

The advanced NMR and surface force techniques demonstrated here are applicable generally to other systems where organic species interact at heterogeneous aluminate, silicate, or aluminosilicate surfaces. Such measurements can be used to establish molecular criteria for the design or selection of saccharide species that mediate surface reactions, such as hydration, corrosion, or adhesion. The resulting insights are expected to contribute directly and broadly toward understanding the molecular-level interactions between saccharides and similar hydrating oxide surfaces, which occur in cements, biomaterials, abiotic syntheses of organic molecules, heterogeneous catalysis of sugars, and corrosion inhibition.

Materials and Methods

Tricalcium aluminate (Ca₃Al₂O₆, CTGroup), tricalcium silicate (Ca₃SiO₅, CTGroup), and calcium sulfate dihydrate (gypsum, CaSO₄·2H₂O, Sigma-Aldrich) were used as received. D-glucose and sucrose, including 99% 13C-enriched species, were obtained from Sigma-Aldrich and used as received. Maltodextrin (Main Street Ingredients) had a dextrose equivalent of 40. Hydrated materials were prepared by mixing the anhydrous materials and saccharide species with water in a high shear blender (Fisher Scientific) at 10,000 rpm for 1 min. The resulting mixtures were measured to be highly alkaline, with pH values of 12.7 (±0.1). Water-to-solids mass ratios of 1.0 and 2.0 were used for systems containing C₃S, and C₃A, respectively. For the cases where saccharides were present, they were added in concentrations of 1.0% by weight of C₃S or C₃A. All C₃A samples were hydrated with calcium sulfate dihydrate present in quantities of 50% by weight of C₃A all C₃S samples were hydrated without gypsum. After mixing, all materials were poured into polyethylene containers and hydrated for 4 h at 95 °C and 100% relative humidity. Following hydration, the products were ground into a powder, immersed in liquid N₂, and evacuated at 0.10 Torr and 233 K to remove unreacted water and quench the hydration process (10). All NMR spectroscopy, SFA, and SEM experimental details are provided in SI Text.

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Supporting Information

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SI Text

Solid-State NMR Experimental Details. Solid-state $^1$H, $^{13}$C, and $^{27}$Al NMR experiments were conducted on a Bruker AVANCE III spectrometer (18.8 T) operating at frequencies of 800.43 MHz for $^1$H, 201.26 MHz for $^{13}$C, and 208.56 MHz for $^{27}$Al and under conditions of magic angle spinning (MAS) at 298 K. Solid-state $^1$H, $^{13}$C, and $^{29}$Si NMR experiments were conducted at 298 K on a Bruker AVANCE-II spectrometer (11.7 T) operating at frequencies of 500.24 MHz for $^1$H, 125.78 MHz for $^{13}$C, and 99.38 MHz for $^{29}$Si. Two-dimensional $^{27}$Al($^1$H), $^{29}$Si($^1$H), and $^{13}$C($^1$H) heteronuclear correlation (HETCOR) experiments were conducted at 298 K under MAS conditions with cross-polarization contact times of 0.5, 1.0, and 1.5 ms, respectively, at 11.7 or 18.8 T for tricalcium silicate and tricalcium aluminate, respectively. The $^1$H, $^{13}$C, and $^{29}$Si chemical shifts were referenced to tetrakis(trimethylsilyl)silane $\left(\left(CH_3\right)_4Si\right)_2Si$ as a secondary standard, and the $^{27}$Al chemical shifts were referenced to an aqueous solution of 0.5 M aluminum nitrate $\left[Al\left(NO_3\right)_3\right]$.

Solid-state 1D single-pulse $^1$H, $^{13}$C, and $^{29}$Si MAS measurements were performed at 11.7 T, 298 K, and under 10-kHz MAS conditions using a Bruker 4-mm H-X double-resonance probehead and zirconia rotors with Kel-F® caps. One-dimensional $^{13}$C single-pulse experiments were conducted using a 90° pulse length of 4.0 μs (3.0 μs), under conditions of proton decoupling (3.4 μs 90° $^1$H pulses, 4.0 μs), and using a recycle delay of 60 s. One-dimensional single-pulse $^{29}$Si experiments were conducted using a 90° pulse length of 3.7 μs (3.0 μs), under conditions of proton decoupling (3.4 μs 90° $^1$H pulses, 4.0 μs), and using a recycle delay of 100 s. One-dimensional single-pulse $^1$H experiments were performed using a 90° pulse length of 3.4 μs (4.0 μs) and a recycle delay of 2 s.

Solid-state 1D single-pulse $^1$H, $^{13}$C, and $^{27}$Al measurements were performed at 18.8 T, 298 K, and under 20-kHz MAS conditions using a Bruker 3.2-mm H-X-Y triple-resonance probehead with zirconia rotors and Kel-F® caps. One-dimensional single-pulse $^{13}$C experiments were conducted using a 90° pulse length of 4.0 μs (−0.19 μs), under conditions of proton decoupling (3.4 μs 90° $^1$H pulses, −0.19 μs), and using a recycle delay of 60 s. One-dimensional single-pulse $^{27}$Al experiments were conducted using a high-power 1.0-μs pulse length (−0.19 μs) for $^{27}$Al, corresponding to a 30° tip angle, and a recycle delay of 10 s. The high magnetic field mitigates the effects of second-order quadrupolar interactions and improves signal sensitivity and resolution of the $^{27}$Al signals. The single-pulse $^{27}$Al NMR measurements were calibrated using a dense 4.7-mg piece of AlN as an external reference for spin counting and establish that >95% of the $^{27}$Al species are NMR visible. One-dimensional single-pulse $^1$H experiments were performed using a 90° pulse length of 3.4 μs (−0.19 μs) and a recycle delay of 2 s.

All solid-state HETCOR NMR spectra were acquired using frequency-switched Lee–Goldberg (FSLG) homonuclear decoupling during the $^1$H evolution period and a radio-frequency field of 70 kHz to enhance resolution in the $^1$H dimension. All 2D $^{13}$C($^1$H) HETCOR spectra were acquired with a 1.5-ms contact time and FSLG homonuclear decoupling. The 2D $^{29}$Si($^1$H) HETCOR spectra were acquired with a 1-μs $^1$H contact pulse to enable efficient $^1$H-$^{29}$Si cross-polarization. The 2D $^{13}$C($^1$H), $^{27}$Al($^1$H), $^{29}$Si($^1$H) experiments were acquired with 64 $t_1$ increments of 24 μs, 3024 transients, and using a recycle delay of 1 s that resulted in an experimental time of 27 h for each 2D experiment.

NMR lineshape analyses were conducted using the software “dmfit #20090330,” with lineshapes fit according to signal amplitude, position, and width (1). One-dimensional single-pulse $^{27}$Al and $^{29}$Si MAS spectra were deconvoluted by collectively fitting peak positions with Gaussian lineshapes that were subsequently kept the same across spectra obtained for similar samples, but with different saccharide species present.

Surface Forces Apparatus Experimental Details. Surface forces measurements were performed using a surface forces apparatus (SFA) 2000 to determine the normal force-distance profiles during approach of the mica surfaces (2). A 1–5-μm-thick mica sheet was glued onto a cylindrical silica disk of radius $R = 1.5$ cm, and then two curved and Ag-backed mica surfaces were mounted in the SFA chamber in a crossed-cylinder geometry. Aqueous solutions were prepared by titrating distilled water with NaOH to pH 12.7 and dissolving glucose or sucrose to form 0.2 wt% solutions. The solutions were comparable to those associated with hydrating aluminate and silicate powders, except for the presence of the Na$^+$ cations, instead of Ca$^{2+}$, which avoided precipitation of Ca(OH)$_2$ that would have interfered with the SFA measurements. After 1 h, approximately 200 μL of the alkaline aqueous solution, with or without saccharide, was injected between the mica surfaces when separated at a relatively large distance (approximately 1 μm) and allowed to equilibrate for 30 min before the initial approach ($v_{\text{approach}} \sim 10$ nm/s). All experiments were performed at 25 °C.

Scanning Electron Microscopy Experimental Details. Scanning electron micrographs were conducted using a FEI XL40 Sirion FEG digital electron scanning microscope at a magnification of 5000x and an electron beam voltage of 10 kV.

Fig. S1. Solid-state $^{27}$Al MAS NMR spectra acquired at 18.8 T, 298 K and 20 kHz MAS for hydrated tricalcium aluminate (4 h, 95 °C) in the presence of CaSO$_4$·2H$_2$O (50% by weight of tricalcium aluminate) and containing: (A) no saccharide, (B) 1% glucose, (C) 1% maltodextrin, or (D) 1% sucrose by weight of tricalcium aluminate. The conversion of NMR-visible $^{27}$Al species is determined by integrating and comparing the relative $^{27}$Al$^{IV}$ and $^{27}$Al$^{VI}$ peak areas, as shown above and tabulated in Table 1.

Fig. S2. Solid-state 2D $^{27}$Al/$^{1}$H HETCOR NMR spectrum acquired at 18.8 T, 298 K, and 10 kHz MAS for hydrated tricalcium aluminate (4 h, 95 °C) without saccharides in the presence of CaSO$_4$·2H$_2$O (50% by weight of tricalcium aluminate). A short spin diffusion time of $t_{sd} = 10 \mu$s was used to probe the immediate molecular proximities (<1 nm) of different resolved $^{27}$Al and $^{1}$H species. One-dimensional single-pulse $^{27}$Al and $^{1}$H spectra are shown along the horizontal and vertical axes, respectively, for comparison with the 1D projections of the 2D spectrum. The much higher resolution of the 2D spectrum allows the $^{27}$Al signals to be assigned (1, 2) to tricalcium aluminate hexahydrate (Ca$_3$Al$_2$O$_6$·6H$_2$O, 11.0 ppm), ettringite (10.0 ppm), calcium aluminate monosulfate (9.3 ppm), and dicalcium aluminate octahydrate (Ca$_2$Al$_2$O$_5$·8H$_2$O, 8.6 ppm). Strong correlated 2D signal intensity observed between the $^{27}$Al signals at 11.0, 10.0, 9.3, and 8.6 ppm and the $^{1}$H signals at 1.0, 1.4, 1.7 and 2.5 ppm, respectively, correspond to hydroxyl groups bound to $^{27}$Al species in the different aluminate hydration products. Gaussian fits to these $^{27}$Al$^{VI}$ signals, which are otherwise only partially resolved in the 1D single-pulse $^{27}$Al MAS spectrum, allow their relative populations to be estimated.

Fig. S3. Solid-state 1D $^{27}$Al MAS NMR spectra acquired at 18.8 T, 298 K, and 20 kHz MAS for hydrated tricalcium aluminate (4 h, 95 °C) in the presence of CaSO$_4$ · 2H$_2$O (50% by weight of tricalcium aluminate) and containing: (A) no saccharide, (B) 1% glucose, (C) 1% maltodextrin, or (D) 1% sucrose by weight of tricalcium aluminate. The $^{27}$Al peaks were fit to Gaussian lineshapes at the same peak locations as resolved in the 2D $^{27}$Al/$^1$H HETCOR spectrum in Fig. S2, allowing the spectra to be deconvoluted and relative $^{27}$Al$^{VI}$ populations estimated, as shown above and tabulated in Table 1.

Fig. S4. Solid-state 2D $^{13}$C/$^1$H HETCOR NMR spectrum acquired at 11.7 T, 298 K and 10 kHz MAS for crystalline sucrose. Intensity correlations are observed between $^{13}$C signals and $^1$H signals centered at 3.6 ppm due to intramolecular -CH- and -COH interactions. Intensity correlations between $^{13}$C signals and $^1$H signals at 4.7 ppm establish the presence of adsorbed water.
Fig. S5. Solid-state 1D single-pulse $^{29}$Si MAS NMR spectra acquired at 11.7 T, 298 K and 10 kHz MAS for hydrated tricalcium silicate (4 h, 95 °C) containing: (A) no saccharide, (B) 1% glucose, (C) 1% maltodextrin, or (D) 1% sucrose by weight of tricalcium silicate. The conversion of NMR-visible $^{29}$Si species is quantified by integrating and comparing the relative $Q^0$ to $Q^1$, $Q^2$, and $Q^2$ $^{29}$Si species peak areas, as shown above and tabulated in Table 2.
Fig. S6. Solid-state 2D $^{29}\text{Si}({}^1\text{H})$ HETCOR NMR spectrum acquired at 11.7 T, 298 K, and 6.5 kHz MAS, for hydrated tricalcium silicate (4 h, 95 °C) without saccharides. A 1-ms contact time was used to probe the immediate molecular proximities (<1 nm) of different resolved $^{29}\text{Si}$ and $^1\text{H}$ species. One-dimensional single-pulse $^{29}\text{Si}$ and $^1\text{H}$ MAS spectra are shown along the horizontal and vertical axes, respectively, for comparison with the 1D projections of the 2D spectrum. Gaussian fits to the $^{29}\text{Si}$ MAS signals for the $Q^0$, $Q^1$, and $Q^2$ $^{29}\text{Si}$ species are shown along the top horizontal axis. Strong correlated 2D signal intensity observed between the $^{29}\text{Si}$ signals at $-79$, $-82$, and $-85$ ppm and the $^1\text{H}$ signals at 1.3, 0.9, and 1.3 ppm, respectively, correspond to $Q^1$, $Q^{2L}$, and $Q^2$ hydroxyl species in calcium-silicate-hydrate. Additional intensity correlations observed between the $^{29}\text{Si}$ signals at $-79$ and $-85$ ppm and the $^1\text{H}$ signal at 4.7 ppm indicate that some adsorbed water is in molecular proximity to the $Q^1$ and $Q^2$ silicate species.