

Exploring the aluminium paradox in calcium-aluminosilicate-hydrate decalcification

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Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This study provides a combined experimental and computational investigation into the influence of aluminum (Al) incorporation on the decalcification of calcium-aluminosilicate-hydrate (C-A-S-H). Atomistic mechanisms and thermodynamics of C-A-S-H decalcification are elucidated through metadynamics simulations, which are rigorously validated by experimental results. This work addresses the complex and often debated effects of Al on C-A-S-H stability by providing fundamental insights into the relationship between coordination structures and dissolution free energy barriers. These findings contribute significantly to our understanding of cementitious material durability and broaden our knowledge of mineral dissolution processes. Given the novelty, rigor, and potential impact, I recommend publication in Nature Communications after addressing the following minor revisions:

1. For the metadynamics simulation of Ca dissolution, the rationale for choosing Ca displacement components as the collective variables, rather than the water coordination number, needs clarification.
2. The description of the Nudged Elastic Band method used to explore minimum free energy pathways in Fig. 3 is insufficient. The Methods section should include a detailed explanation of the NEB implementation for navigating the complex three-dimensional free energy landscape. This level of detail is essential for reproducibility.
3. Please clarify whether Fig. 4a represents actual simulation trajectories or a schematic illustration of the process.
4. The connection between the calculated free energy and the experimental decalcification rates in Fig. 5e requires further explanation. It is difficult to understand how the fitting was conducted.
5. The typical Ca/Si ratio of Portland cement pastes is 1.2~2.3 with a mean of ~1.7 (see Richardson CCR, 1999). While the chosen Ca/Si ratio of 1.25 for C-S-H here is reasonable, it would strengthen the study if the author could explain the reason for using this relatively low Ca/Si ratio.
6. Typo on line 301. Incorrect subscript in "C1.25SH".
7. Comparison and explanation with existing MTD related simulations is critical. Such as: Nature communications, 2022, 13(1): 1253 ; Cement and Concrete Research, 2023, 165: 107092 ; Cement and Concrete Research, 2022, 156: 106767.
8. The authors may consider including the constructed initial C-(A)-S-H crystal information in the supplementary material for future reference and use by other researchers.

Reviewer #2

(Remarks to the Author)

The manuscript by Tao et al. reports on an experimental and computational study of the dissolution of Calcium-Aluminosilicate hydrate.

My report will focus on the computational (metadynamics) part, as it is closer to my area of expertise.

The agreement between the experimental and computationally predicted rates is exceptional, but it is difficult to assess whether this is a coincidence or not. The details of the metadynamics simulations are scarce and even the referenced papers do not provide enough details to allow any reproducibility of the calculations. Moreover, given the complexity of the system, it is quite surprising that a forcefield such as ReaxFF, which has not been calibrated in any way to reproduce the thermodynamics of C-A-S-H, succeeds in predicting the dissolution rates of the material. I don't think that with the provided information it is possible to assess the quality of the molecular dynamics simulations, and as a consequence the soundness of the work reported here. Below I provide some specific points that are missing or needs to be addressed by the authors.

1) There is no mention of the length of the metadynamics simulations and no assessment that the free energy has actually converged. From a quick look at papers referenced here, this seems to also be the case in those articles (Refs 3, 31). Although it is true that the well-tempered metadynamics ensure convergence of the free energy by reducing the height of the gaussians, this is a necessary condition, but it is not sufficient to guarantee that the calculations are converged. In fact, one need to monitor the number of barrier re-crossings events to show that both sides of the barrier are adequately sampled. A bias-factor of 20 is pretty large, hence very long simulation are required to converge the calculations. This is particularly critical for metadynamics simulations with 3 collective variables, which take a long time to converge.

2) Moreover, it is very important that the reactant (adsorbed Ca) and product (Ca in solution) states don't change throughout the simulation to ensure that after each barrier crossing the same states are sampled. It is also important that the recrossing happens along the same pathway so that the corresponding barrier is explored.

While it may be trivial to show that the Ca in solution is always in the same state, this may not be the case for the C-A-S-H surface where the atoms may significantly rearrange after the Ca has been removed. If this is the case, the free energies calculated here probably have very large errors, that cannot be quantified. It would be revealing to repeat the same metadynamics calculation for one site a number of times using different starting condition, which also include starting from the Ca in solution, to demonstrate the variability of the each data point.

3) The Gaussians' deposition rate is very fast 40fs, the system would have no chance of relaxing to the new equilibrium state. Although this a common practice for ab-initio MD simulations, it makes the results very unreliable. A deposition rate in the range 1-2ps would be more appropriate for classical MD simulations.

4) The box restraint used here has a fairly large base (8Å), which likely include several surface states. This means that, during the metadynamics simulations, when the Ca returns towards the surface it may experience different environments than the one where it started from. All these state any have the same z-value but correspond to very different surfaces states, which may make the post-processing quite confusing.

5) The Authors have mis-interpreted what is reported in the paper by Silvestri et al. (Ref 55). Silvestri et al. did not propose a method to increase the efficiency of the calculations, but they suggested a protocol to ensure that the calculated free adsorption/desorption free energy were accurate and, more importantly, referenced to standard conditions, as the experiment should be. In fact, they argue against using a box restraint, as Tao and coworkers are doing here, because that would make the result dependent on the box size and on how much volume of the unbound state is explored. Which in turns makes the reference state of the free energy calculation ill-defined. Silvestri et al. propose to use a linear cylindrical restraint to ensure that the volume of the bound and unbound states are well-defined, which means it is possible to know what the reference state of the calculation is. The free energies contributions to add and remove the restraints also need to be computed. The procedure proposed by Silvestri et al. is designed only to give accurate free energy differences between the adsorbed and desorbed states, not to be efficient.

6) As mentions in the 2012 ReaxFF paper where the forcefield used here was first reported, in the method there are no constraints on the atomic charges, which are calculated at every time step using a charge equilibration scheme. While this may not be trivial to extract from the simulations, it has been reported that the Calcium ion often doesn't have a +2 charge in solution, but some smaller fractional value. If this is the case it may have profound consequences on the results shown here, particularly if in each metadynamics simulation the Ca ion has a different charge in solution, which would imply that the solvation free energy of the ion would be different in different simulations. Another consequence of this is that when the Ca ion leave the surface there is a dipole created in the system (negative surface – Ca ion in solution) and the magnitude of the dipole depends on how the charge equilibration scheme splits the charges. Because of this dipole there is always an attractive force between surface and ion, which gives a spurious contribution to the free energy. It is advisable to run the metadynamics calculations with a charged simulation cell, so that no dipole is created when the Ca ion is removed from the surface.

7) There is also a lack of details about how many surfaces sites have been studied and how the procedure followed to prepare the initial C-A-S-H slab effect the morphology, bond order... a 25Å x 30Å sample is probably not quite representative of a macroscopic system and it would interesting to demonstrate the variability of the results shown here.

8) It is no clear how the "calculated" lines in figure 5e have been obtained. Even with all the caveats mentioned above, the simulations reported in this manuscript did not provide any information about the pre-exponential factor. Was that fitted? Estimated? Guessed?

9) What are the distributions reported in figure 4c and 4g meant to show? The histograms in Figure 4c are clearly not Gaussian distributions. Figure 4g is supposed to show the correlation between bond-order and bond length, so it would be more appropriate to have a trend line or something rather than distributions.

10) Typically, another important aspect of this cementitious materials is the hydroxylation of the surface. Does it play any role here? Should it be considered in the simulations given the experimental samples were prepared in highly caustic solutions?

11) What is the degree of crystallinity of the experimental samples? The simulation cells shown in the SI seem to be mostly crystalline. Maybe an amorphous sample would be a better representation of the surface morphology of the experimental samples. The authors should probably comment on this aspect.

Reviewer #3

(Remarks to the Author)

Yong et al. submitted a full article with the following topic "Understanding calcium-aluminosilicate-hydrate decalcification: The aluminum paradox". In the submitted article, they initially optimized the geometry through DFT computational approach and then used MD equilibration and energy minimization with reactive force field for computation of bulk and surface models of C-(A)-S-H. To understand the impact of Al incorporation, they compared two methods of introducing Al into the C-S-H molecular model with Ca/Si ratio of 1.25 (C1.25A0.2SH). They also linked molecular simulations and experimental observations by investigation of surface configurations. The submitted manuscript may proceed to publication after addressing the following major revision comments (failure to address similar issues in future submissions may result in rejection)!

1) In Fig. 1d, it is not obvious that the ionic bond Ca is saturating the oxygen bonded to two neighboring Si or Si and OH-? It must be shown properly easier for reader to understand! Moreover, it seems that Al has 4-fold coordination including two bonding with oxo bridging from neighboring Si, and two OH-, So since Al is 3+ and can have three ionic bonds with neighboring oxygen, therefore, how possible with four ionic bonds? What can compensate the fourth electron for Al to make 4-fold coordination? It must be something like Na+ from solution to the interlayer (as you mentioned from CASH synthesis from line 343), and it must be included into the calculation.

2) How geometry optimization by DFT implemented when this charge-balancing alkaline cation is not included?

3) Na NMR spectra must be carried to show precisely for samples after decalcification!

4) What is effect of pore solution? It must be discussed!

5) The manuscript includes a significant number of self-citations. While referencing one's own work is valid, it is essential to engage with and incorporate insights from the broader body of literature to ensure a comprehensive and balanced perspective.

6) As I earlier mentioned, the computational modeling mismatched with C-A-S-H synthesis with contribution of Na alkaline cation!

7) Which surface energy of tobermorite selected as the most representative according to low miller index facet for the atomistic mechanism and thermodynamics of CASH decalcification? Have you already computed by DFT and it is needed to add to the manuscript!

8) How did you choose the collective variable for metadynamic computation?

9) The NEB method has been used for Ca dissolution, is it according to DFT calculation as shown in Fig.3a-c? How did you select these intermediate pics for computation of transition state? The methods must be mentioned to make it clearer for reader in section 2! Moreover, FES is shown in figure 3d is also according to metadynamics calculation or DFT? It must be clear to readers!

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The author responded to my questions very well. I suggest accepting this manuscript.

Reviewer #2

(Remarks to the Author)

I've uploaded my comments as a review attachment.

Reviewer #3

(Remarks to the Author)

All the comments have been responded and also implemented in the manuscript properly, therefore, It can be accepted for publication in present form!

Version 2:

Reviewer comments:

Reviewer #4

(Remarks to the Author)

The current reply successfully addresses part of the reviewer's critique. The authors acknowledge the computational tradeoff between AIMD, ReaxFF, and classical MD, making it clear that practical resource limitations affect the level of precision achievable in metadynamics simulations. The authors also explain the rationale for using intermediate metadynamics parameters as a balance between accuracy and computational feasibility, situating ReaxFF between AIMD and classical MD in terms of timescale and sampling quality. In addition, the authors justify focusing on broad sampling across many Ca sites rather than devoting resources to achieve higher precision for a single site, arguing that the variability in dissolution free energies across numerous surface sites is more meaningful for your study than maximizing the accuracy of one calculation. There are several suggestions on data analysis that can be considered when revise the final version of this manuscript:

1. One other possibility is to do reweighting to obtain the metal-water CN information and the associated free energy. Although using the current meta dynamics data for reweighting could be tricky because the CN of metal is not directly biased. The outcome results could be used to compare with the additional simulations results shown in Fig. S12.
2. In Figure S7, the activation energy did not change over time. Will there be less crossing of the energy barrier over time? It seems the in Fig. S7b, the fluctuation of z is not as often as that of x and y over time, especially considering z need to change from 0 to 6 multiple times. Is the crossing of barriers less frequent over time so that the barrier is not properly sampled and appear to be constant? Could you plot the evolution of the 1D free energy profiles and compare the relative energy difference between two reference status?
3. "As shown in Figure S12, the free energy barrier (ΔA) calculated using this {CN_Ow/Oh, dist.z} CV set was higher than the barrier calculated using our original {dist.x, dist.y, dist.z} CV set. This finding indicates that constraining the reaction coordinate to a specific coordination number evolution (the {CN_Ow/Oh, dist.z} path) actually forces the system over an artificially high barrier."

The presence of a higher barrier by using a separate set of CV might imply the earlier energy barrier is underestimated. If the energy barrier from the previous simulation is always the highest value no matter how you change the CV, then it is more likely to conclude that the original choice of CV is appropriate.

Version 3:

Reviewer comments:

Reviewer #4

(Remarks to the Author)

The authors have extended their simulations to longer time scales, included 1D PFM plots to demonstrate profile convergence over time, and revised the text concerning changes in energy barriers. I have no further questions and look forward to seeing this work published soon.

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Responses to Reviewers' Comments

Understanding calcium-aluminosilicate-hydrate decalcification: The aluminium paradox

Yong Tao, Yining Gao, Mohammad Javad Abdolhosseini Qomi, Roland J.-M. Pellenq, Chi Sun Poon

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First and foremost, we would like to express our thanks and appreciation for the referees' reviewing work. Their comments and constructive suggestions are very helpful to further improve the quality of our manuscript. It has now been revised in accordance with the reviewers' comments and suggestions. The revised content in the manuscript is marked in **red**. The point-by-point responses to the reviewers' comments are as follows. The figures and tables used only in this response are numbered as Figure R1, Figure R2, ... Table R1, Table R2, ...

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Replies to Reviewer #1:

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Comment 1. *For the metadynamics simulation of Ca dissolution, the rationale for choosing Ca displacement components as the collective variables, rather than the water coordination number, needs clarification.*

Authors' Reply: Thank you for your valuable comment. We have added a detailed explanation in the revised Methods section to clarify the rationale behind our choice of collective variables (CVs).

We selected the x, y, and z displacement components of the Ca ion as CVs for two main reasons. First, this choice allows us to more accurately distinguish between the various states of the Ca ion during the dissolution process. In our previous studies on Ca dissolution in C-S-H and clinker, we observed that the dissolution pathway of the Ca ion is not a simple linear trajectory perpendicular to the surface. Instead, it follows a more complex, spiral-like path due to the asymmetry in the atomic arrangement of the mineral surface, a characteristic common to most cement minerals. Using only the water coordination number as a CV would fail to adequately differentiate certain intermediate states along this pathway.

Second, the water exchange rate constant of Ca ions in water is significantly higher ($>10^8 \text{ s}^{-1}$)

compared to that of Mg ions ($<10^6 \text{ s}^{-1}$)¹. This rapid exchange ensures that the water coordination number of the Ca ion adjusts automatically as its dissolution state changes. Therefore, it is unnecessary to use the water coordination number as a CV to enforce this adjustment. Additionally, our prior testing confirmed that using the three displacement components as CVs yields the most reasonable results, producing the lowest free energy estimates².

Revisions in manuscript (line 411-422):

The selection has two main reasons. First, the three displacement components allow us to more accurately distinguish between the various states of the Ca ion during the dissolution process. In our previous studies on Ca dissolution in C-S-H and clinker, we observed that the dissolution pathway of the Ca ion is not a simple linear trajectory perpendicular to the surface. Instead, it follows a more complex, spiral-like path due to the asymmetry in the atomic arrangement of the mineral surface, a characteristic common to most cement minerals. Using only the water coordination number as a CV would fail to adequately differentiate certain intermediate states along this pathway. Second, the water exchange rate constant of Ca ions in water is significantly higher ($>10^8 \text{ s}^{-1}$) compared to that of Mg ions ($<10^6 \text{ s}^{-1}$)¹. This rapid exchange ensures that the water coordination number of the Ca ion adjusts automatically as its dissolution state changes. Therefore, it is unnecessary to use the water coordination number as a CV to enforce this adjustment. Additionally, our prior testing confirmed that using the three displacement components as CVs yields the most reasonable results, producing the lowest free energy estimates².

Comment 2. The description of the Nudged Elastic Band method used to explore minimum free energy pathways in Fig. 3 is insufficient. The Methods section should include a detailed explanation of the NEB implementation for navigating the complex three-dimensional free energy landscape. This level of detail is essential for reproducibility.

Authors' Reply: Thank you for your valuable comment. We have added a detailed explanation of the NEB method in the revised Methods section to enhance clarity and reproducibility.

Revisions in manuscript (line 460-472):

Minimum free energy pathway.

The minimum free energy pathway for ion dissolution was explored from the three-dimensional free energy landscape obtained from metadynamics simulations using the NEB method^{3, 4}. Based on the three-dimensional free energy landscape, we identified important intermediate states, which correspond to local energy minima. Between each pair of adjacent minima, several intermediate images were inserted through linear interpolation with a step size of 0.15 Å to construct an initial Ca dissolution pathway. All the images, including the local minima, were then connected with elastic bands using a defined spring constant. The total force acting on each image, which combines contributions from the elastic band and the underlying free energy field, was calculated. This force serves as the driving force

for the optimization process. The images were adjusted iteratively to minimize the total energy of the system using the conjugate gradient algorithm. The optimization was considered complete when the energy difference between consecutive iterations fell below 10^{-4} kJ/mol and the displacement difference between images was less than 10^{-4} Å. For further details on the theoretical framework of the NEB method, we refer readers to Henkelman's papers ^{3, 4}.

Comment 3. *Please clarify whether Fig. 4a represents actual simulation trajectories or a schematic illustration of the process.*

Authors' Reply: Thank you for your comment. Figure 4a represents the C-A-S-H surface configuration obtained from a snapshot of the simulation trajectories. To avoid any ambiguity, we have clarified this in the revised figure caption.

Comment 4. *The connection between the calculated free energy and the experimental decalcification rates in Fig. 5e requires further explanation. It is difficult to understand how the fitting was conducted.*

Authors' Reply: We apologize for the unclear explanation in the original manuscript. In the revised version, we have provided a more detailed description of **Figure 5e** to address this concern.

As shown in the revised Figure 5e, the experimentally measured decalcification rates (k) of C-(A)-S-H at different temperatures (T) were fitted using the Arrhenius equation:

$$\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln k_0$$

where R is the gas constant, and E_a (activation energy) and $\ln k_0$ (a constant) are the fitting parameters. The dotted lines in **Figure 5e** represent the experimental fits, and their slopes ($-\frac{E_a}{R}$) reflect the experimentally determined activation energy for decalcification.

On the other hand, the solid lines in the figure represent Arrhenius-like functions defined as:

$$y = -\frac{A}{R} \frac{1}{T} + B$$

where A is the calculated decalcification free energy (mean values derived from panel d), and B is an adjusted constant.

As seen in **Figure 5e**, the slopes of the dashed lines (based on calculated free energy) closely match those of the dotted lines (based on experimental data). This agreement indicates that the calculated decalcification free energy provides a good prediction of the experimentally observed decalcification rates.

Revisions in manuscript (Figure 5e):

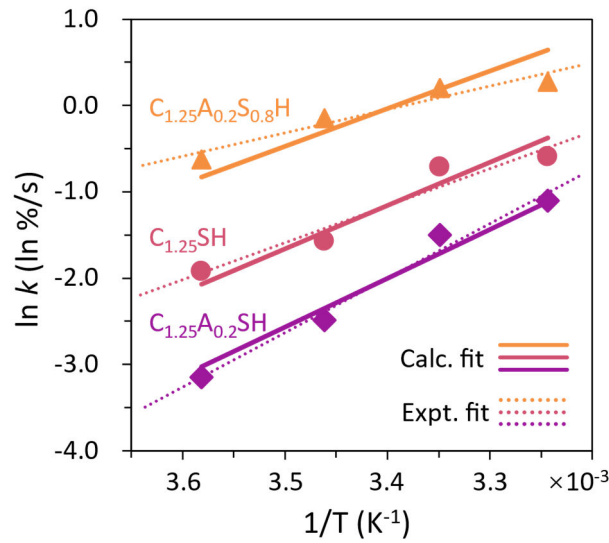


Figure 5e. The experimentally measured decalcification rates (k) of C-(A)-S-H at different temperatures (T) were fitted using the Arrhenius equation: $\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln k_0$, where R is the gas constant, and E_a (activation energy) and $\ln k_0$ (a constant) are the fitting parameters. The dotted lines represent the experimental fits with their slopes ($-\frac{E_a}{R}$) reflecting the experimentally determined activation energy for decalcification. The solid lines represent Arrhenius-like functions defined as: $y = -\frac{A}{R} \frac{1}{T} + B$, where A is the calculated decalcification free energy (mean values derived from panel **d**), and B is an adjusted constant.

Comment 5. The typical Ca/Si ratio of Portland cement pastes is 1.2~2.3 with a mean of ~1.7 (see Richardson CCR, 1999). While the chosen Ca/Si ratio of 1.25 for C-S-H here is reasonable, it would strengthen the study if the author could explain the reason for using this relatively low Ca/Si ratio.

Authors' Reply: Thank you for your insightful comment and suggestion. Indeed, the Ca/Si ratio of mature Portland cement paste typically ranges from 1.2 to 2.3, with a mean of ~1.7. However, when clinker in cementitious formulations is partially replaced by supplementary cementitious materials, the hydration products often exhibit lower Ca/Si ratios, accompanied by the incorporation of Al into the structure⁵. This scenario forms the context of our study. Additionally, C-S-H with a Ca/Si ratio of 1-1.5 is commonly employed as a reference system in studies investigating C-(A)-S-H^{6, 7, 8}. Therefore, the chosen Ca/Si ratio of 1.25 is representative of such systems and aligns well with the objectives of this study.

Revisions in manuscript (line 353-358):

The Ca/Si ratio of mature Portland cement paste typically ranges from 1.2 to 2.3, with a mean of ~1.75⁹. However, when clinker in cementitious formulations is partially replaced by supplementary cementitious materials, the hydration products often exhibit lower Ca/Si ratios, accompanied by the incorporation of Al into the structure⁵. This scenario forms the context of our study. Additionally, C-S-H with a Ca/Si ratio of 1.0 - 1.5 is commonly employed as a reference system in studies investigating C-(A)-S-H^{6, 7, 8}. Therefore, we chose Ca/Si ratio of 1.25 as representative of such systems.

Comment 6. *Typo on line 301. Incorrect subscript in “C1.25SH”.*

Authors’ Reply: Thank you for pointing out this typo. We have revised the subscript in "C_{1.25}SH".

Comment 7. *Comparison and explanation with existing MTD related simulations is critical. Such as: Nature communications, 2022, 13(1): 1253; Cement and Concrete Research, 2023, 165: 107092; Cement and Concrete Research, 2022, 156: 106767.*

Authors’ Reply: Thank you for this valuable suggestion. In the revised manuscript, we have incorporated discussions on the relevant works mentioned.

Comment 8. *The authors may consider including the constructed initial C-(A)-S-H crystal information in the supplementary material for future reference and use by other researchers.*

Authors’ Reply: Thank you for this valuable suggestion. We have included the constructed C-(A)-S-H structures in the Source Data.

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Replies to Reviewer #2:

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***Comment 1.** There is no mention of the length of the metadynamics simulations and no assessment that the free energy has actually converged. From a quick look at papers referenced here, this seems to also be the case in those articles (Refs 3, 31). Although it is true that the well-tempered metadynamics ensure convergence of the free energy by reducing the height of the gaussians, this is a necessary condition, but it is not sufficient to guarantee that the calculations are converged. In fact, one need to monitor the number of barrier recrossings events to show that both sides of the barrier are adequately sampled. A bias-factor of 20 is pretty large, hence very long simulation are required to converge the calculations. This is particularly critical for metadynamics simulations with 3 collective variables, which take a long time to converge.*

Authors' Reply: Thank you for your valuable and insightful comment. We acknowledge that the original manuscript did not provide sufficient convergence testing for the metadynamics simulations, and we appreciate the opportunity to address this important point. In the revised manuscript, we have conducted extensive convergence tests to refine the metadynamics parameters (see **Table R1**) and have recalculated all surface Ca site dissolution free energies accordingly. Below, we summarize our convergence testing process and results:

1. Bias factor testing:

The choice of the bias factor depends on the initial height of the Gaussian potentials. A larger initial height typically requires a smaller bias factor to ensure rapid decay of the Gaussian height, and vice versa. In our study, we set the initial Gaussian height to **1.5 kJ/mol**, which is smaller than the **2.5 kJ/mol** used in prior studies¹⁰. Therefore, a slightly larger bias factor is reasonable. To test this, we compared the free energy calculations using bias factors of 10, 15, and 20, as shown in **Figure S6**. The dissolution process of a Ca ion involves three key states: surface-adsorbed state (S1), inner-sphere adsorbed state (S2), and dissolved state (S3). As expected, increasing the bias factor reduces the simulation time required for the Ca ion to reach the dissolved state. However, the overall dissolution free energies (~30 kJ/mol) are similar across the tested bias factors, although a bias factor of 10 resulted in insufficient sampling at S2 and S3 states within the tested simulation time (25 ns), leading to higher free energy estimates. To balance convergence and computational efficiency, we selected a bias factor of **15**.

2. Simulation time testing:

Figure S7 demonstrates the evolution of metadynamics results with simulation time using the refined parameters in **Table R1**.

In **Figure S7a**, the white dashed line indicates the Ca dissolution pathway identified via the Nudged Elastic Band method. The labels R, P, and TS_{max} represent the reactant (initial surface state), the product (fully dissolved state), and the highest-energy transition state, respectively.

The overall dissolution free energy barrier (ΔA) is calculated as the energy difference between the lowest-energy state and $TS_{\max}$ along the Ca dissolution pathway.

In **Figure S7b**, the collective variables (CVs: x, y, z directional displacement components) show multiple back-and-forth crossings between the surface and solution, confirming adequate sampling of both sides of the barrier. After ~ 10 ns, the free energy near the surface no longer changes significantly, indicating that sampling is sufficient. Although extending the simulation time further could allow for more complete sampling of the solution space, the overall dissolution free energy barrier remains unaffected. Therefore, a simulation time of 15 ns is reasonable for the tested Ca ion site. Overall, for multiple surface Ca sites, the simulation times were determined as **15-30 ns** because Ca sites with higher dissolution free energies require longer metadynamics simulations to dissolve.

3. We would like to share our thoughts about the metadynamics simulations on mineral dissolution:

The total simulation time depends on the metadynamics parameters and the sampling space. While we fully agree that using highly precise parameters and long simulation times usually would yield more accurate results, computational resources often impose practical limitations (**Figure R1**). For instance, classical MD simulations can typically achieve hundreds of nanoseconds of sampling, while ab initio MD (AIMD) simulations are often limited to <1 ns due to their computational cost. Therefore, the parameters of AIMD-based metadynamics are rougher than those of classical MD-based metadynamics, although this will lead to the deterioration of the convergence of the former's calculation results. However, since the accuracy and universality of atomic potential adopted by AIMD is much higher than that of fitted classical force field, AIMD-based metadynamics has its advantages and existence value. In our study, we used ReaxFF-based simulations, which fall between AIMD and classical MD in terms of timescale. Therefore, the precision of our metadynamics parameters is also intermediate between those used in AIMD and classical MD.

This study primarily investigates the impact of surface structures on C-(A)-S-H decalcification thermodynamics. To achieve this, we aimed to sample a large number of surface sites to better represent the dissolution characteristics of amorphous C-(A)-S-H. While higher precision for a single Ca ion site could be achieved by focusing computational resources on one site, the decalcification characteristics of amorphous C-(A)-S-H are better captured by averaging data across a large number of Ca sites. As shown in **Figure 5**, the dissolution free energies for different Ca sites vary significantly, and the differences due to sampling precision for a single site are relatively negligible by comparison. Given that our three C-(A)-S-H models include over 90 surface Ca sites to consider, the refined metadynamics parameters provided in **Table R1** represent the most feasible balance between accuracy and computational cost.

Setting up Verlet run ...

Unit style : real

Current step : 0

Time step : 1

CSH-FF

Per MPI rank memory allocation (min/avg/max) = 55.9 | 55.98 | 56.19 Mbytes

Step	Temp	PotEng	KinEng	TotEng	Press
0	300	-533205.35	6739.9096	-526465.44	8855.7936
5000	298.71679	-536626.53	6711.0806	-529915.45	-781.77601
10000	302.82417	-536560.07	6803.3585	-529756.71	-429.74902
15000	302.47042	-536445.31	6795.4109	-529649.9	-104.96386
20000	303.97315	-536553.26	6829.1718	-529724.08	448.78684
25000	301.34128	-536531.8	6770.0433	-529761.76	-579.64256
30000	298.83022	-536352.59	6713.6288	-529638.96	-432.42943
35000	301.65813	-536373.32	6777.1617	-529596.15	-1423.2495
40000	297.98829	-536621.37	6694.7137	-529926.65	-317.47433
45000	296.55724	-536463.44	6662.5633	-529800.88	1260.2172
50000	301.89564	-536628.94	6782.4978	-529846.44	-22.222381

Loop time of 410.037 on 56 procs for 50000 steps with 7538 atoms

Performance: 10.536 ns/day, 2.278 hours/ns, 121.940 timesteps/s, 919.185 katom-step/s
98.9% CPU use with 56 MPI tasks x 1 OpenMP threads

Setting up Verlet run ...

Unit style : real

Current step : 0

Time step : 0.2

ReaxFF

Per MPI rank memory allocation (min/avg/max) = 110.4 | 112.6 | 115.2 Mbytes

Step	Temp	PotEng	KinEng	TotEng	Press
0	300	-759695.28	6739.9096	-752955.37	306670.55
5000	304.099	-792896.95	6831.9991	-786064.95	-312.78417
10000	299.82466	-793265.57	6735.9702	-786529.6	3530.6225
15000	300.80859	-793351.52	6758.0758	-786593.44	-1967.4335
20000	301.40183	-793433.52	6771.4036	-786662.12	-1724.8357
25000	306.17387	-793667.09	6878.614	-786788.48	706.49695
30000	302.60598	-793581.95	6798.4565	-786783.5	-352.45107
35000	299.29453	-793620.56	6724.0603	-786896.5	-50.472955
40000	300.40476	-793768.36	6749.0031	-787019.36	-60.756155
45000	302.10037	-793567.41	6787.0973	-786780.32	-1305.5851
50000	303.91285	-793733.24	6827.8172	-786905.43	-1352.9761

Loop time of 1736.11 on 56 procs for 50000 steps with 7538 atoms

Performance: 0.498 ns/day, 48.225 hours/ns, 28.800 timesteps/s, 217.094 katom-step/s
99.2% CPU use with 56 MPI tasks x 1 OpenMP threads

Figure R1. Comparison of the simulation efficiency of classical force field CSH-FF and reactive force field ReaxFF. The testing model, a C-S-H slab model filling with water with a total number of atoms of 7538, was simulated on a 56-core CPU. The ReaxFF simulation is only 4.7% of the efficiency of the CSH-FF simulation.

Table R1. Comparison of the original and refined parameters for metadynamics simulations.

parameters	original	refined
Gaussian width	0.1 Å	0.1 Å
Gaussian initial height	1.5 kJ/mol	1.5 kJ/mol
Gaussian deposition pace	every 200 steps	every 600 steps
Bias factor	20	15
sampling region	8Å × 8Å × 9Å, cuboid	r=2.8Å, h=7Å, cylinder
simulation time	4 ~ 8 ns	15 ~ 30 ns

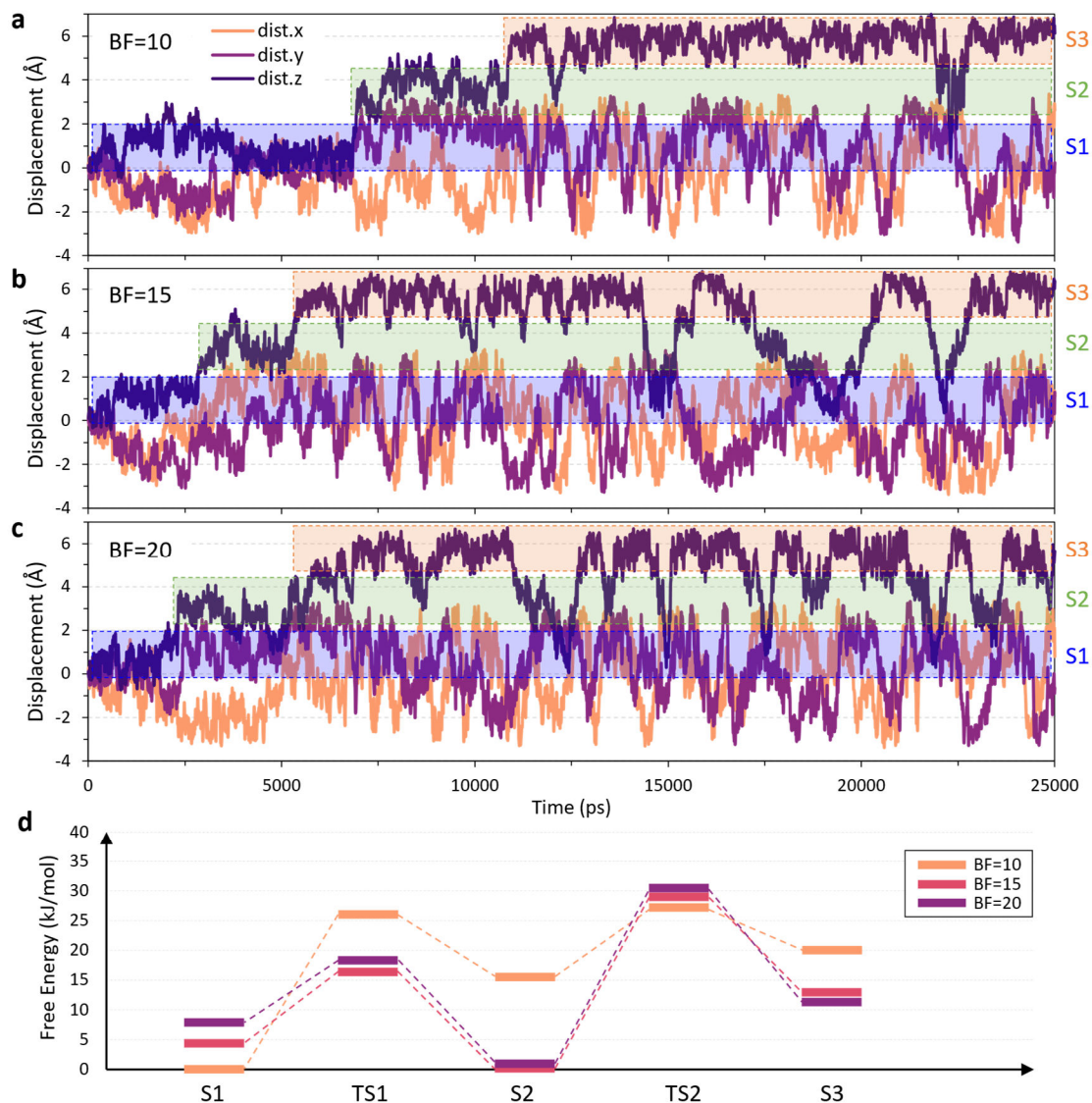


Figure S6. Tests of the bias factor for well-tempered metadynamics. **a-c**, The evolution of collective variables (dissolution displacement components in x, y, and z directions: dist.x, dist.y, and dist.z) for well-tempered metadynamics simulations using bias factors (BF) of 10, 15, and 20 respectively. The width, initial height, and deposition pace of Gaussian penalty potentials are 0.1 Å, 1.5 kJ/mol, and every 600 steps respectively. Three distinct states of calcium ions are observed during the dissolution process: initial surface-adsorbed state (S1), inner-sphere adsorbed state (S2), and fully dissolved state (S3). **d**, The calculated dissolution free energy barriers from S1 to S3.

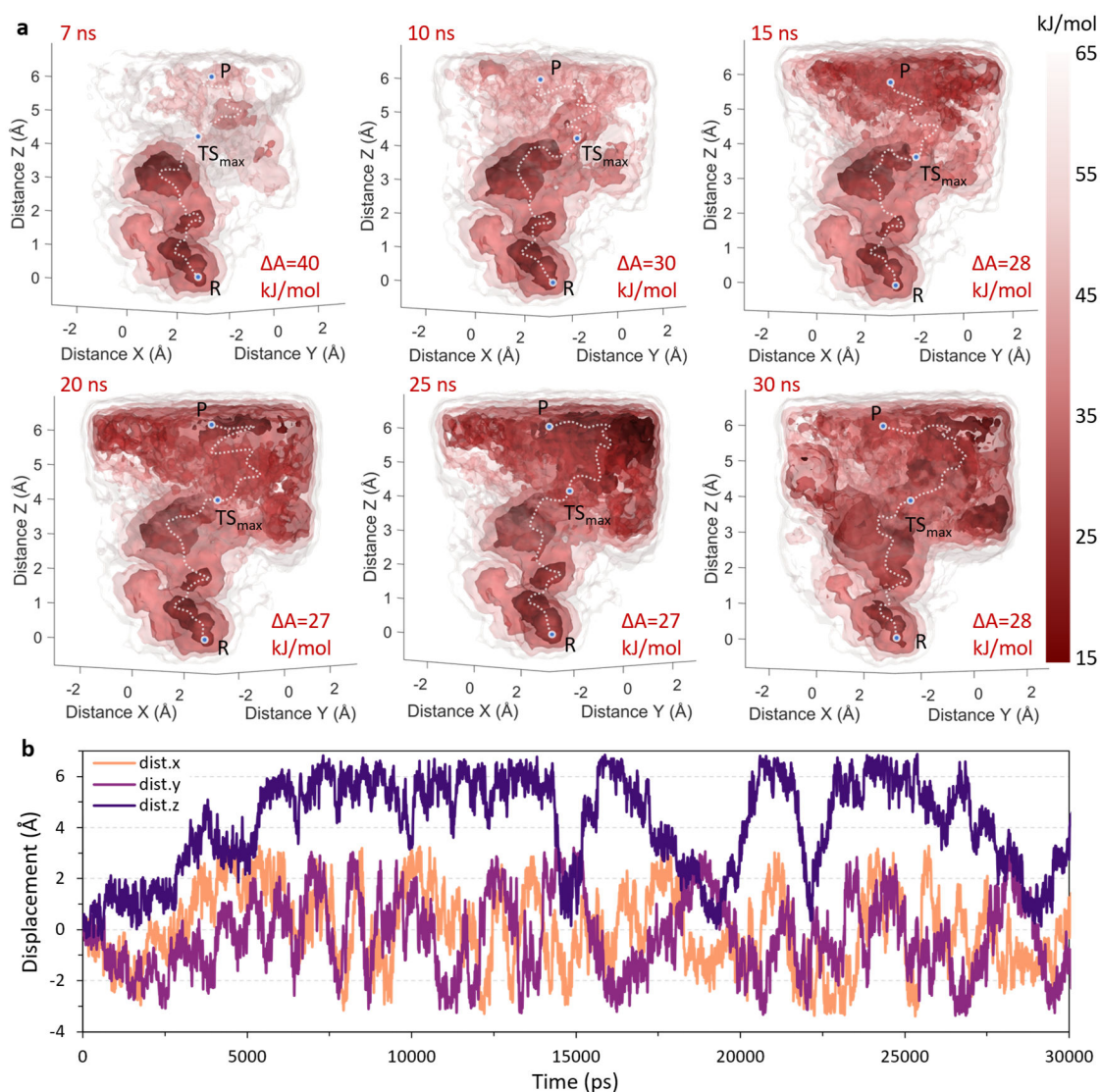


Figure S7. Tests of simulation time for well-tempered metadynamics. **a**, The evolution of the three-dimensional free energy landscape of calcium dissolution with simulation time. The white dashed line indicates the Ca dissolution pathway identified via the Nudged Elastic Band method. The labels R, P, and TS_{max} represent the reactant (initial surface state), the product (fully dissolved state), and the highest-energy transition state, respectively. The overall dissolution free energy barrier (ΔA) is calculated as the energy difference between the lowest-energy state and TS_{max} along the Ca dissolution pathway. **b**, The evolution of collective variables (dissolution displacement components in x, y, and z directions: dist.x, dist.y, and dist.z) with simulation time. For these well-tempered metadynamics tests, the width, initial height and deposition pace of Gaussian penalty potentials, and bias factor are 0.1 Å, 1.5 kJ/mol, every 600 steps, and 15 respectively.

Revisions in manuscript (line 423-445):

The total simulation time depends on the metadynamics parameters and the sampling space. While we acknowledge that using highly precise parameters and long simulation times usually would yield more accurate results, computational resources often impose practical limitations. For instance, classical MD simulations can typically achieve hundreds of nanoseconds of sampling^{11, 12, 13}, while ab initio MD (AIMD) simulations are often limited to < 1 ns due to their computational cost^{14, 15}. Therefore, the parameters of AIMD-based metadynamics are rougher than those of classical MD-based metadynamics, although this will lead to the deterioration of the convergence of the former's calculation results. However, since the accuracy and universality of atomic potential adopted by AIMD is much higher than

that of fitted classical force field, AIMD-based metadynamics has its advantages and existence value. In this study, we used reactive force field simulations, which fall between AIMD and classical MD in terms of timescale. Therefore, the precision of our metadynamics parameters is also intermediate between those used in AIMD and classical MD. More importantly, this study primarily investigates the impact of surface structures on C-(A)-S-H decalcification thermodynamics. To achieve this, we aimed to sample a large number of surface sites to better represent the dissolution characteristics of amorphous C-(A)-S-H. While higher precision for a single Ca ion site could be achieved by focusing computational resources on one site, the decalcification characteristics of amorphous C-(A)-S-H are better captured by averaging data across a large number of Ca sites. As shown in **Figure 5**, the dissolution free energies for different Ca sites vary significantly, and the differences due to sampling precision for a single site are relatively negligible by comparison. Given that our three C-(A)-S-H models include over 90 surface Ca sites to consider, we conducted extensive tests (**Figures S6, S7, S9**) on metadynamics parameters to seek the most feasible balance between accuracy and computational cost. Based on the tests, Gaussian bias potentials with a width of 0.1 Å and an initial height of 1.5 kJ/mol were deposited every 600 MD steps, coupling with a bias factor of 15 to dynamically adjust the height of the Gaussian potentials. For multiple surface Ca sites, the simulation times were determined as 15 - 30 ns because Ca sites with higher dissolution free energies require longer metadynamics simulations to dissolve.

Comment 2. *Moreover, it is very important that the reactant (adsorbed Ca) and product (Ca in solution) states don't change throughout the simulation to ensure that after each barrier crossing the same states are sampled. It is also important that the recrossing happens along the same pathway so that the corresponding barrier is explored.*

While it may be trivial to show that the Ca in solution is always in the same state, this may not be the case for the C-A-S-H surface where the atoms may significantly rearrange after the Ca has been removed. If this is the case, the free energies calculated here probably have very large errors, that cannot be quantified. It would be revealing to repeat the same metadynamics calculation for one site a number of times using different starting condition, which also include starting from the Ca in solution, to demonstrate the variability of the each data point.

Authors' Reply: Thank you for your insightful comment. We fully agree that revisiting the initial states and ensuring consistency in the sampled states is an important criterion for assessing the convergence and reliability of free energy calculations. Below, we address your concerns and provide additional testing to support the robustness of our results:

1. In our simulations, we observed that the C-(A)-S-H surface structure remained relatively stable during the simulation, even after the complete dissolution of a Ca ion. This is because C-(A)-S-H is a mineral with low solubility, and its surface atoms are relatively stable over short simulation times. As shown in **Figure S7b**, the CVs dist.x, dist.y, and dist.z (displacements in the x, y, and z directions) indicate that, after dissolution, the Ca ion revisits the initial position (dist.x=0, dist.y=0, dist.z=0) region multiple times. This suggests that the local surface environment near the Ca ion remains accessible and does not undergo significant rearrangement.

2. To further validate the convergence of our metadynamics calculations, we conducted additional tests starting from different initial configurations along the dissolution pathway. As shown in **Figure S8**, we released the Ca ion from three distinct positions along the dissolution pathway: **S1**: The surface-adsorbed state (initial position). **S2**: The inner-sphere adsorbed state. **S3**: The fully dissolved state. In all three cases, the Ca ion successfully sampled all three states (S1, S2, S3), and the overall dissolution free energy barriers (TS2) were found to be similar across the different starting configurations.

The concern you raised highlights an important point about the balance between simulation time and the stability of the studied system. While longer simulation times can improve sampling, they may also lead to undesirable changes in the system, such as significant rearrangement of the surface structure. For example, in systems with unstable initial configurations, long simulations might result in alterations to the phase space (e.g., significant surface restructuring), making the original reactant state inaccessible. Artificially constraining the initial structure (e.g., restricting the movement of atoms near the initial configuration) could prevent such rearrangements, but this would compromise the realism of the simulated reaction process. Therefore, the simulation time of metadynamics is not simply the longer the better, but must be carefully tailored to the specific system being studied.

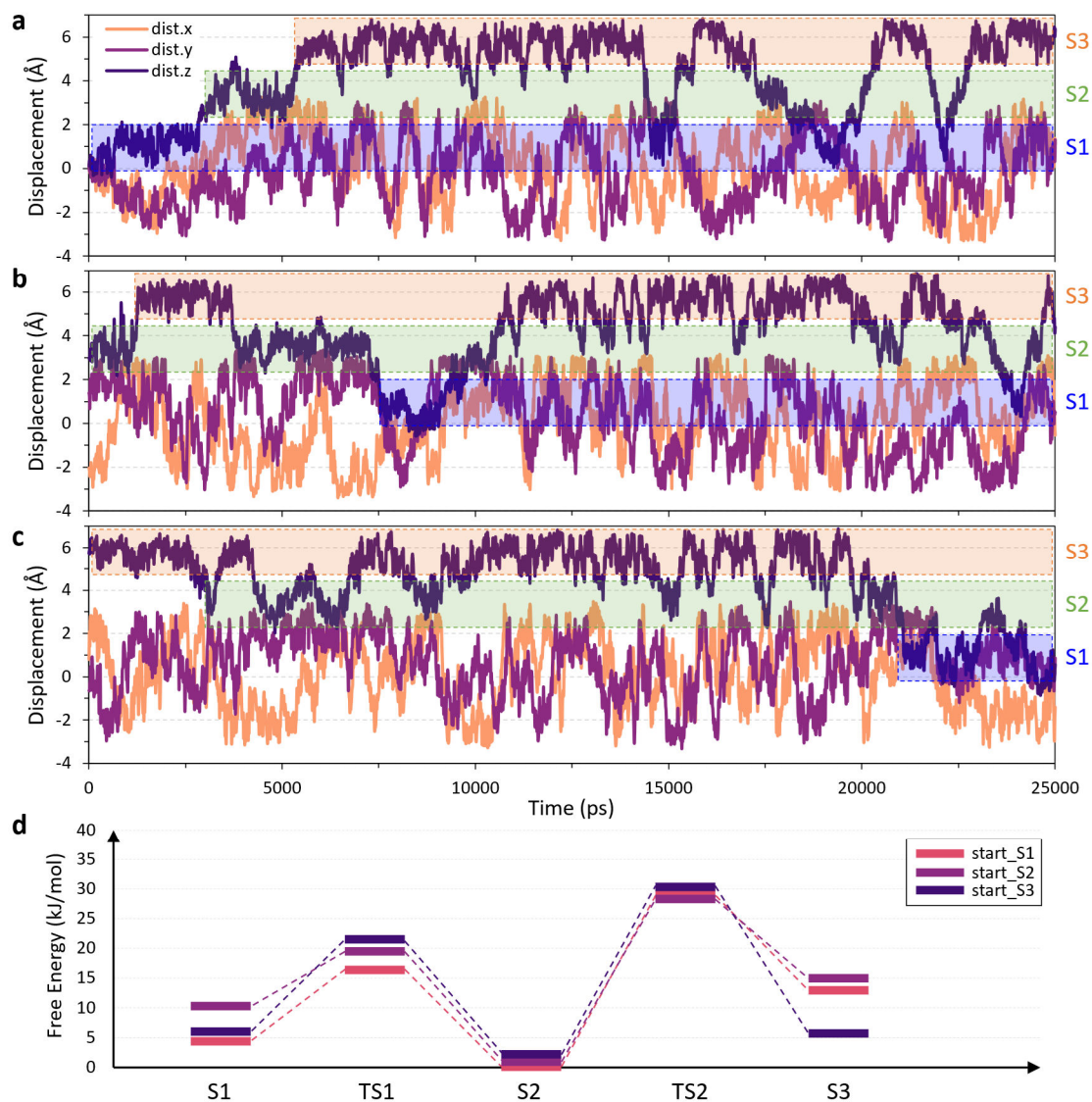


Figure S8. Tests of different starting points along the dissolution pathway for well-tempered metadynamics. **a-c**, The evolution of collective variables (dissolution displacement components in x, y, and z directions: dist.x, dist.y, and dist.z) with simulation time. **d**, Calcium dissolution energetics encompassing all intermediate states (S1-3) and transition states (TS1-2). The total dissolution free energy barriers (ΔA) are the free energy differences between the lowest-energy intermediate state and the highest-energy TS along the dissolution pathway. We released the Ca ion from three distinct positions along the dissolution pathway: S1: The surface-adsorbed state (initial position). S2: The inner-sphere adsorbed state. S3: The fully dissolved state. For these well-tempered metadynamics tests, the width, initial height and deposition pace of Gaussian penalty potentials, and bias factor are 0.1 Å, 1.5 kJ/mol, every 600 steps, and 15 respectively.

Revisions in manuscript (line 455-459):

To evaluate the convergence of metadynamics calculations, we conducted tests starting from different initial states along the Ca dissolution pathway including 1) the surface-adsorbed state (initial position); 2) the inner-sphere adsorbed state; and 3) the fully dissolved state (**Figure S8**). In all three cases, the Ca ion successfully sampled all three states, and the overall dissolution free energy barriers were found to be similar across the different starting configurations.

Comment 3. The Gaussians' deposition rate is very fast 40fs, the system would have no chance of relaxing to the new equilibrium state. Although this a common practice for ab-initio MD simulations, it makes the results very unreliable. A deposition rate in the range 1-2ps would be more appropriate for classical MD simulations.

Authors' Reply: Thank you for your insightful comment. We agree that a fast Gaussian deposition pace can potentially prevent the system from fully relaxing to equilibrium after each bias is applied, which could impact the accuracy of the results. Below, we address this concern and explain the rationale for our choice of deposition pace, as well as the tests we performed to ensure the reliability of our results.

The deposition pace in metadynamics is a critical parameter that directly affects the total simulation time and the system's ability to relax between Gaussian depositions. The optimal pace depends on the simulation method used. AIMD simulations typically use a very high deposition pace (e.g., adding Gaussians every few tens of steps) because the total simulation time is often limited to less than 1 ns due to computational constraints. Classical MD simulations can afford much longer total simulation times (e.g., >100 ns), allowing for lower deposition paces (e.g., adding Gaussians every 1000 steps). Our simulations use ReaxFF MD, which falls between AIMD and classical MD in terms of computational efficiency and achievable simulation times. Therefore, in our revised simulations, we selected an intermediate deposition pace of adding Gaussians every 600 steps to balance computational efficiency and the system's relaxation time.

We also want to emphasize that the deposition pace should be evaluated in terms of the number of simulation steps rather than absolute simulation time. This is because the timestep size determines how much the system evolves in each step. In our ReaxFF MD simulations, the timestep is 0.2 fs, meaning that each step induces only 20% of the relative perturbation caused by a classical MD step where the timestep is typically 1 fs. Consequently, the system requires less time to relax after each Gaussian deposition. Thus, the deposition pace of 600 steps in our ReaxFF MD simulations is comparable to the deposition pace commonly used in classical MD (e.g., 100-1000 steps)^{11, 12, 13}.

To evaluate the impact of deposition pace on the accuracy and convergence of our results, we tested metadynamics calculations using deposition paces of 400 steps, 600 steps, and 800 steps as shown in **Figure S9**. As expected, decreasing the deposition pace significantly increased the simulation time required for the Ca ion to dissolve. The overall free energy barriers calculated using the three deposition paces were similar, except that the 400-step pace was slightly higher. Given that our study involves metadynamics calculations for over 90 Ca ion sites, it is essential to balance computational efficiency with accuracy. Based on the testing results, we therefore chose a deposition pace of 600 steps.

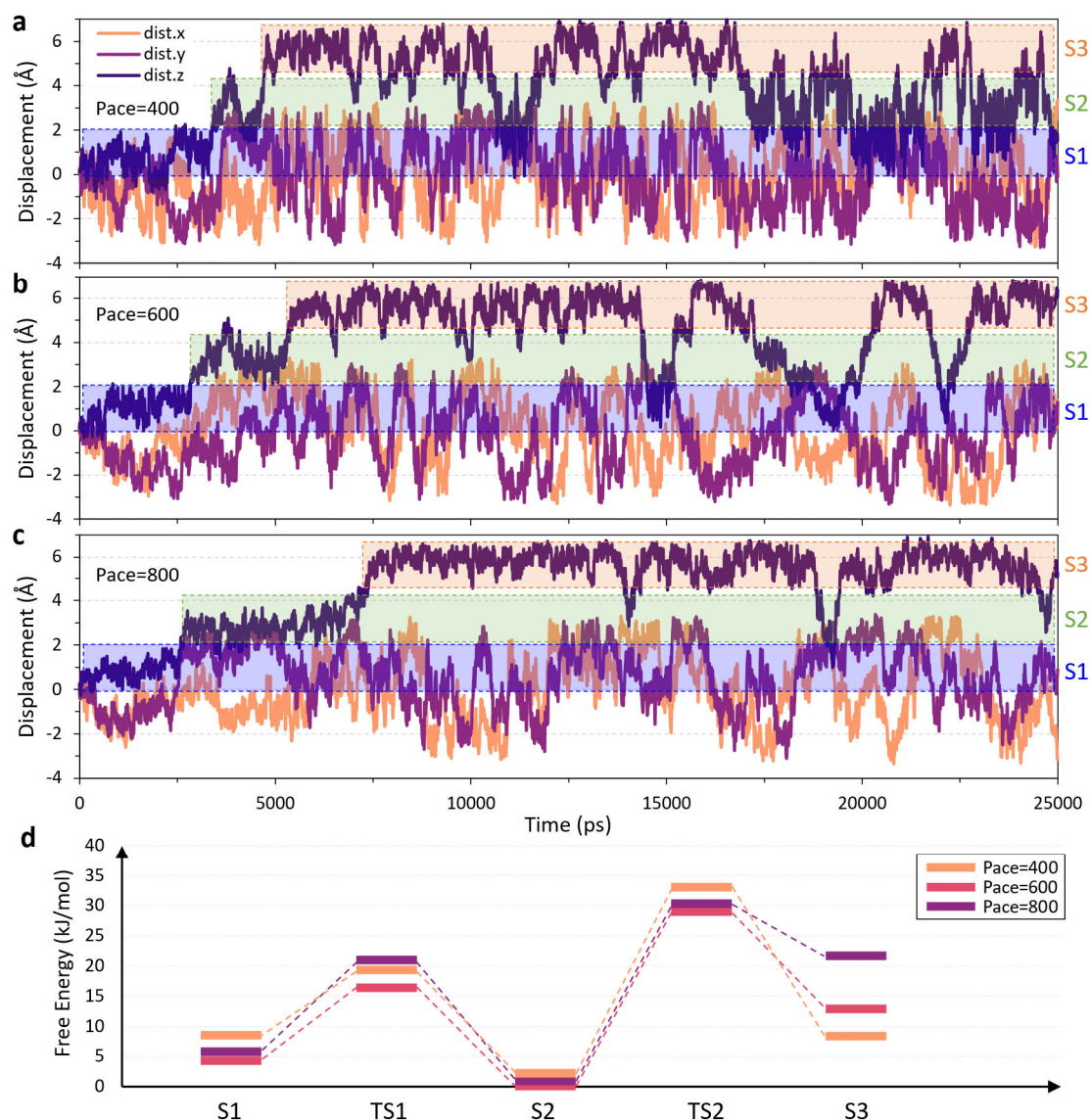


Figure S9. Tests of Gaussian deposition rates for well-tempered metadynamics. a-c, The evolution of collective variables (dissolution displacement components in x, y, and z directions: dist.x, dist.y, and dist.z) with simulation time using different Gaussian deposition paces (every 400, 600, and 800 steps). **d,** Calcium dissolution energetics encompassing all intermediate states (S1-3) and transition states (TS1-2). The total dissolution free energy barriers (ΔA) are the free energy differences between the lowest-energy intermediate state and the highest-energy TS along the dissolution pathway. For these well-tempered metadynamics tests, the width and initial height of Gaussian penalty potentials, and bias factor are 0.1 Å, 1.5 kJ/mol, and 15 respectively.

Revisions in manuscript (line 423-445):

The total simulation time depends on the metadynamics parameters and the sampling space. While we acknowledge that using highly precise parameters and long simulation times usually would yield more accurate results, computational resources often impose practical limitations. For instance, classical MD simulations can typically achieve hundreds of nanoseconds of sampling^{11, 12, 13}, while ab initio MD (AIMD) simulations are often limited to < 1 ns due to their computational cost^{14, 15}. Therefore, the parameters of AIMD-based metadynamics are rougher than those of classical MD-based metadynamics, although this will lead to the deterioration of the convergence of the former's calculation results. However, since the accuracy and universality of atomic potential adopted by AIMD is much higher than that of fitted classical force field, AIMD-based metadynamics has its advantages and existence value.

In this study, we used reactive force field simulations, which fall between AIMD and classical MD in terms of timescale. Therefore, the precision of our metadynamics parameters is also intermediate between those used in AIMD and classical MD. More importantly, this study primarily investigates the impact of surface structures on C-(A)-S-H decalcification thermodynamics. To achieve this, we aimed to sample a large number of surface sites to better represent the dissolution characteristics of amorphous C-(A)-S-H. While higher precision for a single Ca ion site could be achieved by focusing computational resources on one site, the decalcification characteristics of amorphous C-(A)-S-H are better captured by averaging data across a large number of Ca sites. As shown in **Figure 5**, the dissolution free energies for different Ca sites vary significantly, and the differences due to sampling precision for a single site are relatively negligible by comparison. Given that our three C-(A)-S-H models include over 90 surface Ca sites to consider, we conducted extensive tests (**Figures S6, S7, S9**) on metadynamics parameters to seek the most feasible balance between accuracy and computational cost. Based on the tests, Gaussian bias potentials with a width of 0.1 Å and an initial height of 1.5 kJ/mol were deposited every 600 MD steps, coupling with a bias factor of 15 to dynamically adjust the height of the Gaussian potentials. For multiple surface Ca sites, the simulation times were determined as 15 - 30 ns because Ca sites with higher dissolution free energies require longer metadynamics simulations to dissolve.

Comment 4. *The box restraint used here has a fairly large base (8Å), which likely include several surface states. This means that, during the metadynamics simulations, when the Ca returns towards the surface it may experience different environments than the one where it started from. All these states have the same z-value but correspond to very different surface states, which may make the post-processing quite confusing.*

Authors' Reply: Thank you for this insightful comment. We agree that a large sampling space can lead to the Ca ion exploring multiple surface states when returning to the surface, potentially complicating the post-processing and reducing the efficiency of the metadynamics simulations. To address this issue, we performed additional tests to refine the sampling space, as described below.

To minimize interference from multiple surface states while ensuring that the natural dissolution pathway of the Ca ion is preserved, we revised the sampling space to a cylindrical restraint with a radius of **2.8 Å** and a height of **7 Å**. The radius of the sampling space was determined based on the structural features of the C-(A)-S-H surface (see **Figure S10a**). This radius is small enough to limit the Ca ion's interaction with other surface states, yet large enough to allow the Ca ion to explore its natural dissolution pathway without artificial constraints.

We tested sampling spaces with radii of 2 Å, 2.8 Å, and 4 Å. The free energy profiles for these cases are shown in **Figure S10b-d**. For radius = 4 Å (**Figure S10d**), While the forward dissolution pathway (from surface to solution) was not significantly affected, the Ca ion frequently revisited other surface states when returning to the surface. This behavior reduced the convergence efficiency of the metadynamics simulations and introduced ambiguity in the post-processing. For radius = 2 Å (**Figure S10b**), restricting the sampling space to a smaller radius excluded an important intermediate state near coordinates (-2.2, 1.3, 3.0), which was

observed in the larger sampling spaces (**Figure S10c, d**). This exclusion led to an artificially higher free energy barrier for Ca dissolution, indicating that a 2 Å radius was overly restrictive and interfered with the natural dissolution pathway. Based on these results, we selected a radius of **2.8 Å** as the optimal sampling space and recalculated the dissolution free energies for all surface Ca ions.

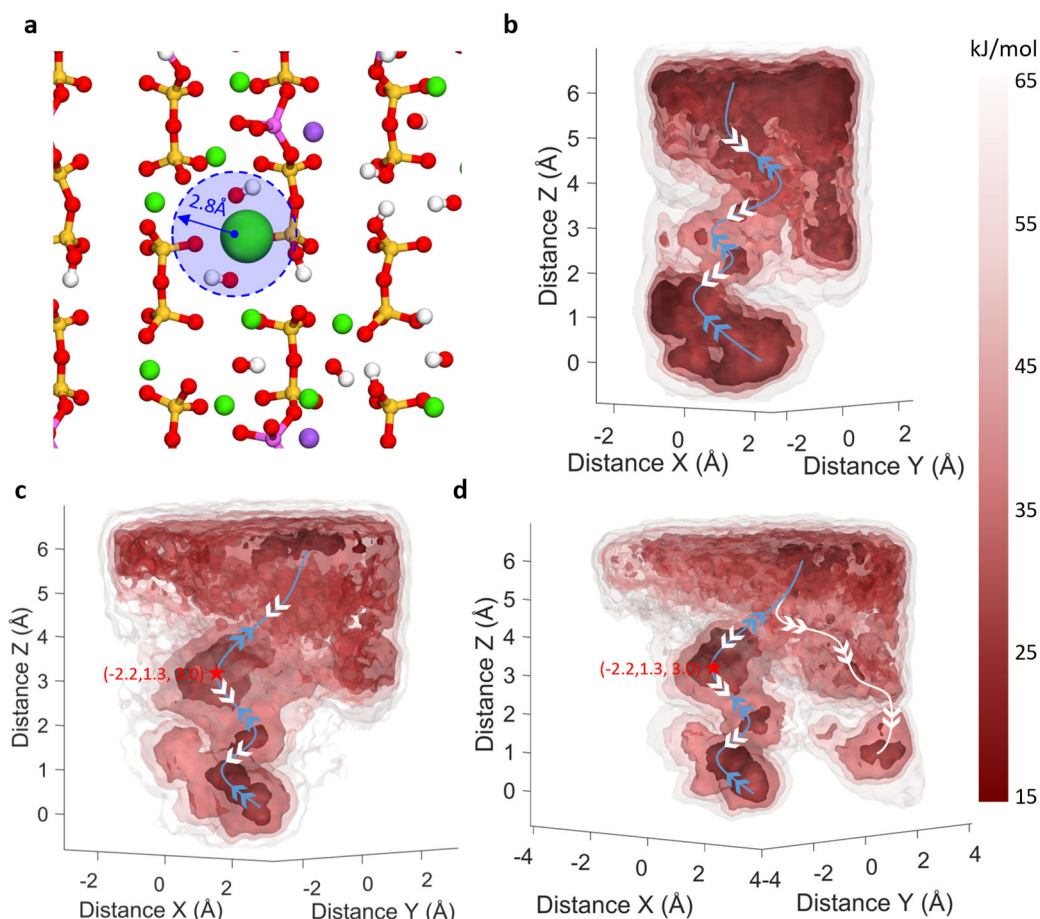


Figure S10. Tests of sampling space size for well-tempered metadynamics. **a**, C-A-S-H surface structures using $\text{C}_{1.25}\text{A}_{0.2}\text{S}_{0.8}\text{H}$ as an example. The yellow, red, white, pink, purple, green spheres are Si, O, H, Al, Na, and Ca ions respectively. Water molecules and free hydroxyl groups are partly hidden for clarity. **b-d**, The calculated three-dimensional free energy landscape of calcium dissolution using confined sampling spaces with radii of 2 Å, 2.8 Å, and 4 Å respectively. The blue arrows indicate the forward dissolution pathway (from surface to solution) while the white arrows indicate the backward pathway (from solution to surface). For these well-tempered metadynamics tests, the width, initial height and deposition pace of Gaussian penalty potentials, and bias factor are 0.1 Å, 1.5 kJ/mol, every 600 steps, and 15 respectively.

Revisions in manuscript (line 446-454):

Since we are sampling a three-dimensional phase space, the dissolved Ca ion may explore multiple surface states when returning to the surface, potentially complicating the post-processing and reducing the efficiency of the metadynamics simulations. To minimize interference from multiple surface states while ensuring that the natural dissolution pathway of the Ca ion is preserved, we confined the sampling space to a cylindrical region with a radius of 2.8 Å in x-y plane and a height of 7 Å in z direction using quadratic walls with a strength of 150 kJ/mol. The radius of the sampling space was determined based on the structural features of the C-(A)-S-H surface (see **Figure S10a**). Our simulation tests (**Figures S10b-d**) showed that this radius is small enough to limit the Ca ion's interaction with other surface

states, yet large enough to allow the Ca ion to explore its natural dissolution pathway without artificial constraints.

Comment 5. *The Authors have mis-interpreted what is reported in the paper by Silvestri et al. (Ref 55). Silvestri et al. did not propose a method to increase the efficiency of the calculations, but they suggested a protocol to ensure that the calculated free adsorption/desorption free energy were accurate and, more importantly, referenced to standard conditions, as the experiment should be. In fact, they argue against using a box restraint, as Tao and coworkers are doing here, because that would make the result dependent on the box size and on how much volume of the unbound state is explored. Which in turns makes the reference state of the free energy calculation ill-defined. Silvestri et al. propose to use a linear cylindrical restraint to ensure that the volume of the bound and unbound states are well-defined, which means it is possible to know what the reference state of the calculation is. The free energies contributions to add and remove the restraints also need to be computed. The procedure proposed by Silvestri et al. is designed only to give accurate free energy differences between the adsorbed and desorbed states, not to be efficient.*

Authors' Reply: Thank you for your comment and for pointing out our misinterpretation of the work by Silvestri et al. We sincerely apologize for the misunderstanding in the original manuscript and have carefully revisited their work to clarify its relevance and implications for our study. Below, we address the distinctions between the approach of Silvestri et al. and the methods employed in our research, as well as the rationale behind our chosen methodology.

As highlighted, Silvestri et al. proposed a rigorous protocol for accurately calculating adsorption/desorption free energies under **standard conditions**, using a cylindrical restraint with a radius of zero. Their approach ensured the volumes of both the bound and unbound states were clearly defined, making it possible to compute **standard free energy differences** comparable to experimental values, such as solubility or equilibrium constants. In addition, by restricting the ion's pathway to a linear cylindrical restraint, they avoided sampling other surface sites, enabling convergence of detachment/attachment free energies with minimal bias.

In contrast, the goals and focus of our study differ significantly from those of Silvestri et al. Our primary objective is to calculate the **activation free energy barriers** for the dissolution of Ca ions from the C-(A)-S-H surface. These barriers represent **non-equilibrium properties**, such as the energy required to transition through the rate-limiting step of the dissolution process, rather than the standard free energy of dissolution.

As we know, fully sampling the reverse process of ion dissolution (ion reattachment to the surface) requires extended simulation times due to the large configurational space in solution. Thus, achieving convergence for the backward (reattachment) process is computationally prohibitive. While Silvestri et al.'s cylindrical restraint (radius = 0) effectively accelerates the convergence of detachment/attachment free energies, it enforces an artificial linear pathway for ion dissolution. However, as their results showed, a linear pathway may not reflect the true

dissolution mechanism. When the spring strength of their restraint was reduced, the dissolution free energy barrier decreased, indicating that the natural pathway is not linear. Therefore, in our study, we use a cylindrical restraint with a radius of 2.8 Å, selected based on the structural characteristics of the C-(A)-S-H surface, to balance computational efficiency and physical realism.

Comment 6. *As mentioned in the 2012 ReaxFF paper where the forcefield used here was first reported, in the method there are no constraints on the atomic charges, which are calculated at every time step using a charge equilibration scheme. While this may not be trivial to extract from the simulations, it has been reported that the Calcium ion often doesn't have a +2 charge in solution, but some smaller fractional value. If this is the case it may have profound consequences on the results shown here, particularly if in each metadynamics simulation the Ca ion has a different charge in solution, which would imply that the solvation free energy of the ion would be different in different simulations. Another consequence of this is that when the Ca ion leave the surface there is a dipole created in the system (negative surface – Ca ion in solution) and the magnitude of the dipole depends on how the charge equilibration scheme splits the charges. Because of this dipole there is always an attractive force between surface and ion, which gives a spurious contribution to the free energy. It is advisable to run the metadynamics calculations with a charged simulation cell, so that no dipole is created when the Ca ion is removed from the surface.*

Authors' Reply: Thank you for raising this important and insightful comment. We acknowledge that the effective charge of the Ca ion in solution is not the formal +2 charge commonly assumed in classical force fields. Instead, the ReaxFF force field, which calculates atomic charges dynamically using a charge equilibration scheme, provides a more realistic representation of the fractional charge of ions in solution.

1. Variability in the charge of Ca ions:

To validate the accuracy of the ReaxFF charge equilibration scheme, we compared the charges calculated by ReaxFF to those obtained from DFT calculations for a C_{1.25}SH model (see **Figure S11a**). The results show excellent agreement between ReaxFF and DFT charges. The aqueous Ca ions (Cac), primarily coordinated with water and hydroxyl groups, have a slightly higher charge than solid-state Ca ions (Cao) in the interlayer. However, the difference in charge between Cac and Cao is small, indicating that ReaxFF provides a consistent and realistic description of the system.

In addition, we monitored the charge of the Ca ion during the dissolution process (see **Figure S11b**). When the Ca ion is fully dissolved, its charge slightly increases, consistent with the expected behavior of ions in solution. The charge changes reversibly as the Ca ion moves back and forth between the surface and solution, reflecting the dynamic nature of charge equilibration. More importantly, the Ca charge variation is small and consistent across different surface Ca sites, minimizing concerns about variability in the solvation free energy of the Ca

ion in different simulations.

2. Surface charge and dipole effects:

The surface Ca ions in C-(A)-S-H are typically coordinated with free hydroxyl groups. As shown in **Figure 3d**, these hydroxyl groups often dissolve together with the Ca ion, partially compensating for the charge defect caused by dissolution. This phenomenon is consistent with experimental observations, where Ca ion dissolution is often accompanied by an increase in solution pH.

On the other hand, unlike simple crystalline minerals (e.g., NaCl), C-(A)-S-H is an amorphous mineral with a complex surface chemistry. Experimental studies have shown that the dissolution of C-(A)-S-H is not stoichiometric. The dissolution rate of Ca ions is significantly higher than that of anionic groups (e.g., $[\text{SiO}_4]$ tetrahedra), especially when the Ca/Si ratio is greater than 1 (see **Figure R2**)^{13, 14}. As a result, the surface of C-(A)-S-H in contact with solution is often negatively charged^{16, 17}. For long time dissolution, positive ions from the solution may adsorb onto the C-(A)-S-H surface, neutralizing the surface charge over time. The final surface charge depends on the equilibrium activity of Ca ions in solution (see **Figure R3**)¹⁷. Our simulations focus on the initial, non-equilibrium dissolution stage of C-(A)-S-H. During this stage, the surface produced by Ca ion dissolution is expected to carry a negative charge, especially when the dissolved hydroxyl groups are insufficient to fully compensate for the charge defect. This behavior is consistent with the real dissolution characteristics of C-(A)-S-H.

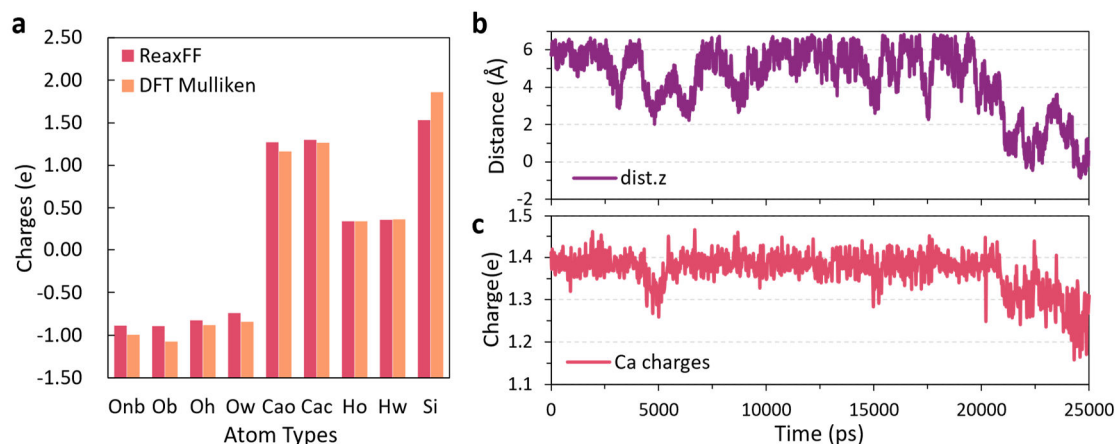


Figure S11. Tests of atomic charges. **a**, Comparison of the atomic charges calculated by ReaxFF to those obtained from DFT calculations for a $\text{C}_{1.25}\text{SH}$ model. **b** and **c**, The evolution of dissolution distance in z direction and the atomic charge of the Ca ion with metadynamics simulation time respectively.

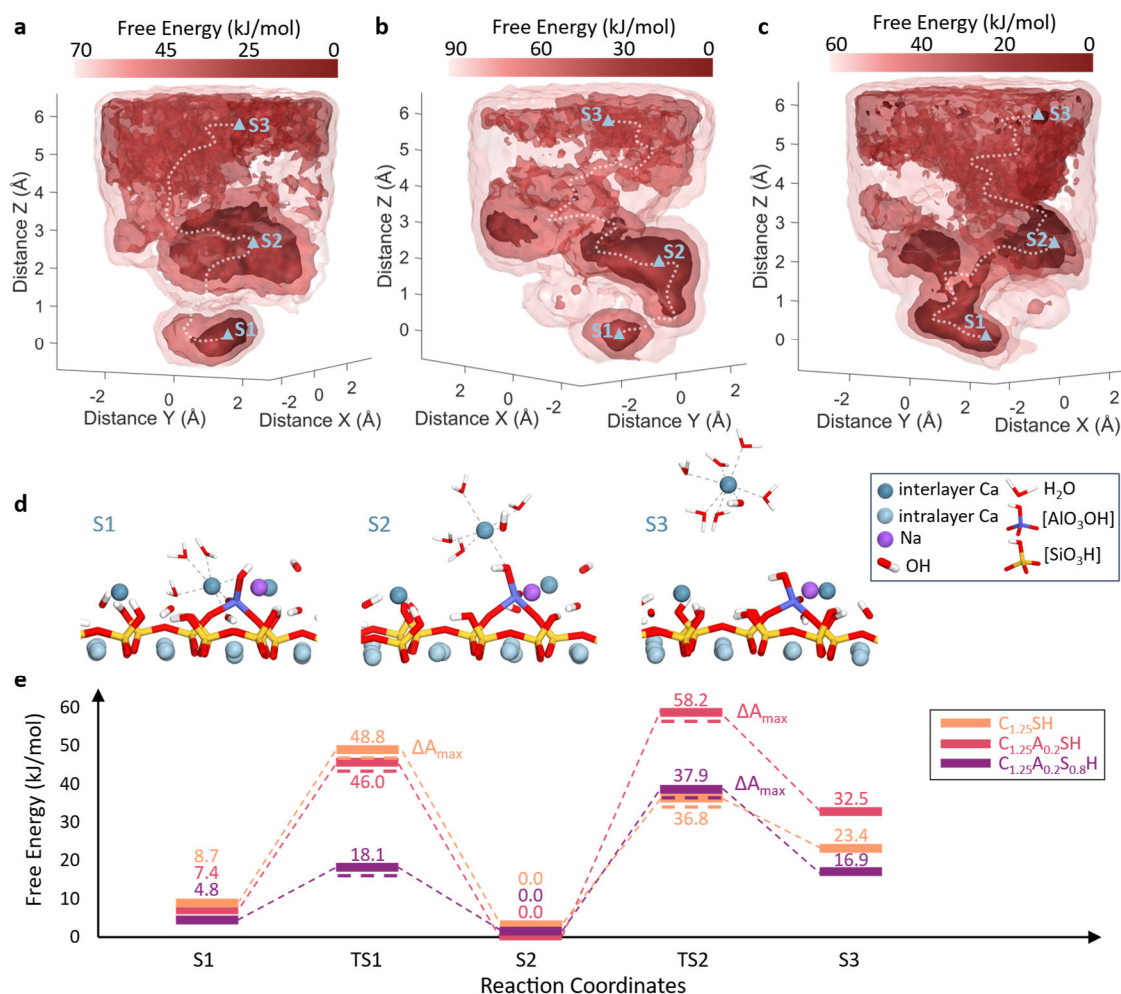


Figure 3. Atomistic mechanisms and thermodynamics of C-(A)-S-H decalcification. **a-c**, Representative three-dimensional free energy landscapes for calcium dissolution from $C_{1.25}SH$, $C_{1.25}A_{0.2}SH$, and $C_{1.25}A_{0.2}S_{0.8}H$ respectively. These landscapes depict the free energy as a function of calcium dissolution displacement along the x, y, and z axes. The origin (0, 0, 0) represents the initial state (S1) of the calcium ion. Dotted lines trace the minimum free energy pathway for calcium dissolution explored using NEB method, while wathet triangles mark key intermediate states (local free energy minima, S1-S3) along the pathway. **d**, Simulation snapshots showing calcium dissolution stages using the $C_{1.25}A_{0.2}SH$ system as a paradigm: S1 (surface-adsorbed state), S2 (inner-sphere adsorbed state), and S3 (fully dissolved state). **e**, Calcium dissolution energetics encompassing all intermediate states (S1-3) and transition states (TS1-2) obtained from . The total dissolution free energy barriers (ΔA_{max}) are the free energy differences between the lowest-energy intermediate state and the highest-energy TS along the dissolution pathway.

[Figure Redacted]

Figure R2. Changes of surface Ca/Si ratio with decalcification time¹⁸

[Figure Redacted]

Figure R3. Zeta potential determined from GCMC (solid curve) and electrophoretic mobility experiments (empty circles) versus bulk $\text{Ca}(\text{OH})_2$ for a C-S-H dispersion in pure lime solutions. The results of the mean field theory (dashed curve) are given for comparison¹⁷.

Revisions in manuscript (line 388-396):

It should be noted that the effective charge of the Ca ion in solution is not the formal +2 charge commonly assumed in classical force fields. Instead, ReaxFF calculates atomic charges dynamically using a charge equilibration scheme, providing a more realistic representation of the fractional charge of ions in solution. To validate the accuracy of the ReaxFF charge equilibration scheme, we compared the charges calculated by ReaxFF to those obtained from DFT calculations for a $\text{C}_{1.25}\text{SH}$ model (see **Figure S11a**). The results show excellent agreement between ReaxFF and DFT charges. In addition, we monitored the charge of the Ca ion during the dissolution process (see **Figure S11b**). When the Ca ion is fully dissolved, its charge slightly increases, consistent with the expected behavior of ions in solution. The charge changes reversibly as the Ca ion moves back and forth between the surface and solution, reflecting the dynamic nature of charge equilibration.

***Comment 7.** There is also a lack of details about how many surfaces sites have been studied and how the procedure followed to prepare the initial C-A-S-H slab effect the morphology, bond order... a $25\text{\AA} \times 30\text{\AA}$ sample is probably not quite representative of a macroscopic system and it would interesting to demonstrate the variability of the results shown here.*

Authors' Reply: Thank you for your valuable comment. Below, we address your concerns by providing additional details about the structural models, surface sites studied, and the representativeness of the C-(A)-S-H slab models used in this study.

Unlike crystalline phases in hydrated cement (e.g., portlandite), whose grain sizes can reach the micrometer scale, amorphous C-(A)-S-H gel is composed of nanoscale particles. As shown in **Figure 1a-b**, the basic particle size of C-(A)-S-H is typically only a few nanometers¹⁹.

The slab models used in this study ($25 \text{ \AA} \times 30 \text{ \AA}$ in the x-y plane) are representative of the nanoscale C-(A)-S-H particles observed in real systems. These dimensions ensure that the models capture the structural and chemical heterogeneity of C-(A)-S-H surfaces while remaining computationally feasible.

C-(A)-S-H is an amorphous material with significant chemical heterogeneity, particularly at its surfaces. The broken silicate chains on the surface lead to a lack of symmetry, resulting in varying local chemical environments for the surface Ca ions. These variations are critical for understanding the dissolution behavior of C-(A)-S-H. The slab models constructed in this study ($\text{C}_{1.25}\text{SH}$, $\text{C}_{1.25}\text{A}_{0.2}\text{SH}$, and $\text{C}_{1.25}\text{A}_{0.2}\text{S}_{0.8}\text{H}$) have surfaces (including both the top and bottom) containing **32 Ca ions** each. We calculated the dissolution free energy for **all 32 Ca ions** on each slab model, ensuring comprehensive coverage of the surface chemical variability. The calculated dissolution free energies were subjected to statistical analysis to account for the variability in chemical environments. This approach allows us to compare the results with experimental decalcification kinetics, which capture the overall behavior of the heterogeneous C-(A)-S-H system.

[Figure Redacted]

Figure 1. Molecular structures of C-(A)-S-H. **a**, Schematic illustration of C-(A)-S-H nanoparticle packing ¹⁹. **b**, Interface between C-S-H and the surrounding gel pore solution. The C-S-H model has a Ca/Si ratio of 1.25 and is denoted as $\text{C}_{1.25}\text{SH}$. **c**, Interface between C-A-S-H and pore solution. The present C-A-S-H model exemplifies the “Al addition” mechanism, one of the two modes of Al incorporation. The C-(A)-S-H interfacial models have dimensions of $\sim 25 \text{ \AA} \times 30 \text{ \AA} \times 75 \text{ \AA}$. **d**, The two mechanisms of aluminum incorporation into $\text{C}_{1.25}\text{SH}$: “substitution” and “addition” with the compositions of $\text{C}_{1.25}\text{A}_{0.2}\text{S}_{0.8}\text{H}$ and $\text{C}_{1.25}\text{A}_{0.2}\text{SH}$ respectively. The black dashed lines depict the calcium-oxygen and sodium-oxygen bonds.

Revisions in manuscript (line 363-367, line 404-406):

The triclinic primitive cell of 14 Å tobermorite was first converted into an orthorhombic unit cell and then extended to a supercell with dimensions of $\sim 25 \text{ Å} \times 30 \text{ Å} \times 35 \text{ Å}$, which represents the nanoscale C-(A)-S-H particles observed in real systems¹⁹. These dimensions ensure that the models capture the structural and chemical heterogeneity of C-(A)-S-H surfaces while remaining computationally feasible.

The constructed slab models of $C_{1.25}SH$, $C_{1.25}A_{0.2}SH$, and $C_{1.25}A_{0.2}S_{0.8}H$ have surfaces (including both the top and bottom) containing 32 Ca ions each. We calculated the dissolution free energy for all 32 Ca ions on each slab model, ensuring comprehensive coverage of the surface chemical variability.

Comment 8. *It is no clear how the “calculated” lines in figure 5e have been obtained. Even with all the caveats mentioned above, the simulations reported in this manuscript did not provide any information about the pre-exponential factor. Was that fitted? Estimated? Guessed?*

Authors’ Reply: Thank you for your comment and for pointing out the need for clarification regarding Figure 5e. We acknowledge that the original explanation may have been insufficient and have revised the manuscript to better describe how the “calculated” lines in Figure 5e were obtained. Below, we provide a detailed explanation of the methodology and assumptions used to construct these lines.

As shown in the revised **Figure 5e**, the experimentally measured decalcification rates (k) of C-(A)-S-H at different temperatures (T) were fitted using the Arrhenius equation: $\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln k_0$, where R is the gas constant, and E_a (activation energy) and $\ln k_0$ (a constant) are the fitting parameters. The dotted lines in **Figure 5e** represent the experimental fits, and their slopes ($-\frac{E_a}{R}$) reflect the experimentally determined activation energy for decalcification.

On the other hand, the solid lines in the figure represent Arrhenius-like functions defined as: $y = -\frac{A}{R} \frac{1}{T} + B$, where A is the calculated decalcification free energy (mean values derived from **Figure 5d**), and B is an adjusted constant that includes contributions from the pre-exponential factor ($\ln k_0$) and other terms. The constant B was adjusted to align the dashed lines with the general magnitude of the experimental data. This adjustment was necessary because our simulations do not explicitly provide information about the pre-exponential factor ($\ln k_0$), which depends on complex dynamical properties not captured in the free energy calculations.

The comparison between the slopes of the dotted lines (experimentally fitted) and solid lines (calculated) provides insight into the agreement between our simulations and experimental data: the calculated calcium dissolution free energies provide a reasonable prediction of the experimental decalcification activation energies.

Revisions in manuscript (Figure 5e):

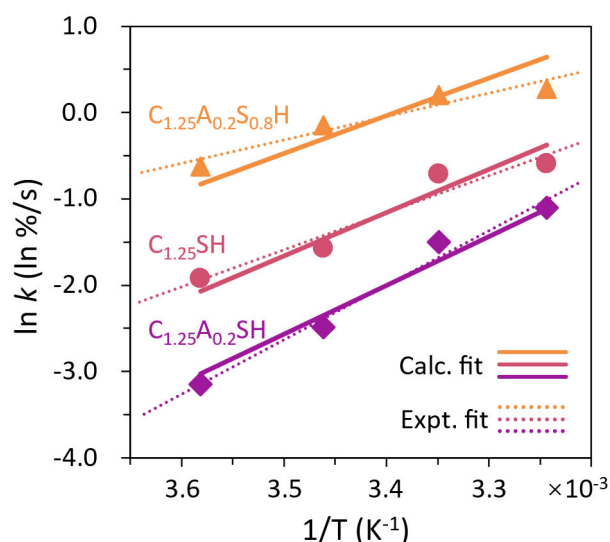


Figure 5e. The experimentally measured decalcification rates (k) of C-(A)-S-H at different temperatures (T) were fitted using the Arrhenius equation: $\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln k_0$, where R is the gas constant, and E_a (activation energy) and $\ln k_0$ (a constant) are the fitting parameters. The dotted lines represent the experimental fits with their slopes ($-\frac{E_a}{R}$) reflecting the experimentally determined activation energy for decalcification. The solid lines represent Arrhenius-like functions defined as: $y = -\frac{A}{R} \frac{1}{T} + B$, where A is the calculated decalcification free energy (mean values derived from panel d), and B is an adjusted constant.

Comment 9. What are the distributions reported in figure 4c and 4g meant to show? The histograms in Figure 4c are clearly not Gaussian distributions. Figure 4g is supposed to show the correlation between bond-order and bond length, so it would be more appropriate to have a trend line or something rather than distributions.

Authors' Reply: Thank you for your comment. We acknowledge that the original explanation may have been unclear and have revised our analysis and visualizations to better convey the intended information.

We agree that Gaussian distribution fitting may not be suitable for the histograms of **Figure 4c**. We have used the Kernel Smoother method to estimate the histogram distribution. **Figure 4c** is intended to compare the number of Ca-Os bonds per surface Ca ion across the three C-(A)-S-H systems ($C_{1.25}SH$, $C_{1.25}A_{0.2}SH$, and $C_{1.25}A_{0.2}S_{0.8}H$). This comparison helps us understand how the surface coordination environment influences the decalcification energy barriers. **Figure 4c** shows that the number of Ca-Os bonds for surface Ca ions in $C_{1.25}SH$ and $C_{1.25}A_{0.2}S_{0.8}H$ is similar. In contrast, surface Ca ions in $C_{1.25}A_{0.2}SH$ have significantly more Ca-Os bonds. This difference in bond numbers, to some extent, explains why the decalcification energy barriers for $C_{1.25}A_{0.2}SH$ are higher compared to the other two systems, as more bonds increase the surface binding strength of Ca ions.

For **Figure 4g**, the negative correlation between bond length and bond order is not surprising, as bond order reflects bond strength, which is inversely related to bond length. **Figure 4g** is intended to compare the characteristics of Ca-Os bond length and bond order across the three C-(A)-S-H systems. $C_{1.25}SH$ has more tightly clustered bond lengths (top distribution) and

higher bond orders (right distribution) compared to $C_{1.25}A_{0.2}SH$ and $C_{1.25}A_{0.2}S_{0.8}H$. These differences suggest that the Ca-Os bonds in $C_{1.25}SH$ are slightly stronger than those in the other two systems, potentially contributing to its relatively higher decalcification energy barriers compared to $C_{1.25}A_{0.2}S_{0.8}H$.

Revisions in manuscript (Figure 4):

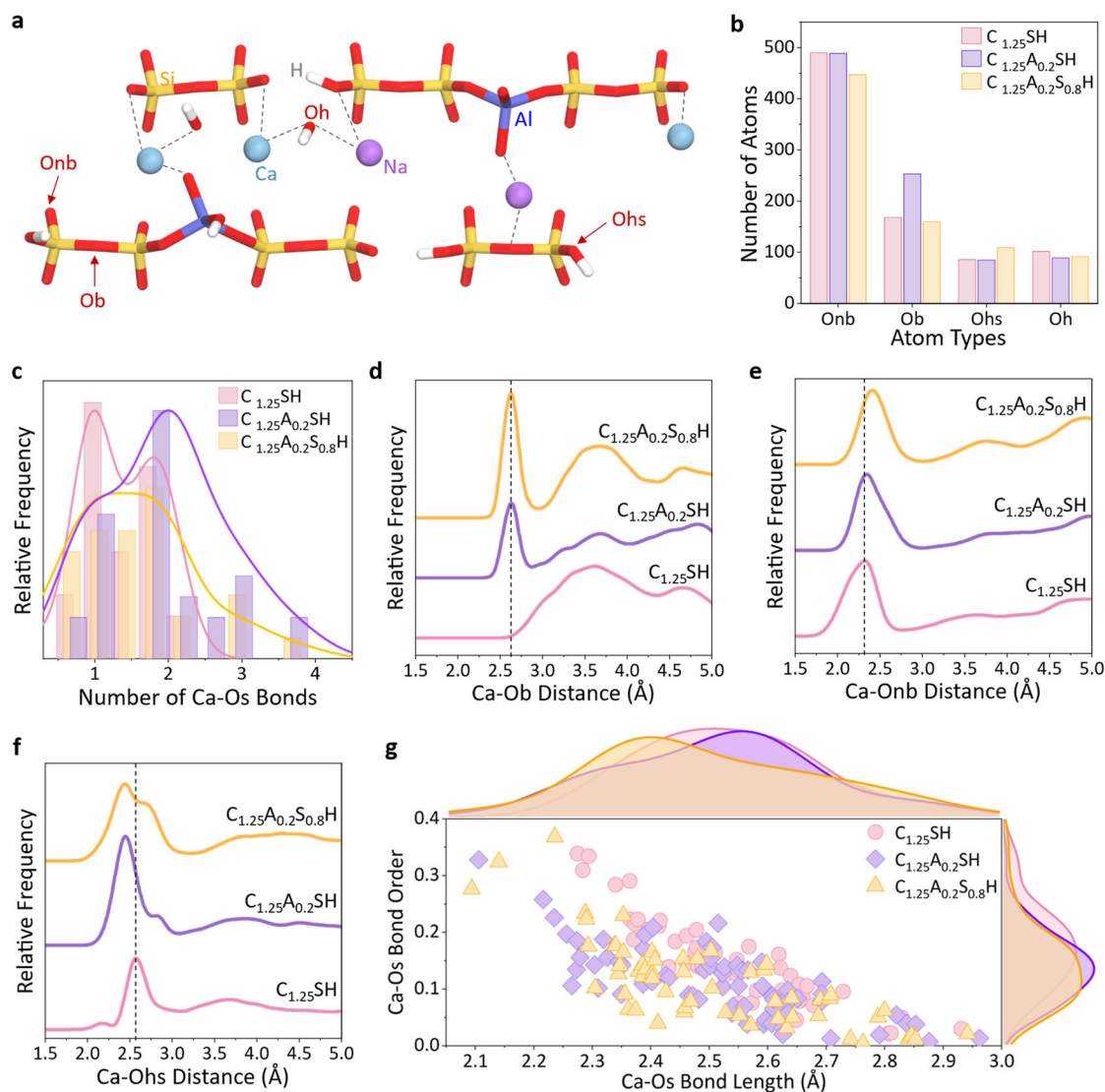


Figure 4. Ca coordination structures in C-(A)-S-H. **a**, Simulation snapshots showing the different atom types in C-(A)-S-H. Water molecules are hidden for clarity. Oxygen atoms within aluminosilicate chains, including bridging (Ob), non-bridging (Onb), and silanol/aluminol group (Ohs) sites, are collectively referred to as silicate oxygen (Os). Black dashed lines represent chemical bonds between calcium ions and coordinated Os ions. **b**, Contents of different oxygen types in C-(A)-S-H. **c**, Distributions of the number of Ca-Os bonds for surface calcium ions in C-(A)-S-H. The fractional Ca-Os bond counts arise from the use of a switching function to represent coordination numbers as continuous functions of the interatomic distance. **d-f**, Pair distribution functions of Ca-Ob, Ca-Onb, and Ca-Ohs in bulk C-(A)-S-H. **g**, Ca-Os bond order and bond length assembly for the three C-(A)-S-H systems. The top and right panels illustrate the distributions of bond lengths and bond orders, respectively.

Comment 10. Typically, another important aspect of this cementitious materials is the hydroxylation of the surface. Does it play any role here? Should it be considered in the

simulations given the experimental samples were prepared in highly caustic solutions?

Authors' Reply: Thank you for your insightful comment. Indeed, surface hydroxylation is an important characteristic of cementitious materials, particularly for C-(A)-S-H, and it influences surface chemistry and dissolution behavior.

As described in the Methods section, we employed the ReaxFF reactive force field for the annealing and equilibration of the C-(A)-S-H slab models. This process naturally results in the formation of stable, hydroxylated surfaces. The final surfaces of the C-(A)-S-H slabs exhibit hydroxyl groups bonded to surface silicate (Si-OH) and calcium (Ca-OH) sites, as shown in **Figure 4a**.

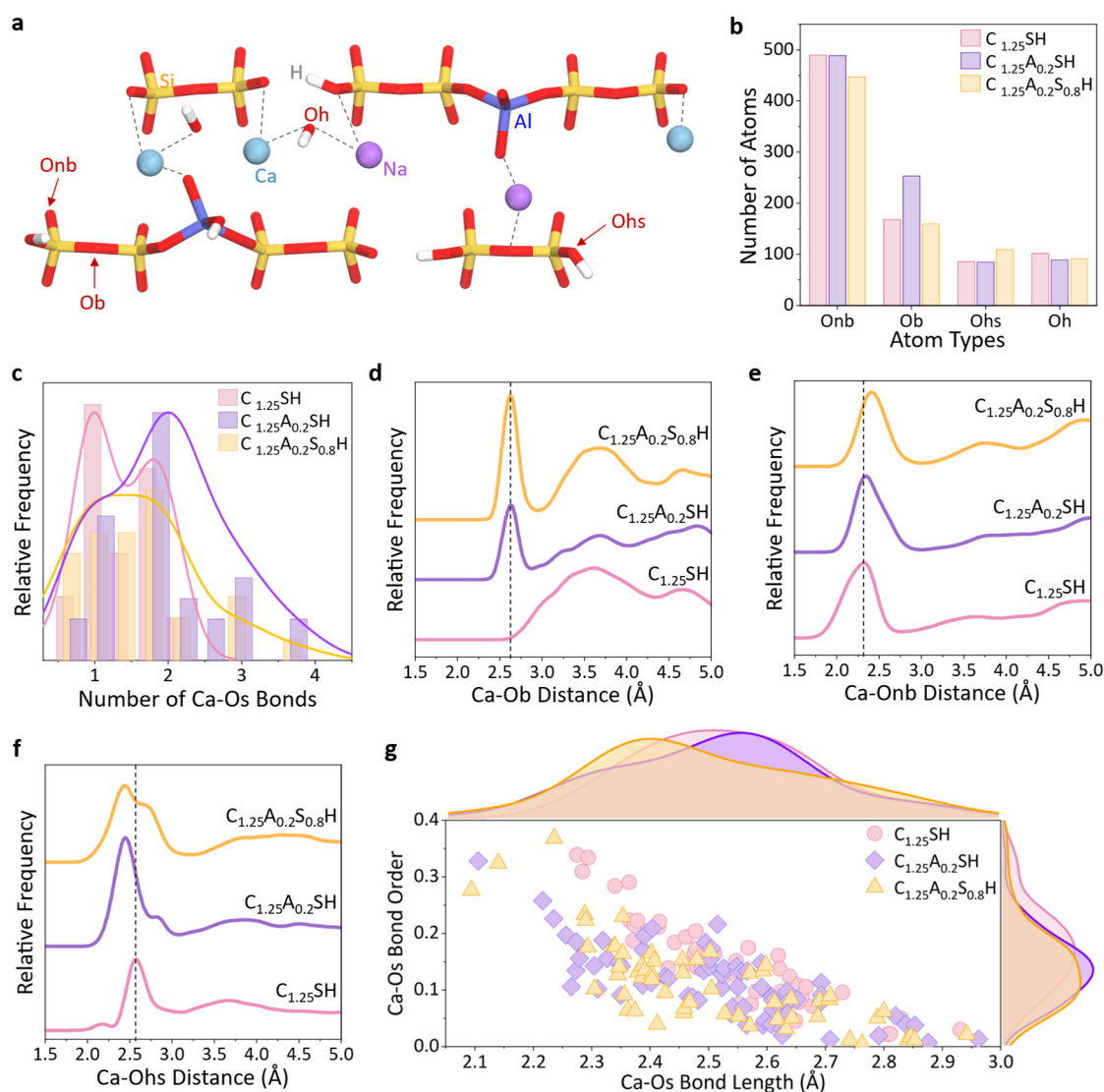


Figure 4. Ca coordination structures in C-(A)-S-H. **a**, Simulation snapshots showing the different atom types in C-(A)-S-H. Water molecules are hidden for clarity. Oxygen atoms within aluminosilicate chains, including bridging (Ob), non-bridging (Onb), and silanol/aluminol group (Ohs) sites, are collectively referred to as silicate oxygen (Os). Black dashed lines represent chemical bonds between calcium ions and coordinated Os ions. **b**, Contents of different oxygen types in C-(A)-S-H. **c**, Distributions of the number of Ca-Os bonds for surface calcium ions in C-(A)-S-H. The fractional Ca-Os bond counts arise from the use of a switching function to represent coordination numbers as continuous functions of the interatomic distance. **d-f**, Pair distribution functions of Ca-Ob, Ca-Onb, and Ca-Ohs in bulk C-(A)-S-H. **g**, Ca-Os bond order and bond length assembly for the three C-(A)-S-H systems. The top and right panels illustrate the distributions of bond lengths and bond orders, respectively.

Comment 11. What is the degree of crystallinity of the experimental samples? The simulation cells shown in the SI seem to be mostly crystalline. Maybe an amorphous sample would be a better representation of the surface morphology of the experimental samples. The authors should probably comment on this aspect.

Authors' Reply: Thank you for your valuable comment.

The structure of C-(A)-S-H is distinct from both fully amorphous materials (e.g., glass) and well-ordered crystalline minerals. C-(A)-S-H is commonly referred to as an “amorphous gel” in the literature because it lacks the long-range three-dimensional order found in highly crystalline phases like portlandite. This gel-like nature is due to its disordered silicate chains and variable Ca/Si ratios. However, C-(A)-S-H exhibits a layered structure similar to clay minerals, with well-defined interlayer regions and calcium aluminosilicate sheets. This structural organization makes it more ordered than a fully amorphous material. Its structural similarities to clay minerals have led researchers to use classical force fields, such as ClayFF, to study the properties of C-(A)-S-H^{20, 21, 22}.

Because the structure of C-(A)-S-H gel is close to the crystalline layered mineral tobermorite except that C-(A)-S-H has a higher Ca/Si ratio and shorter aluminosilicate chains, the tobermorite crystal has been widely adopted a structural prototype to construct C-(A)-S-H gel model. Following the widely accepted approach²³, we began with the crystalline tobermorite structure as a base. To mimic the amorphous gel-like characteristics of C-(A)-S-H, we introduced structural disorder by breaking silicate chains: Removing portions of the silicate chains to create finite-length chains, which increases disorder and achieves the higher Ca/Si ratios typical of C-(A)-S-H gels. Then, we used reactive force field simulations to anneal the modified structure. This process introduces additional structural relaxation and hydroxylation, resulting in a more realistic representation of C-(A)-S-H gel.

Revisions in manuscript (line 358-361):

Since the structure of C-(A)-S-H gel is close to the crystalline layered mineral tobermorite except that C-(A)-S-H has a higher Ca/Si ratio and shorter aluminosilicate chains, the most widely accepted method for constructing amorphous C-S-H molecular models is to remove the bridge [SiO₂] groups of the silicate chains from crystalline tobermorite^{23, 24, 25}.

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Replies to Reviewer #3:

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Comment 1. *In Fig. 1d, it is not obvious that the ionic bond Ca is saturating the oxygen bonded to two neighboring Si or Si and OH-? It must be shown properly easier for reader to understand! Moreover, it seems that Al has 4-fold coordination including two bonding with oxo bridging from neighboring Si, and two OH-, So since Al is 3+ and can have three ionic bonds with neighboring oxygen, therefore, how possible with four ionic bonds? What can compensate the fourth electron for Al to make 4-fold coordination? It must be something like Na+ from solution to the interlayer (as you mentioned from CASH synthesis from line 343), and it must be included into the calculation.*

Authors' Reply: Thank you for pointing out these important issues. We have carefully addressed your concerns by revising the C-(A)-S-H structural models and updating the corresponding calculations. Below, we provide detailed responses and describe the specific changes made.

1. Revised surface structure representation (**Figure 1d**):

We have revised **Figure 1d** to explicitly display the ionic bonds formed between surface Ca and Na ions and neighboring oxygen atoms. Basically, the surface Ca ions coordinate with oxygen atoms of [SiO₄] (or [AlO₄]) groups and free OH⁻ groups that are attached to the surface.

[Figure Redacted]

Figure 1. Molecular structures of C-(A)-S-H. **a**, Schematic illustration of C-(A)-S-H nanoparticle packing ¹⁹. **b**, Interface between C-S-H and the surrounding gel pore solution. The C-S-H model has a Ca/Si ratio of 1.25 and is denoted as C_{1.25}SH. **c**, Interface between C-A-S-H and pore solution. The present C-A-S-H model exemplifies the “Al addition” mechanism, one of the two modes of Al incorporation. The C-(A)-S-H interfacial models have dimensions of ~ 25 Å × 30 Å × 75 Å. **d**, The two mechanisms of aluminum incorporation into C_{1.25}SH: “substitution” and “addition” with the compositions of C_{1.25}A_{0.2}S_{0.8}H and C_{1.25}A_{0.2}SH respectively. The black dashed lines depict the calcium-oxygen and sodium-oxygen bonds.

2. Incorporation of Na ions in the model:

Previously we used proton (H⁺) to balance the charge of Al substitution. We agree that Na ions should be important charge compensation species to be considered in our models. Here, we conducted X-ray fluorescence (XRF) spectrometry to determine the Na content in our experimental C-(A)-S-H samples. The results, presented in **Table S1**, reveal that the samples do contain a measurable amount of Na ions. However, the measured Na/Si and Al/Si ratios are not equal, which means the Na ion is not the only charge compensation specie for the Al substitution. Therefore, we introduced the specific Na contents into the C-(A)-S-H models based on the XRF results and used additional H⁺ or OH⁻ ions to balance the net charges. Specifically, for C_{1.25}SH and C_{1.25}A_{0.2}SH, where Na/Si is higher than Al/Si, OH⁻ ions are introduced to maintain charge neutrality. For C_{1.25}A_{0.2}S_{0.8}H, where Na/Si is lower than Al/Si, the Na ions are insufficient to fully compensate for the charge defects. In this case, we introduced H⁺ by protonating the oxygen atoms of the aluminosilicate chains. The revised structural models, incorporating Na, H⁺, and OH⁻ ions as appropriate, are presented in **Figures S1–S3** of the Supplementary Information. These models better reflect the chemical composition and charge balance of the experimental samples.

Table S1. The designed and real composition of C-(A)-S-H samples. The real composition is determined by X-ray fluorescence spectrometric analysis.

Sample	Notation	SiO ₂ (wt.%)	Na ₂ O (wt.%)	CaO (wt.%)	Al ₂ O ₃ (wt.%)	others (wt.%)	Real Composition				Designed Composition		
							Ca/Si	Al/Si	Ca/(Si+Al)	Na/Si	Ca/Si	Al/Si	Ca/(Si+Al)
1	C _{1.25} SH	43.8	2.03	52.33	0.00	1.84	1.28	/	1.28	0.09	1.25	/	1.25
2	C _{1.25} A _{0.2} SH	40.6	4.40	46.61	6.55	1.85	1.23	0.19	1.03	0.21	1.25	0.20	1.04
3	C _{1.25} A _{0.2} S _{0.8} H	37.7	2.33	52.43	6.72	0.82	1.49	0.21	1.23	0.12	1.56	0.25	1.25

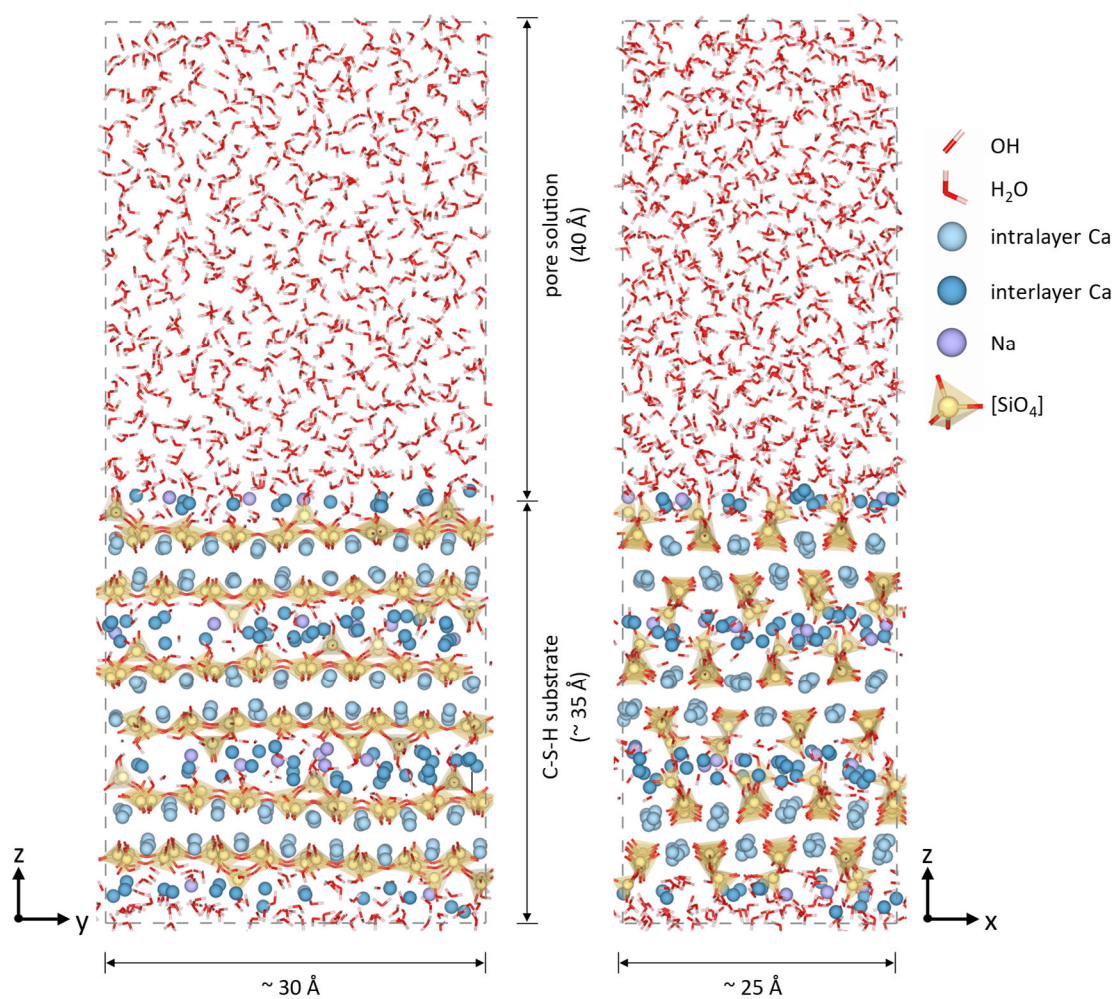


Figure S1. The interfacial model of $C_{1.25}SH$.

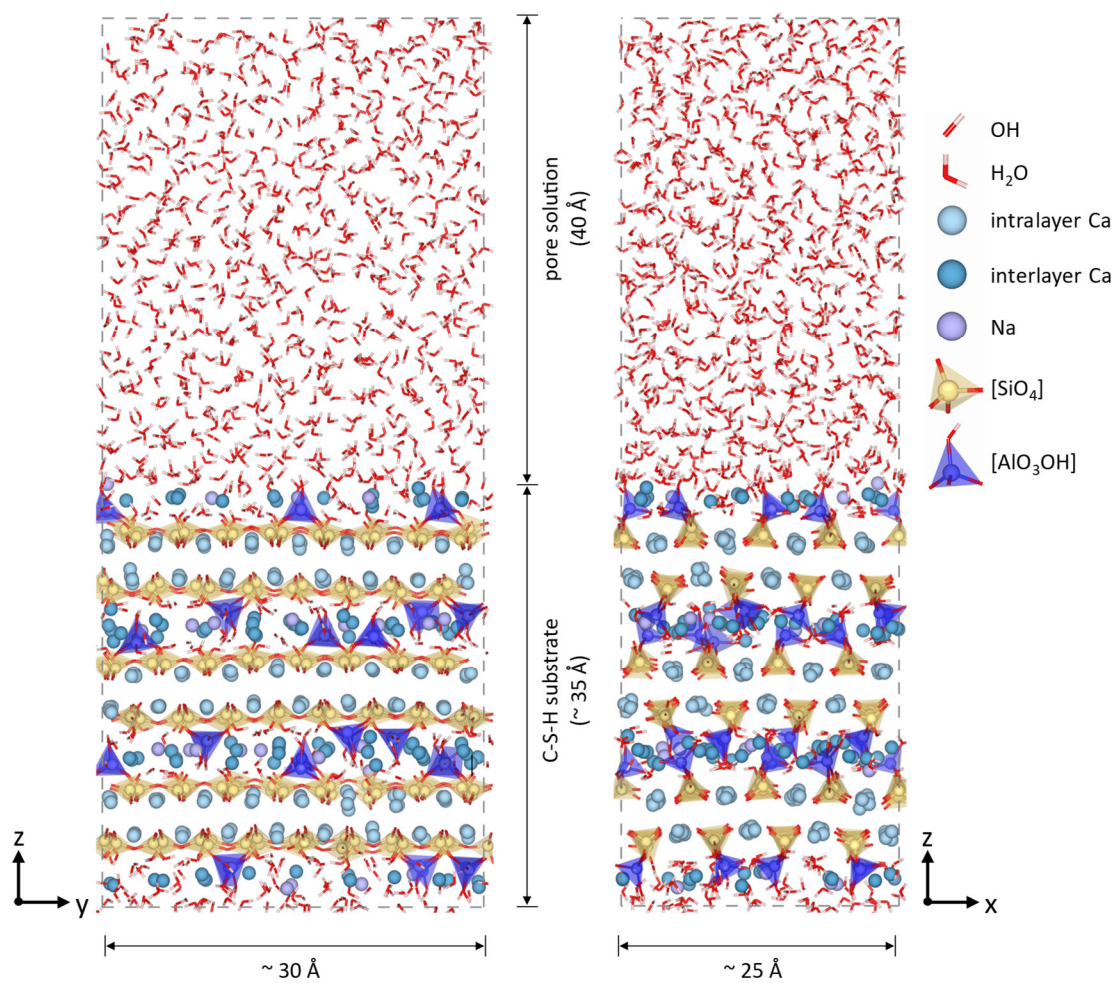


Figure S2. The interfacial model of $C_{1.25}A_{0.2}S_{0.8}H$.

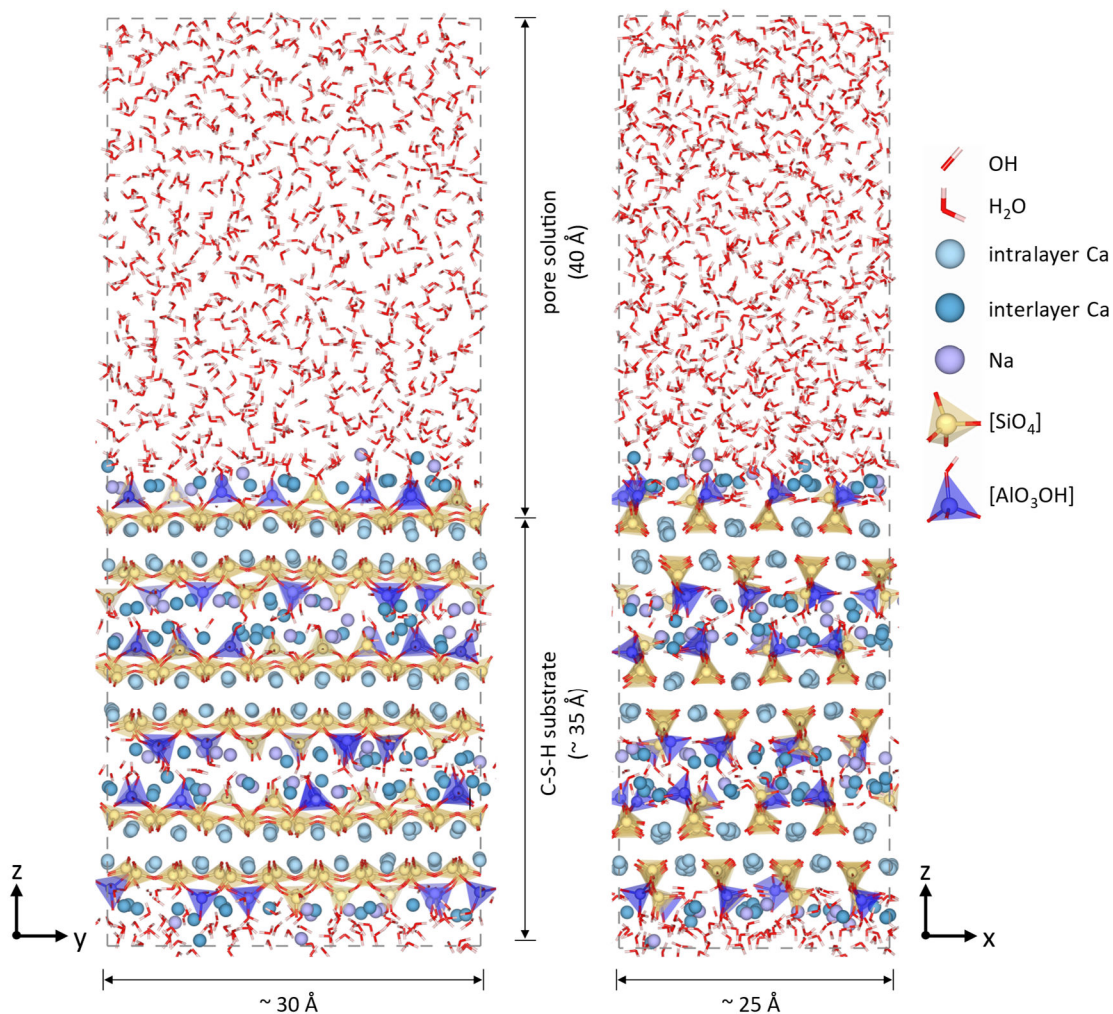


Figure S3. The interfacial model of $C_{1.25}A_{0.2}SH$.

Revisions in manuscript (line 373-382):

To construct a more accurate C-(A)-S-H model, we conducted X-ray fluorescence (XRF) spectrometry to determine the element composition in our experimental C-(A)-S-H samples. It is observed that the samples contain a measurable amount of Na ions (**Table S1**), which agrees with previous studies that Al incorporation usually involves alkali metal ions for charge balance^{26, 27, 28, 29}. However, the measured Na/Si and Al/Si ratios are not equal, which means the Na ion is not the only charge compensation species for the Al incorporation. Therefore, we introduced the specific Na contents into the C-(A)-S-H models based on the XRF results and used additional H^+ or OH^- ions to balance the net charges. Specifically, for $C_{1.25}SH$ and $C_{1.25}A_{0.2}SH$, where Na/Si ratio was found higher than Al/Si, OH^- ions were introduced to maintain charge neutrality. For $C_{1.25}A_{0.2}S_{0.8}H$, where Na/Si was found lower than Al/Si, the Na ions are insufficient to fully compensate for the charge defects. In this case, we introduced H^+ by protonating the oxygen atoms of the aluminosilicate chains.

Comment 2. How geometry optimization by DFT implemented when this charge-balancing alkaline cation is not included?

Authors' Reply: Thank you for your comment. In the original version of our work, we achieved charge neutrality in the system by introducing H^+ ions (via protonation of silicate oxygen atoms) to balance the charge defects caused by Al substitution. While this approach ensured that the system was overall electrically neutral, it did not explicitly account for the presence of Na ions, which are known to exist in experimental samples. Therefore, in the revised version of the manuscript, based on your suggestion and additional experimental data, we incorporated explicit Na ions into the structural models.

Comment 3. *Na NMR spectra must be carried to show precisely for samples after decalcification!*

Authors' Reply: Thank you for this valuable suggestion. We have conducted additional experiments, including ^{23}Na NMR spectroscopy, to investigate the leaching behavior of sodium ions after decalcification and. This analysis allowed us to better understand the sodium leaching behavior in C-(A)-S-H decalcification. In addition, to further explore the role of sodium leaching in C-(A)-S-H decalcification, we calculated the dissolution free energies and rate constants for three representative leaching scenarios (**Figure 6c** and **Figure 6d**). We have added a comprehensive discussion on the role of Na leaching in C-(A)-S-H decalcification in Section 5 of the revised manuscript as shown below.

Revisions in manuscript (line 271-302):

5. Role of Na leaching in C-(A)-S-H decalcification

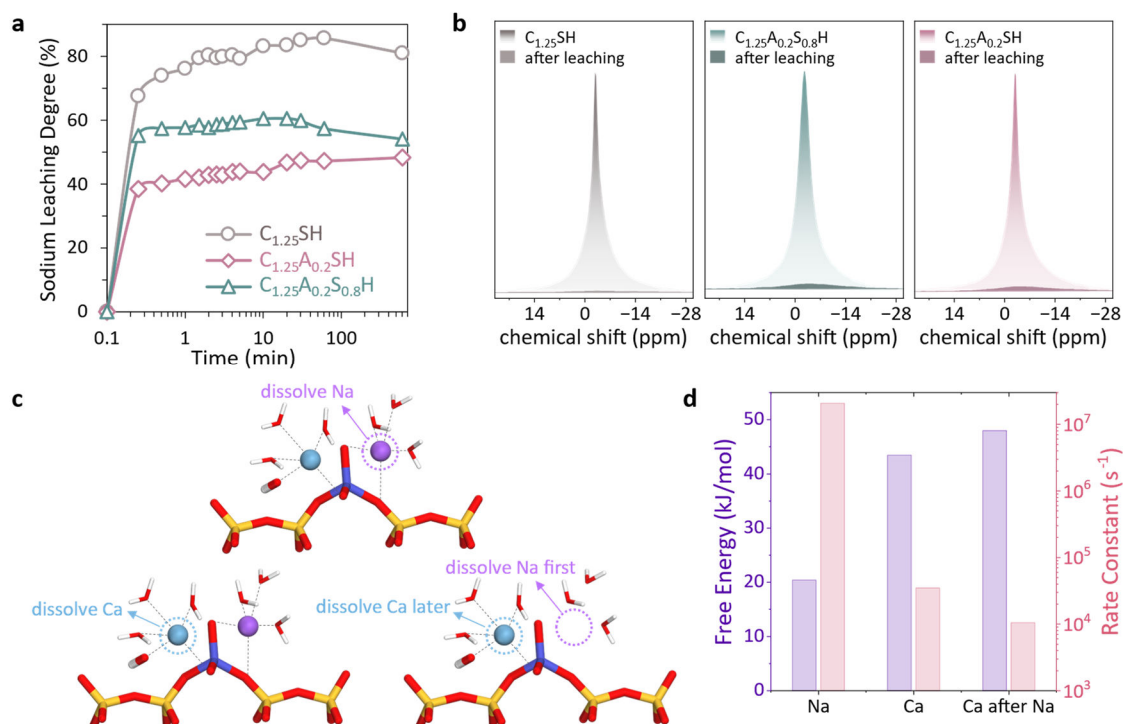


Figure 6. Effect of sodium leaching on C-A-S-H decalcification. **a**, Sodium leaching degree of $C_{1.25}\text{SH}$, $C_{1.25}\text{A}_{0.2}\text{SH}$, and

C_{1.25}A_{0.2}S_{0.8}H as a function of time. **b**, ²³Na MNR spectra of the C-(A)-S-H samples before and after leaching. **c**, Three dissolution scenarios: dissolve a sodium ion, dissolve a calcium ion, dissolve the calcium after dissolving the sodium. **d**, Dissolution free energies and rate constants of the three dissolution scenarios.

In C-(A)-S-H systems, the incorporation of Al is frequently associated with the presence of Na ions as charge-balancing species^{26, 28, 30}, which are susceptible to leaching as widely recognized in alkali-activated materials^{31, 32}. Therefore, we also characterized Na leaching behaviors experimentally and calculated their influence on C-(A)-S-H decalcification thermodynamics. The comparison of Ca and Na leaching kinetics across C_{1.25}SH, C_{1.25}A_{0.2}SH, and C_{1.25}A_{0.2}S_{0.8}H (**Figure 2a** and **Figure 6a**) reveals that both the leaching rates and equilibrium leaching degrees of Na ions are substantially greater than those of Ca ions. As demonstrated by ²³Na NMR spectroscopy (**Figure 6b**), the almost complete disappearance of Na signals in the leached C_{1.25}SH system indicates a near-total removal of Na ions, consistent with its high leaching degree (>80%) observed in **Figure 6a**. Conversely, in the leached C_{1.25}A_{0.2}SH and C_{1.25}A_{0.2}S_{0.8}H systems, the persistence of Na signals suggests that a significant fraction of Na ions remains in the solid phase, corresponding to their lower Na leaching degrees (~50%) in **Figure 6a**. This phenomenon can be attributed to the requirement for Na ions to compensate for the charge imbalance of Al replacing Si within the C-A-S-H framework. Analogous to the previously discussed influence of aluminosilicate chain length on C-A-S-H decalcification behavior, the greater integrity of the aluminosilicate chains in the C_{1.25}A_{0.2}SH system impedes Na leaching, thereby resulting in lower Na leaching rates and degrees compared to the C_{1.25}A_{0.2}S_{0.8}H system.

To gain further insight into the thermodynamics underlying Na dissolution and its impact on C-(A)-S-H decalcification, we calculated dissolution free energies and rate constants for three representative scenarios (**Figure 6c** and **Figure 6d**): 1) single Ca ion leaching; 2) single Na ion leaching; and 3) sequential Ca ion leaching after Na ion removal. The calculated free energy barrier for Na dissolution (20.4 kJ/mol) is markedly lower than that for Ca dissolution (43.4 kJ/mol), which agrees with their experimentally observed leaching kinetics. Importantly, when Na ion is preferentially leached, the subsequent energy barrier for Ca ion dissolution increases to 48.0 kJ/mol, which is due to the enhanced electrostatic attraction between Ca ion and the negatively charged aluminosilicate chain generated upon Na ion removal. The calculated dissolution rate constants further corroborate these findings: the intrinsic rate constant for Na dissolution ($2.07 \times 10^7 \text{ s}^{-1}$) significantly exceeds that for Ca ion ($3.49 \times 10^4 \text{ s}^{-1}$), while the rate constant for Ca ion dissolution following Na ion removal decreases further to $1.05 \times 10^4 \text{ s}^{-1}$. These results indicate that the preferential dissolution of Na ions in C-(A)-S-H phases effectively suppresses the dissolution of Ca ions. It may to some extent explain the better durability of alkali-activated materials with C-N,K-A-S-H (N for sodium and K for potassium) as the main hydration products compared to Portland cement systems³³.

Comment 4. *What is effect of pore solution? It must be discussed!*

Authors' Reply: Thank you for your insightful comment. We have added a discussion on the effect of pore solution on C-(A)-S-H decalcification in the revised manuscript as shown below.

Revisions in manuscript (line 320-325):

Beyond solid-phase composition, pore solution chemistry—including pH, ionic strength, and cation

content—significantly affects the decalcification kinetics of C-(A)-S-H. Incorporation of Al is typically accompanied by charge-balancing alkali ions such as Na and K ions ^{26, 28}, whose dissolution elevates the pore solution pH and stabilizes the aluminosilicate chains, thereby inhibiting decalcification. This effect becomes more pronounced in alkali-rich C-(A)-S-H such as alkali-activated material systems ³², where extensive leaching of alkali ions increases the negative surface charge, enhancing electrostatic interactions that further suppress Ca ions dissolution.

Comment 5. *The manuscript includes a significant number of self-citations. While referencing one's own work is valid, it is essential to engage with and incorporate insights from the broader body of literature to ensure a comprehensive and balanced perspective.*

Authors' Reply: Thank you for your valuable feedback. We have expanded the discussion in the manuscript to include key studies from other researchers in the field, ensuring a more comprehensive and balanced perspective. If there are any specific references or studies that you believe we should include to further strengthen the manuscript, we would greatly appreciate your suggestions.

Added relevant references in manuscript:

1. Bonk F, Schneider J, Cincotto MA, Panepucci H. Characterization by Multinuclear High-Resolution NMR of Hydration Products in Activated Blast-Furnace Slag Pastes. *Journal of the American Ceramic Society* 86, 1712-1719 (2003).
2. Walkley B, Rees GJ, San Nicolas R, van Deventer JSJ, Hanna JV, Provis JL. New Structural Model of Hydrous Sodium Aluminosilicate Gels and the Role of Charge-Balancing Extra-Framework Al. *The Journal of Physical Chemistry C* 122, 5673-5685 (2018).
3. Walkley B, Provis JL. Solid-state nuclear magnetic resonance spectroscopy of cements. *Materials Today Advances* 1, 100007 (2019).
4. Yan Y, et al. Kinetics of Al uptake in synthetic calcium silicate hydrate (C-S-H). *Cement and Concrete Research* 172, 107250 (2023).
5. Liu C, Li Z, Nie S, Skibsted J, Ye G. Structural evolution of calcium sodium aluminosilicate hydrate (C-(N-)A-S-H) gels induced by water exposure: The impact of Na leaching. *Cement and Concrete Research* 178, (2024).
6. Provis JL, Palomo A, Shi C. Advances in understanding alkali-activated materials. *Cement and Concrete Research* 78, 110-125 (2015).
7. Myers RJ, L'Hopital E, Provis JL, Lothenbach B. Composition-solubility-structure relationships in calcium (alkali) aluminosilicate hydrate (C-(N,K-)A-S-H). *Dalton transactions* 44, 13530-13544 (2015).

Comment 6. *As I earlier mentioned, the computational modeling mismatched with C-A-S-H synthesis with contribution of Na alkaline cation!*

Authors' Reply: Thank you for your valuable comment. In the original manuscript, we acknowledged that the computational models did not explicitly account for the contribution of Na ions. In response to your feedback, we have conducted additional experimental analyses and updated our computational models to better align with the synthesis of C-(A)-S-H.

We conducted X-ray fluorescence (XRF) spectrometry to determine the Na content in our experimental C-(A)-S-H samples. The results, presented in **Table S1**, reveal that the samples do contain a measurable amount of Na ions. However, the measured Na/Si and Al/Si ratios are not equal, which means the Na ion is not the only charge compensation specie for the Al substitution. Therefore, we introduced the specific Na contents into the C-(A)-S-H models based on the XRF results and used additional H^+ or OH^- ions to balance the net charges. Specifically, for $C_{1.25}SH$ and $C_{1.25}A_{0.2}SH$, where Na/Si is higher than Al/Si, OH^- ions are introduced to maintain charge neutrality. For $C_{1.25}A_{0.2}S_{0.8}H$, where Na/Si is lower than Al/Si, the Na ions are insufficient to fully compensate for the charge defects. In this case, we introduced H^+ by protonating the oxygen atoms of the aluminosilicate chains. The revised structural models, incorporating Na, H^+ , and OH^- ions as appropriate, are presented in **Figures S1–S3** of the Supplementary Information. These models better reflect the chemical composition and charge balance of the experimental samples.

Table S1. The designed and real composition of C-(A)-S-H samples. The real composition is determined by X-ray fluorescence spectrometric analysis.

Sample	Notation	SiO ₂ (wt.%)	Na ₂ O (wt.%)	CaO (wt.%)	Al ₂ O ₃ (wt.%)	others (wt.%)	Real Composition				Designed Composition		
							Ca/Si	Al/Si	Ca/(Si+Al)	Na/Si	Ca/Si	Al/Si	Ca/(Si+Al)
1	$C_{1.25}SH$	43.8	2.03	52.33	0.00	1.84	1.28	/	1.28	0.09	1.25	/	1.25
2	$C_{1.25}A_{0.2}SH$	40.6	4.40	46.61	6.55	1.85	1.23	0.19	1.03	0.21	1.25	0.20	1.04
3	$C_{1.25}A_{0.2}S_{0.8}H$	37.7	2.33	52.43	6.72	0.82	1.49	0.21	1.23	0.12	1.56	0.25	1.25

Comment 7. *Which surface energy of tobermorite selected as the most representative according to low miller index facet for the atomistic mechanism and thermodynamics of CASH decalcification? Have you already computed by DFT and it is needed to add to the manuscript!*

Authors' Reply: Thank you for raising this important point. We fully agree that calculating the surface energies of low-index facets is generally crucial for determining the most stable surface when constructing surface models of crystalline materials. However, tobermorite (prototype for C-(A)-S-H gel model), as a layered mineral, presents a unique case. It is formed by the stacking of calcium silicate layers in one direction, with interlayer interactions significantly weaker than those in other directions. Consequently, cleavage along the interlayer

space is the dominant pathway.

As shown in **Figure R4**, the interlayer space of the silicate layer is filled with water and free ions. Cleavage at this location primarily involves breaking hydrogen bonds of water, resulting in a relatively low cleavage energy. Furthermore, the presence of water and ions on the resulting surfaces can further reduce the surface energy. Cleavage in other directions would inevitably involve breaking strong Si-O and Ca-O bonds, leading to much higher cleavage energies. For this reason, C-(A)-S-H surface models are almost exclusively constructed via interlayer cleavage. We have added explanations to the manuscript to clarify this point.

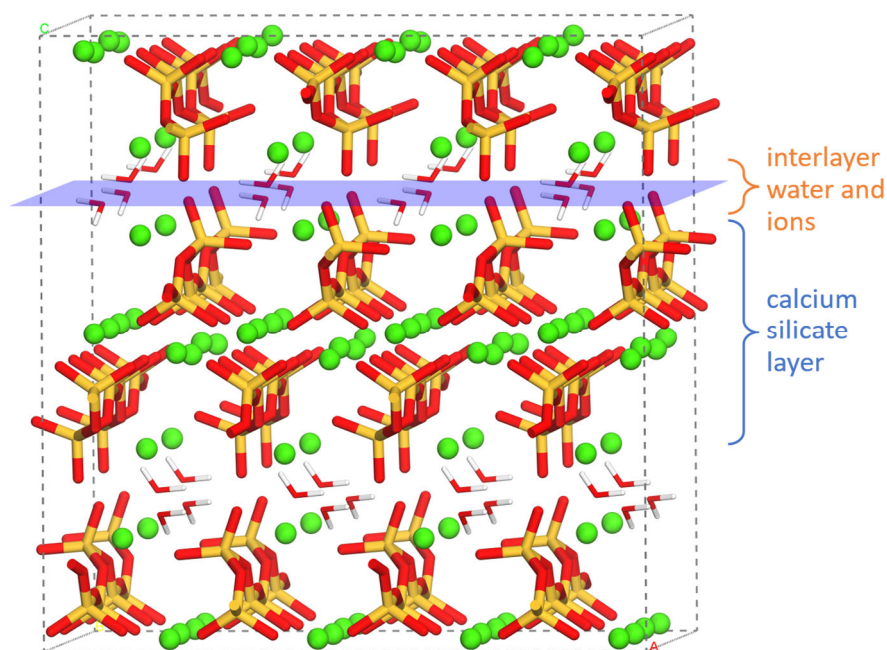


Figure R4. Bulk crystal model of tobermorite.

Revisions in manuscript (line 399-404):

Normally, we need to calculate the surface energies of low-index facets to determine the most stable surface when constructing surface models of crystalline materials. However, tobermorite (prototype for C-(A)-S-H gel model), as a layered mineral, presents a unique case. It is formed by the stacking of calcium silicate layers in one direction, with interlayer interactions significantly weaker than those in other directions. Consequently, cleavage along the interlayer space is the dominant pathway.

Comment 8. *How did you choose the collective variable for metadynamic computation?*

Authors' Reply: Thank you for your valuable comment. We have added a detailed explanation in the revised Methods section to clarify the rationale behind our choice of collective variables (CVs).

We selected the x, y, and z displacement components of the Ca ion as CVs for two main

reasons. First, this choice allows us to more accurately distinguish between the various states of the Ca ion during the dissolution process. In our previous studies on Ca dissolution in C-S-H and clinker, we observed that the dissolution pathway of the Ca ion is not a simple linear trajectory perpendicular to the surface. Instead, it follows a more complex, spiral-like path due to the asymmetry in the atomic arrangement of the mineral surface, a characteristic common to most cement minerals. Using only the water coordination number as a CV would fail to adequately differentiate certain intermediate states along this pathway.

Second, the water exchange rate constant of Ca ions in water is significantly higher ($>10^8 \text{ s}^{-1}$) compared to that of Mg ions ($<10^6 \text{ s}^{-1}$)¹. This rapid exchange ensures that the water coordination number of the Ca ion adjusts automatically as its dissolution state changes. Therefore, it is unnecessary to use the water coordination number as a CV to enforce this adjustment. Additionally, our prior testing confirmed that using the three displacement components as CVs yields the most reasonable results, producing the lowest free energy estimates².

Revisions in manuscript (line 411-422):

The selection has two main reasons. First, the three displacement components allow us to more accurately distinguish between the various states of the Ca ion during the dissolution process. In our previous studies on Ca dissolution in C-S-H and clinker, we observed that the dissolution pathway of the Ca ion is not a simple linear trajectory perpendicular to the surface. Instead, it follows a more complex, spiral-like path due to the asymmetry in the atomic arrangement of the mineral surface, a characteristic common to most cement minerals. Using only the water coordination number as a CV would fail to adequately differentiate certain intermediate states along this pathway. Second, the water exchange rate constant of Ca ions in water is significantly higher ($>10^8 \text{ s}^{-1}$) compared to that of Mg ions ($<10^6 \text{ s}^{-1}$)¹. This rapid exchange ensures that the water coordination number of the Ca ion adjusts automatically as its dissolution state changes. Therefore, it is unnecessary to use the water coordination number as a CV to enforce this adjustment. Additionally, our prior testing confirmed that using the three displacement components as CVs yields the most reasonable results, producing the lowest free energy estimates².

Comment 9. *The NEB method has been used for Ca dissolution, is it according to DFT calculation as shown in Fig.3a-c? How did you select these intermediate pics for computation of transition state? The methods must be mentioned to make it clearer for reader in section 2! Moreover, FES is shown in figure 3d is also according to metadynamics calculation or DFT? It must be clear to readers!*

Authors' Reply: Thank you for your insightful comment. We appreciate the opportunity to clarify the application of the NEB method in our study. The NEB method was employed to explore the transition states within the three-dimensional free energy landscape (**Figure 3a-c**) obtained from our metadynamics simulations.

We understand that the NEB method is also commonly used in conjunction with DFT calculations to search for transition states on the potential energy surface. However, our approach differs in that we utilize the pre-existing three-dimensional free energy landscape generated by metadynamics. This landscape provides us with information about intermediate states (free energy local minima). Therefore, we use the NEB method to determine the minimum free energy pathway between these intermediate states within the three-dimensional free energy space.

To address your concern about clarity, we have added a detailed explanation of our specific implementation of the NEB method to the revised Methods section.

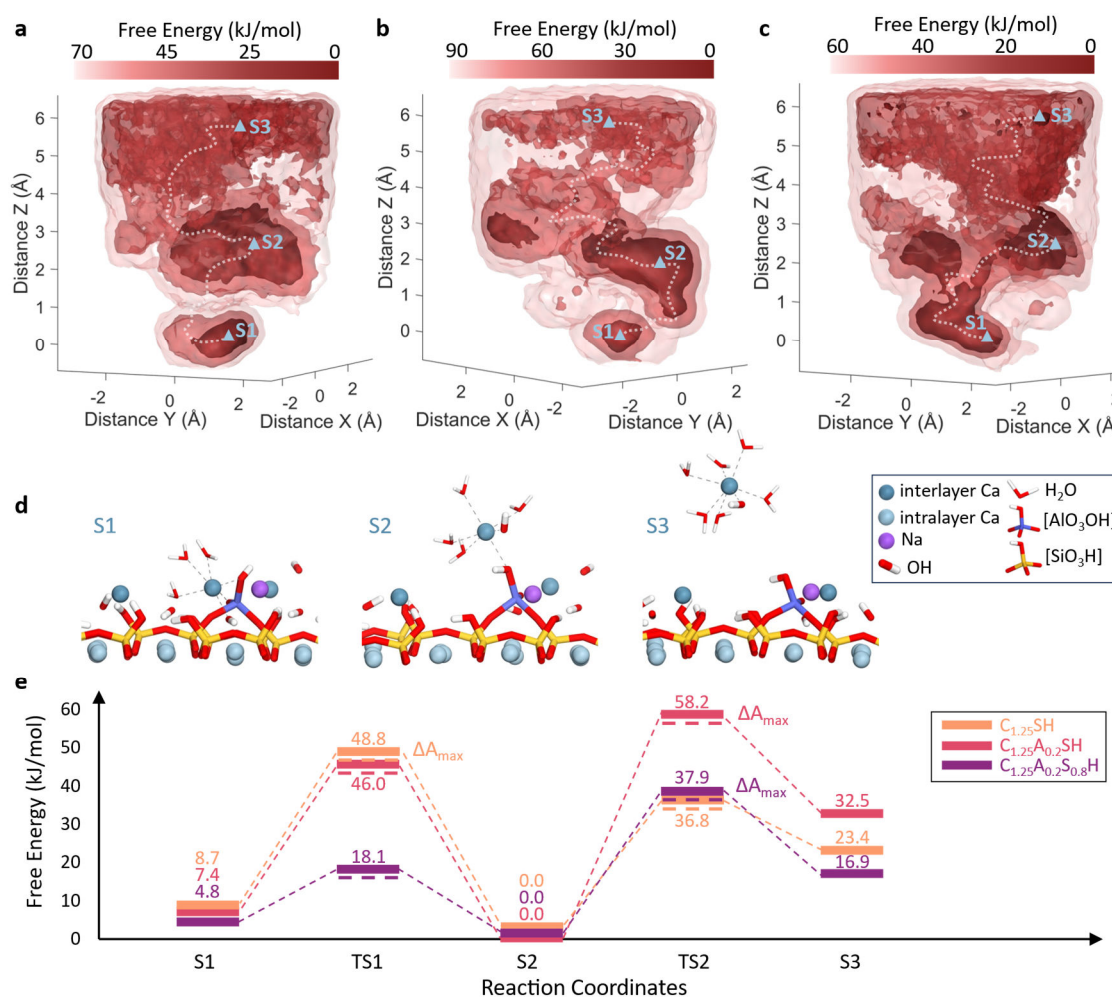


Figure 3. Atomistic mechanisms and thermodynamics of C-(A)-S-H decalcification. **a-c**, Representative three-dimensional free energy landscapes for calcium dissolution from $C_{1.25}SH$, $C_{1.25}A_{0.2}SH$, and $C_{1.25}A_{0.2}S_{0.8}H$ respectively. These landscapes depict the free energy as a function of calcium dissolution displacement along the x, y, and z axes. The origin (0, 0, 0) represents the initial state (S1) of the calcium ion. Dotted lines trace the minimum free energy pathway for calcium dissolution explored using NEB method, while wathet triangles mark key intermediate states (local free energy minima, S1-S3) along the pathway. **d**, Simulation snapshots showing calcium dissolution stages using the $C_{1.25}A_{0.2}SH$ system as a paradigm: S1 (surface-adsorbed state), S2 (inner-sphere adsorbed state), and S3 (fully dissolved state). **e**, Calcium dissolution energetics encompassing all intermediate states (S1-3) and transition states (TS1-2) obtained from . The total dissolution free energy barriers (ΔA_{max}) are the free energy differences between the lowest-energy intermediate state and the highest-energy TS along the dissolution pathway.

Revisions in manuscript (line 460-472):

Minimum free energy pathway

The minimum free energy pathway for ion dissolution was explored from the three-dimensional free energy landscape obtained from metadynamics simulations using the NEB method^{3, 4}. Based on the three-dimensional free energy landscape, we identified important intermediate states, which correspond to local energy minima. Between each pair of adjacent minima, several intermediate images were inserted through linear interpolation with a step size of 0.15 Å to construct an initial Ca dissolution pathway. All the images, including the local minima, were then connected with elastic bands using a defined spring constant. The total force acting on each image, which combines contributions from the elastic band and the underlying free energy field, was calculated. This force serves as the driving force for the optimization process. The images were adjusted iteratively to minimize the total energy of the system using the conjugate gradient algorithm. The optimization was considered complete when the energy difference between consecutive iterations fell below 10⁻⁴ kJ/mol and the displacement difference between images was less than 10⁻⁴ Å. For further details on the theoretical framework of the NEB method, we refer readers to Henkelman's papers^{3, 4}.

REFERENCES

1. Helm L, Merbach AE. Water exchange on metal ions: experiments and simulations. *Coordination Chemistry Reviews* **187**, 151-181 (1999).
2. Tao Y, Martin P, Manzano H, Qomi MJA. Mesoscopic mechanisms of dicalcium silicate dissolution. *Cement and Concrete Research* **189**, 107660 (2025).
3. Henkelman G, Uberuaga BP, Jónsson H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics* **113**, 9901-9904 (2000).
4. Henkelman G, Jónsson H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *The Journal of Chemical Physics* **113**, 9978-9985 (2000).
5. Zhu X, Richardson IG. Morphology-structural change of C-A-S-H gel in blended cements. *Cement and Concrete Research* **168**, 107156 (2023).
6. Zhu X, *et al.* Nature of aluminates in C-A-S-H: A cryogenic stability insight, an extension of DNA-code rule, and a general structural-chemical formula. *Cement and Concrete Research* **167**, 107131 (2023).
7. Jin M, *et al.* Multi-scale investigation on composition-structure of C-(A)-S-H with different Al/Si ratios under attack of decalcification action. *Cement and Concrete Research* **172**, 107251 (2023).
8. Pardal X, Pochard I, Nonat A. Experimental study of Si–Al substitution in calcium-silicate-hydrate (C-S-H) prepared under equilibrium conditions. *Cement and Concrete Research* **39**, 637-643 (2009).

9. Richardson IG. The nature of C-S-H in hardened cements. *Cement and Concrete Research* **29**, 1131-1147 (1999).
10. Silvestri A, Raiteri P, Gale JD. Obtaining consistent free energies for ion binding at surfaces from solution: Pathways versus alchemy for determining kink site stability. *Journal of chemical theory and computation*, (2022).
11. Stack AG, Raiteri P, Gale JD. Accurate rates of the complex mechanisms for growth and dissolution of minerals using a combination of rare-event theories. *Journal of the American Chemical Society* **134**, 11-14 (2012).
12. Bracco JN, *et al.* Simultaneous adsorption and incorporation of Sr^{2+} at the barite (001)–water interface. *The Journal of Physical Chemistry C* **123**, 1194-1207 (2018).
13. Shen Z, Kerisit SN, Stack AG, Rosso KM. Free-energy landscape of the dissolution of gibbsite at high pH. *The journal of physical chemistry letters* **9**, 1809-1814 (2018).
14. Li Y, Pan H, Li Z. Ab initio metadynamics simulations on the formation of calcium silicate aqua complexes prior to the nucleation of calcium silicate hydrate. *Cement and Concrete Research* **156**, (2022).
15. Li Y, Pan H, Liu Q, Ming X, Li Z. Ab initio mechanism revealing for tricalcium silicate dissolution. *Nature communications* **13**, 1253 (2022).
16. Labbez C, Pochard I, Jönsson B, Nonat A. C-S-H/solution interface: Experimental and Monte Carlo studies. *Cement and Concrete Research* **41**, 161-168 (2011).
17. Labbez C, Jönsson B, Pochard I, Nonat A, Cabane B. Surface charge density and electrokinetic potential of highly charged minerals: experiments and Monte Carlo simulations on calcium silicate hydrate. *The Journal of Physical Chemistry B* **110**, 9219-9230 (2006).
18. Sun C, Liu L, Du Y. Analyses of decalcification process of calcium silicate hydrate (CSH) phase. In: *IOP Conference Series: Materials Science and Engineering*. IOP Publishing (2019).
19. Allen AJ, Thomas JJ, Jennings HM. Composition and density of nanoscale calcium–silicate–hydrate in cement. *Nature Materials* **6**, 311-316 (2007).
20. Duque-Redondo E, Bonnaud PA, Manzano H. A comprehensive review of C-S-H empirical and computational models, their applications, and practical aspects. *Cement and Concrete Research* **156**, (2022).
21. Mishra RK, *et al.* **cemff**: A force field database for cementitious materials including validations, applications and opportunities. *Cement and Concrete Research* **102**, 68-89 (2017).

22. Hou D, Li T, Wang P. Molecular Dynamics Study on the Structure and Dynamics of NaCl Solution Transport in the Nanometer Channel of CASH Gel. *ACS Sustainable Chemistry & Engineering* **6**, 9498-9509 (2018).
23. Abdolhosseini Qomi MJ, *et al.* Combinatorial molecular optimization of cement hydrates. *Nature communications* **5**, 4960 (2014).
24. Pellenq RJ-M, *et al.* A realistic molecular model of cement hydrates. *Proceedings of the National Academy of Sciences* **106**, 16102-16107 (2009).
25. Tao Y, Gao Y, Sun Y, Pellenq RJM, Poon CS. C-S-H decalcification in seawater: The view from the nanoscale. *Cement and Concrete Research* **175**, 107385 (2024).
26. Yan Y, *et al.* Kinetics of Al uptake in synthetic calcium silicate hydrate (C-S-H). *Cement and Concrete Research* **172**, 107250 (2023).
27. Walkley B, Provis JL. Solid-state nuclear magnetic resonance spectroscopy of cements. *Materials Today Advances* **1**, 100007 (2019).
28. Walkley B, Rees GJ, San Nicolas R, van Deventer JSJ, Hanna JV, Provis JL. New Structural Model of Hydrated Sodium Aluminosilicate Gels and the Role of Charge-Balancing Extra-Framework Al. *The Journal of Physical Chemistry C* **122**, 5673-5685 (2018).
29. Bonk F, Schneider J, Cincotto MA, Panepucci H. Characterization by Multinuclear High-Resolution NMR of Hydration Products in Activated Blast-Furnace Slag Pastes. *Journal of the American Ceramic Society* **86**, 1712-1719 (2003).
30. Myers RJ, L'Hopital E, Provis JL, Lothenbach B. Composition-solubility-structure relationships in calcium (alkali) aluminosilicate hydrate (C-(N,K-)A-S-H). *Dalton transactions* **44**, 13530-13544 (2015).
31. Liu C, *et al.* Dissolution of cations in C-(N,K-)A-S-H gels at the nanoscale. *Composites Part B: Engineering* **297**, 112337 (2025).
32. Liu C, Li Z, Nie S, Skibsted J, Ye G. Structural evolution of calcium sodium aluminosilicate hydrate (C-(N-)A-S-H) gels induced by water exposure: The impact of Na leaching. *Cement and Concrete Research* **178**, (2024).
33. Provis JL, Palomo A, Shi C. Advances in understanding alkali-activated materials. *Cement and Concrete Research* **78**, 110-125 (2015).

Responses to Reviewers' Comments

Understanding calcium-aluminosilicate-hydrate decalcification: The aluminium paradox

Yong Tao, Yining Gao, Mohammad Javad Abdolhosseini Qomi, Roland J.-M. Pellenq, Chi Sun Poon

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First and foremost, we would like to express our thanks and appreciation for the referees' reviewing work. Their comments and constructive suggestions are very helpful to further improve the quality of our manuscript. It has now been revised in accordance with the reviewers' comments and suggestions. The revised content in manuscript is marked in red. The point-by-point responses to the reviewers' comments are as follows. The figures and tables used only in this response are numbered as Figure R1, Figure R2, ... Table R1, Table R2, ...

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Replies to Reviewer #2:

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Comment 1. "3. We would like to share our thoughts about the metadynamics simulations on mineral dissolution:

The total simulation time depends on the metadynamics parameters and the sampling space. While we fully agree that using highly precise parameters and long simulation times usually would yield more accurate results, computational resources often impose practical limitations (Figure R1). For instance, classical MD simulations can typically achieve hundreds of nanoseconds of sampling, while ab initio MD (AIMD) simulations are often limited to <1 ns due to their computational cost. Therefore, the parameters of AIMD-based metadynamics are rougher than those of classical MD-based metadynamics, although this will lead to the deterioration of the convergence of the former's calculation results. However, since the accuracy and universality of atomic potential adopted by AIMD is much higher than that of fitted classical force field, AIMD-based metadynamics has its advantages and existence value. In our study, we used ReaxFF-based simulations, which fall between AIMD and classical MD in terms of timescale. Therefore, the precision of our metadynamics parameters is also intermediate between those used in AIMD and classical MD.

This study primarily investigates the impact of surface structures on C-(A)-S-H decalcification thermodynamics. To achieve this, we aimed to sample a large number of surface sites to better represent the dissolution characteristics of amorphous C-(A)-S-H. While higher precision for a single Ca ion site could be achieved by focusing computational resources on one site, the decalcification characteristics of amorphous C-(A)-S-H are better captured by averaging data across a large number of Ca sites. As shown in Figure 5, the dissolution free energies for different Ca sites vary significantly, and the differences due to sampling precision for a single site are relatively negligible by comparison. Given that our three C-(A)-S-H models include over 90 surface Ca sites to consider, the refined metadynamics parameters provided in Table R1 represent the most feasible balance between accuracy and computational cost."

The atomistic mechanisms of aqueous mineral processes are largely dominated by the water dynamics and the entropy associated with the water exchange is one of the main contributions to the free energy, there is ample evidence of that, and the authors themselves discussed that the change in coordination environment of the Ca ion between the CASH, adsorbed and solution states. Therefore, having a correct sampling of the water dynamics is at least as important as having an accurate description of the interatomic interactions. Using "rough" metadynamics parameters and short simulations times, would lead to errors that can easily be larger than any gain in the accuracy of the molecular interactions that can be achieved by using an AIMD method.

One can simply test this by taking an empirical forcefield, and computing a well converged free energy, say for the ion-pairing, using proper metadynamics parameters, and then parameters typically used in AIMD (or those used in this work) and compare the results. For the short simulations, one should also test how the computed free energy depends on the starting configuration.

Moreover, no evidence is provided here that the ReaxFF model used by the authors is more accurate than a classical forcefield. In fact, see below, the authors show that the model predicts a partial charge for the solvated Ca^{2+} ion of +1, which is completely unphysical. Therefore, in my opinion, any quantitative agreement with the experimental dissolution activation energies for a gel/amorphous material is fortuitous. To the best of my knowledge, ReaxFF also doesn't use the Ewald summation method, hence the long range electrostatic effects may not be captured correctly.

Authors' Reply: We sincerely thank you for these insightful and challenging comments. Your feedback has pushed us to more deeply consider the critical balance between force field precision and sampling accuracy, and to more rigorously justify our chosen methodology. We have carefully considered all points and provide our clarifications below.

1. Balance Between Sampling Accuracy and Methodological Scope

We completely agree that the dynamics of water and the associated entropic contributions are paramount in mineral dissolution processes. This is precisely why, in our previous revision, we undertook a comprehensive re-evaluation of our simulation protocol. We conducted extensive parameter testing (as detailed in **Figures S7-S10**) to establish a robust and efficient metadynamics protocol for this complex system and redid all metadynamics simulations with the most reasonable parameters and simulation times within our computational power.

We wish to clarify the primary objective of our study. Our goal is not to compute the standard dissolution free energy (ΔG) for C-(A)-S-H, but rather to investigate how the vast structural heterogeneity of an amorphous surface impacts the non-equilibrium decalcification energetics (activation energy, ΔA). Our central scientific question is: what are the relative differences in dissolution free energy (referring to ΔA in the following replies) among the dozens of distinct Ca sites on the C-(A)-S-H surface, and how do these differences relate to the local silicate and aluminate coordination environments? To answer this, sampling a large number of representative sites (>90 in our case) is essential to capture the statistical nature of the amorphous material.

For this purpose, we conducted comprehensive parameter testing (**Figures S7-S10**) to find the optimal balance between accuracy and efficiency within our computational power. Our convergence tests (taking **Figure S7** as an example) demonstrate that the free energy barriers (ΔA) of the forward dissolution reaction stabilize within 20 ns. This indicates that our simulations adequately capture the primary energetic cost associated with detaching the Ca ion from the surface and reorganizing its immediate hydration shell, the key events that define the dissolution barrier. While we acknowledge that achieving full convergence of the solvated state far from the surface would require significantly longer simulation times, this would primarily refine the absolute value of the free energy in the dissolved basin, having a minor effect on the height of the barrier itself. Therefore, for the purpose of comparing the relative barriers across many sites, our protocol represents a rational and well-justified balance between computational feasibility and the accuracy required to support our conclusions. We acknowledge that the complete sampling of the solvated states far from the surface is

essential (while time-consuming) to construct the standard dissolution/precipitation free energies^{1,2,3}, which however is not the purpose of this study.

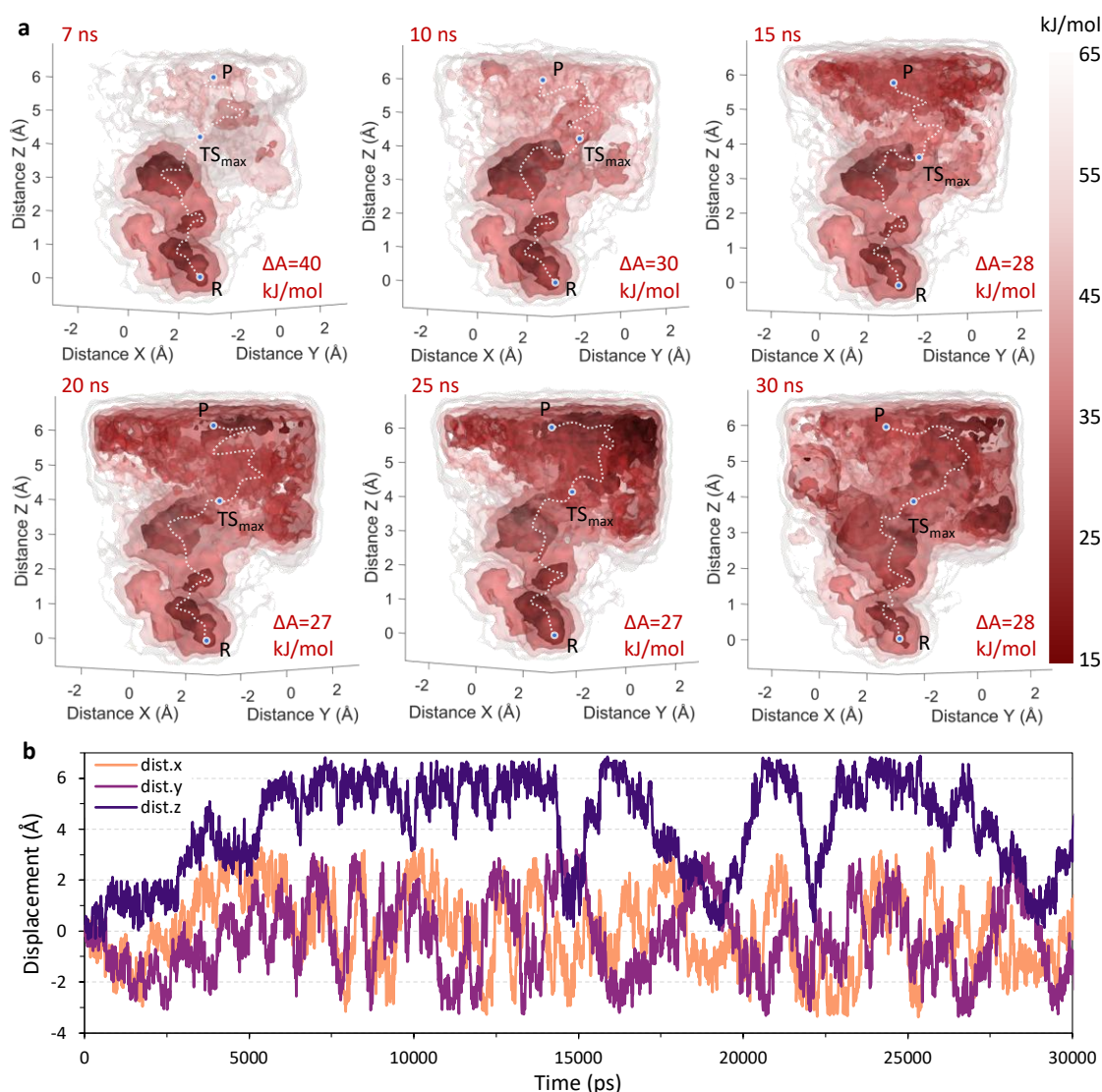


Figure S7. Tests of simulation time for well-tempered metadynamics. **a**, The evolution of the three-dimensional free energy landscape of calcium dissolution with simulation time. The white dashed line indicates the Ca dissolution pathway identified via the Nudged Elastic Band method. The labels R, P, and TS_{max} represent the reactant (initial surface state), the product (fully dissolved state), and the highest-energy transition state, respectively. The overall dissolution free energy barrier (ΔA) is calculated as the energy difference between the lowest-energy state and TS_{max} along the Ca dissolution pathway. **b**, The evolution of collective variables (dissolution displacement components in x, y, and z directions: dist.x, dist.y, and dist.z) with simulation time. For these well-tempered metadynamics tests, the width, initial height and deposition pace of Gaussian penalty potentials, and bias factor are 0.1 Å, 1.5 kJ/mol, every 600 steps, and 15 respectively.

2. Rationale and Validity of ReaxFF

We apologize for the statements in our previous reply that may have misled readers that “ReaxFF is more accurate than classical force fields”. We recognize every force field has its specific domain of applicability (bulk properties, interfacial interaction, aqueous dynamics ...) and limitations beyond that. We offer the following points to justify why ReaxFF is a well-suited choice for this specific case.

Regarding the physical realism of partial charges, you raised a crucial point regarding the seemingly “unphysical” charge on the solvated Ca ion (about +1.40, see **Figure S11c**). We must clarify that this is the atomic partial charge calculated by the Charge Equilibration (QE) method inherent to ReaxFF, not the formal charge of the ion. In polarizable, charge-equilibration force fields like ReaxFF, electron density dynamically shifts in response to the

local chemical environment. This behavior is a cornerstone of modern polarizable models. It reflects the physical reality of electronic polarization: when a Ca ion is solvated, electron density is drawn from the coordinating water molecules, effectively screening the cation's charge. Consequently, the Ca atom itself holds a partial charge less than +2, while the surrounding water molecules become more polarized. This is a physically realistic representation of electronic polarization.

As shown in the revised **Figure S11a**, DFT calculations consistently show that both Bader and Mulliken partial charges of solvated Ca ions (q_{Ca}) are significantly less than their formal +2 charge and comparable to the ReaxFF charges. Also, previous ab initio calculations on tobermorite (C-S-H like crystals) also showed that the Ca ions feature partial charges of +1.66 ~ +1.7 rather than the formal +2 charge⁴. For the same reason, classical force fields like CSH-FF and INTERFACE FF also use point charges (+1.7e) to describe the aqueous Ca ions in the C-S-H like minierals^{4,5}. These confirm that the dynamic partial charges in ReaxFF are not an artifact, but rather a more physically realistic representation than the fixed integer charges used in non-polarizable force fields, which cannot capture these crucial polarization and charge transfer effects.

Regarding the long-range electrostatic interactions, you are correct that standard ReaxFF implementations do not use Ewald summation, relying instead on a distance-dependent shielded Coulomb potential that tapers to zero. We acknowledge this is an approximation for long-range electrostatics. However, for interfacial reactions like dissolution, the dominant energetic contributions arise from short-range interactions: the breaking of covalent/ionic Ca-O bonds at the surface and the dynamic reorganization of the first and second hydration shells. The ReaxFF formalism is specifically calibrated without Ewald to capture these local, coordination-dependent effects accurately. Numerous studies on mineral-water interfaces have successfully employed ReaxFF with this approximation^{6,7,8,9,10}, indicating its suitability for such systems.

Finally, a critical reason for choosing ReaxFF is its ability to model water auto-dissociation and surface hydroxylation. The surface of C-(A)-S-H is complex, featuring varying degrees of hydroxylation depending on the local Ca/Si and Al/Si ratios. A classical non-reactive force field cannot capture the dynamic formation of silanol (Si-OH) groups or the proton transfer events that stabilize the hydrated surface. ReaxFF allows us to first anneal our C-(A)-S-H models in water to achieve a chemically realistic, equilibrated hydrated surface, which is the necessary starting point for our subsequent dissolution studies. This capability is indispensable for our system and represents a key advantage over classical potentials.

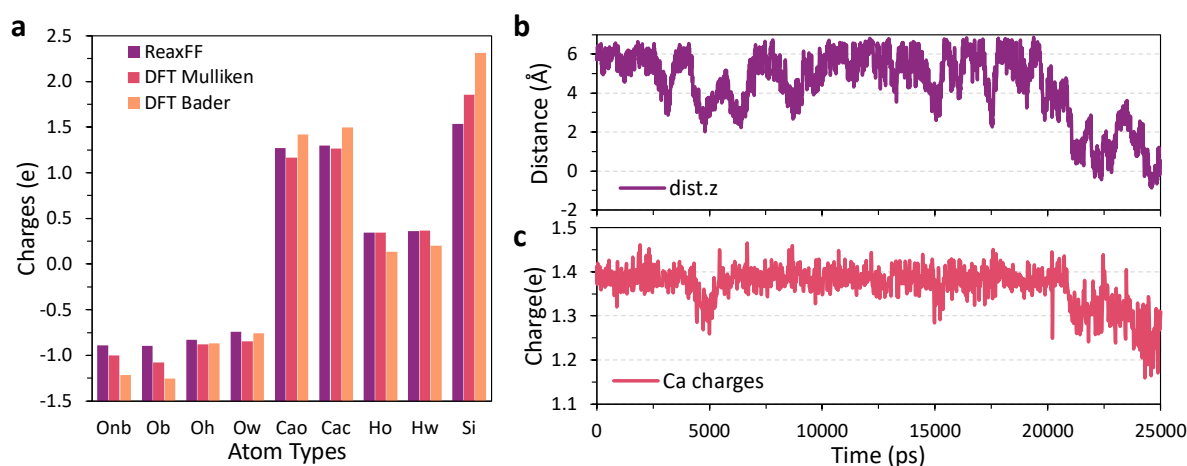


Figure S11. Tests of atomic charges. **a**, Comparison of the atomic charges calculated by ReaxFF to those obtained from DFT calculations for a $C_{1.25}SH$ model. **b** and **c**, The evolution of dissolution distance in z direction and the atomic charge of the Ca ion with metadynamics simulation time respectively. The Ca ion was initially put in the solution above the surface and pushed back to its original position on the C-(A)-S-H surface.

Comment 2. “We also want to emphasize that the deposition pace should be evaluated in terms of the number of simulation steps rather than absolute simulation time. This is because the timestep size determines how much the system evolves in each step. In our ReaxFF MD simulations, the timestep is 0.2 fs, meaning that each step induces only 20% of the relative perturbation caused by a classical MD step where the timestep is typically 1 fs. Consequently, the system requires less time to relax after each Gaussian deposition. Thus, the deposition pace of 600 steps in our ReaxFF MD simulations is comparable to the deposition pace commonly used in classical MD (e.g., 100-1000 steps)”

This is incorrect, and it is actually the opposite of what the authors say. The system will take the same time to relax after each Gaussian deposition, this is an intrinsic time that is related to the diffusivity of the species, which need to have the time to diffuse further than the Gaussian’s width. This means that with 0.2fs timestep, the system will take 5 times more MD steps to relax than if the simulation was run with a 1fs timestep. The deposition rate measured in (1/ps) should be the same, while the rate measured in (1/timesteps) should be slower for simulations with a shorter timestep, not faster. This is again easy to test with a simple model system.

Figures S6-S9

Looking at the various test that the authors have performed, it appears that the S2 state (inner-sphere adsorbed state) is always the most stable configuration, and that there is a huge variability in the relative free energy of the dissolved state, from ~5 to ~20 kJ/mol higher. This would suggest that the simulation protocol used here is extremely sensitive to the metadynamics parameters, and to the choice the initial set up.

Moreover, it’s not very clear why the Ca should dissolve if the adsorbed state is the most stable configuration.

Authors’ Reply:

1. Deposition Pace of Gaussian Potentials

We are deeply grateful to the reviewer for pointing out the error in our previous reasoning regarding the deposition pace. You are absolutely correct, and we sincerely apologize for the mistake. The physical relaxation time of the system is indeed independent of the simulation timestep, and a smaller timestep requires more steps to achieve the same relaxation duration.

While our previous explanation was flawed, the chosen deposition pace (every 600 steps, which is 120 fs) was based on a pragmatic balance between computational cost and ensuring

the system does not deviate drastically from equilibrium, which is a common practice in expensive metadynamics studies. While a slower deposition rate is ideal, it is computationally prohibitive for systems of our complexity when sampling over 90 distinct sites using ReaxFF. The key to selecting deposition pace is not to eliminate bias-induced non-equilibrium effects entirely, but to ensure they do not fundamentally alter the transition pathways and the determined energy barriers. Our tests in **Figure S9** provide concrete support that although the absolute free energies of solvated Ca show some sensitivity, the identification of the primary dissolution barrier (ΔA , energy barrier between TS2 and S2) remains consistent across the tested paces. The 600-step pace emerged as the most efficient choice that still produced a stable barrier height comparable to the slower 800-step pace.

2. Free Energy Variations of the Dissolved State

The phase space of a solvated ion, once it has detached from the surface, is immense and relatively flat. Exhaustively sampling this entire region to obtain a fully converged absolute free energy for the S3 state requires computational resources that are far beyond what is feasible for a study involving over 90 distinct sites with a reactive force field. As shown in our simulation time test (**Figure S7**), while ΔA stabilizes relatively quickly, the free energy of the S3 basin continues to decrease with longer simulation times. We fully expect that with sufficient (and likely prohibitive) sampling time, the S3 state would indeed become the global free energy minimum, yielding the correct thermodynamic sign for spontaneous Ca dissolution in pure water ($\Delta G < 0$). Therefore, at the current stage, we can only conclude that S2 (inner-sphere adsorbed state) is the most stable state before the Ca ion is fully dissolved. It actually agrees with previous simulations on barite dissolution ¹¹.

ΔA is determined by local events, the breaking of Ca-O bonds and the reorganization of the immediate hydration shells. These processes occur within a more constrained region of phase space, and thus the barrier height converges relatively rapidly. Our tests in **Figure S7** and **Figure S9** demonstrate that ΔA is stable and robust within our simulation protocol. In contrast, ΔG depends on the energy difference between two vast and distinct basins (surface-bound vs. fully solvated). Its convergence is limited by the slowest part of the process, which is the exhaustive sampling of the S3 state. Given this, the primary objective of our study is not to report a precise, standard ΔG for C-(A)-S-H dissolution. Rather, our central scientific contribution is to investigate how surface structural heterogeneity affects dissolution kinetics by comparing the relative differences in activation energies (ΔA) across a large ensemble of sites. This comparative analysis remains valid and robust even if the absolute ΔG is not fully converged.

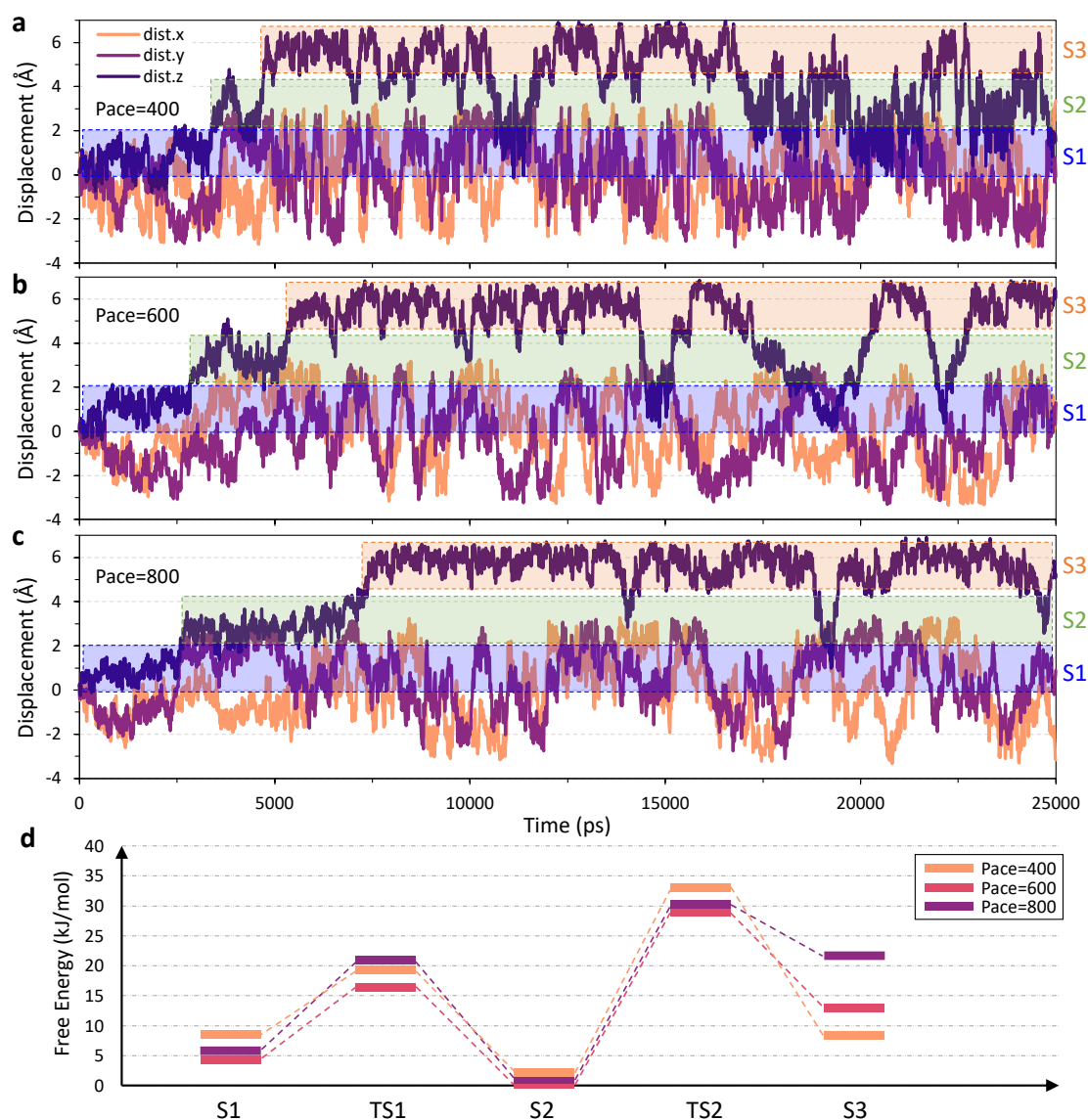


Figure S9. Tests of Gaussian deposition rates for well-tempered metadynamics. **a-c**, The evolution of collective variables (dissolution displacement components in x, y, and z directions: dist.x, dist.y, and dist.z) with simulation time using different Gaussian deposition paces (every 400, 600, and 800 steps). **d**, Calcium dissolution energetics encompassing all intermediate states (S1-3) and transition states (TS1-2). The total dissolution free energy barriers (ΔA) are the free energy differences between the lowest-energy intermediate state and the highest-energy TS along the dissolution pathway. For these well-tempered metadynamics tests, the width and initial height of Gaussian penalty potentials, and bias factor are 0.1 Å, 1.5 kJ/mol, and 15 respectively.

Comment 3. “The concern you raised highlights an important point about the balance between simulation time and the stability of the studied system. While longer simulation times can improve sampling, they may also lead to undesirable changes in the system, such as significant rearrangement of the surface structure. For example, in systems with unstable initial configurations, long simulations might result in alterations to the phase space (e.g., significant surface restructuring), making the original reactant state inaccessible. Artificially constraining the initial structure (e.g., restricting the movement of atoms near the initial configuration) could prevent such rearrangements, but this would compromise the realism of the simulated reaction process. Therefore, the simulation time of metadynamics is not simply the longer the better, but must be carefully tailored to the specific system being studied.”

I disagree with that statement.

A longer metadynamics simulation is always better. It ensures that the simulation explores as much as possible the configurational space, including possible slow degrees of freedom that have not been included in the CVs, which can manifest itself as hysteresis, large variability of the free energy differences, CV(s) being stuck at a given value and more.

If the surface (or the system in general) changes conformation/geometry during the

simulation, then appropriate restraints need to be added to the simulation to prevent this from happening (and the corresponding free energy contributions need to be accounted for). In my view, running a short simulation, which is likely to produce a semi-random non-converged free energy value is not a better outcome.

Also, the fact that the chosen method (ReaxFF or AIMD) is slow is not a good reason to report non converged and unreliable free energy values. Given that a large fraction of the free energy contributions for aqueous processes comes from the water entropy, a more “approximate” method that allows for proper sampling the water dynamics can potentially produce more reliable results. I would indeed argue that a carefully parameterised classical forcefield that reproduces the experimental thermodynamic properties of the bulk and aqueous species can provide better results due to being able to achieve a more complete sampling of the entropic contributions.

Authors’ Reply: We thank you for this comprehensive and thought-provoking critique. You have articulated the central, challenging trade-offs that exist at the heart of computational materials chemistry. We agree with the fundamental principles you’ve outlined: in an ideal scenario, all simulations should be run until full convergence is achieved, and sampling of all degrees of freedom, especially solvent entropy, is paramount. However, the specific nature of our scientific problem—elucidating the atomistic mechanisms of decalcification from a chemically complex, amorphous surface—necessitates a carefully considered methodological compromise.

1. Surface Relaxation, Restraints, and Simulation Time

We respectfully disagree with the statement that simply running a longer simulation is always the better or correct approach for this specific system, particularly if it requires adding structural restraints.

C-(A)-S-H is an amorphous, metastable solid. Its surface is not a static, perfect crystal lattice. When a Ca ion is removed, the local silicate/aluminate network is expected to relax and reorganize to some extent. This surface relaxation is an intrinsic and crucial part of the overall dissolution process. Applying restraints to prevent this rearrangement, as suggested, would artificially suppress this physical reality. The resulting free energy would not correspond to the dissolution from a real C-(A)-S-H surface, but from a hypothetical, structurally “frozen” one. Our goal is to understand the process in its full complexity, including this surface response.

2. Choice of ReaxFF over Classical Potentials

You have raised the critical question of whether a well-sampled classical potential could outperform a less-sampled reactive potential. This choice is dictated by the fundamental physics we aim to capture.

The proton transfer and surface hydroxylation are active processes that happen during the detachment of a Ca ion from the C-(A)-S-H surface. A classical, non-reactive force field cannot describe these O-H bond-breaking and bond-forming events. While it would excel at sampling water dynamics far from the surface, it would fail to capture the core chemical event at the interface, which can be one of the determinants of the activation barrier. ReaxFF was chosen precisely because it is one of the few computationally tractable methods capable of simulating these chemical reactions within a large, condensed-phase system. It correctly describes the surface protonation and water splitting reactions. The cost of this higher physical fidelity is slower sampling. Given that our scientific question is about the mechanism and activation energy of this chemical reaction, prioritizing the accuracy of the reaction itself over the

sampling of distant water molecules is a deliberate and, we argue, a necessary scientific choice.

In conclusion, we are not using the computational cost of ReaxFF as an “excuse” for reporting non-converged results. Rather, we are presenting a comprehensive study on the relative dissolution barriers across a heterogeneous surface, a scientific question for which ReaxFF is the most appropriate tool. We have rigorously tested the convergence of this relative metric (ΔA) and found it to be robust. We acknowledge the limitations regarding the full convergence of absolute free energies and have made this explicitly clear in our revised manuscript. We believe this approach, despite its inherent compromises, provides novel and valuable insights into C-(A)-S-H chemistry that would be inaccessible using classical force fields.

Comment 4. “Variability in the charge of Ca ions: To validate the accuracy of the ReaxFF charge equilibration scheme, we compared the charges calculated by ReaxFF to those obtained from DFT calculations for a C1.25SH model (see **Figure S11a**). The results show excellent agreement between ReaxFF and DFT charges. The aqueous Ca ions (Cac), primarily coordinated with water and hydroxyl groups, have a slightly higher charge than solid-state Ca ions (Cao) in the interlayer. However, the difference in charge between Cac and Cao is small, indicating that ReaxFF provides a consistent and realistic description of the system.

In addition, we monitored the charge of the Ca ion during the dissolution process (see **Figure S11b**). When the Ca ion is fully dissolved, its charge slightly increases, consistent with the expected behavior of ions in solution. The charge changes reversibly as the Ca ion moves back and forth between the surface and solution, reflecting the dynamic nature of charge equilibration. More importantly, the Ca charge variation is small and consistent across different surface Ca sites, minimizing concerns about variability in the solvation free energy of the Ca ion in different simulations.”

Since there is no experimental evidence that the Ca^{2+} solvated ion has an effective charge of around +1, these results suggest that the ReaxFF model employed here has unphysical properties. If Ca^{2+} has a charge of +1, which other part of the system has lost an electron?

The partitioning of the electronic density into atomic partial charges in DFT is an arbitrary process that requires the definition of a criterion to assign what charge belongs to each atom. The Mulliken charges are one of such methods, which is typically extremely inaccurate. One can simply compare Mulliken charges, with Bader charges, Hirschfeld charges, Wannier charges... to see how wildly the atomic partial charges can change. Hence, the fact that the ReaxFF partial charges agree with the Mulliken charges is not an indication that they are accurate, quite the contrary. What the authors are observing is an artifact of DFT which doesn't localise the charge very well with standard methods (there's no mention in the authors' reply of what DFT method they have used), and that ReaxFF suffers of the same problem.

Hybrid methods, with large fraction of exact exchange are usually required to better localise the charge, but Mulliken charges is not a good indication of where the charge is.

Authors' Reply: Thank you for your valuable comment. You are absolutely correct that a solvated Ca ion usually exists as a formal “+2” species. The fractional charge of about +1.4e observed in ReaxFF is not a formal ionic charge, but rather an effective atomic partial charge resulting from the charge equilibration (QEq) scheme.

This fractional value reflects a well-understood physical phenomenon: covalent interaction and charge transfer from the ligands (water molecules) to the cation. When a Ca^{2+} ion is solvated, the highly electronegative oxygen atoms of the coordinating water molecules donate a small amount of electron density towards the cation. This electron density does not fully “reduce” the calcium, but rather occupies the space between the Ca core and the water ligands, effectively

screening the +2 nuclear charge. Consequently, the Ca atom itself holds a partial charge less than +2, while the surrounding water molecules become more polarized. This is a physically realistic representation of electronic polarization.

As shown in the revised **Figure S11a**, DFT calculations consistently show that both Bader and Mulliken partial charges of solvated Ca ions (Cac) are significantly less than their formal +2 charge and comparable to the ReaxFF charges. Also, previous ab initio calculations on tobermorite (C-S-H like crystals) also showed that the Ca ions feature partial charges of 1.66 ~ 1.7 rather than the formal +2 charge⁴. For the same reason, classical force fields like CSH-FF and INTERFACE FF also use point charges (+1.7e) to describe the aqueous Ca ions in the C-S-H like minerals^{4,5}. These confirm that the dynamic partial charges in ReaxFF are not an artifact, but rather a more physically realistic representation than the fixed integer charges used in non-polarizable force fields, which cannot capture these crucial polarization and charge transfer effects. The DFT calculation procedures are provided in the “METHODS: Density functional theory calculations” section.

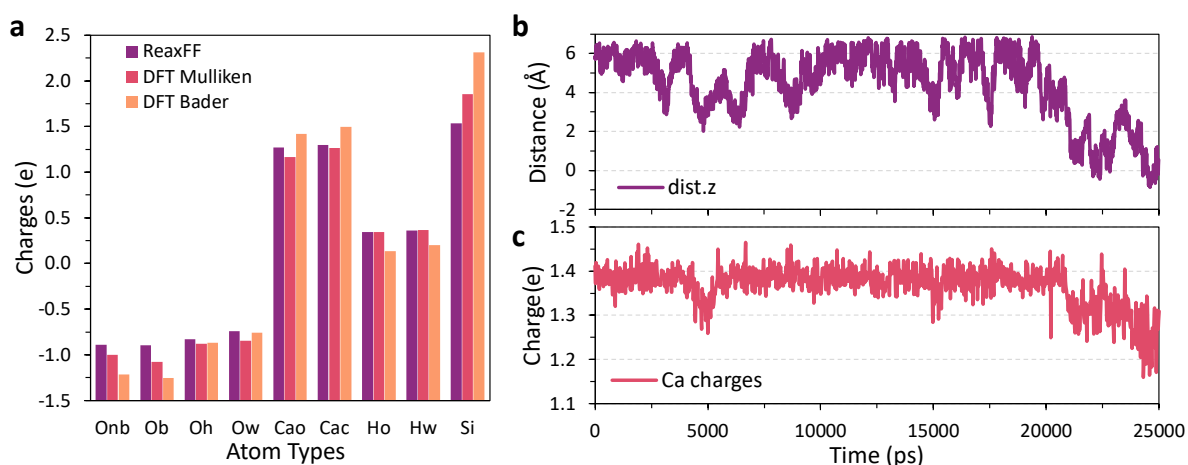


Figure S11. Tests of atomic charges. **a**, Comparison of the atomic charges calculated by ReaxFF to those obtained from DFT calculations for a C_{1.25}SH model. **b** and **c**, The evolution of dissolution distance in z direction and the atomic charge of the Ca ion with metadynamics simulation time respectively. The Ca ion was initially put in the solution above the surface and pushed back to its original position on the C-(A)-S-H surface.

Comment 5. “Surface charge and dipole effects:

The surface Ca ions in C-(A)-S-H are typically coordinated with free hydroxyl groups. As shown in **Figure 3d**, these hydroxyl groups often dissolve together with the Ca ion, partially compensating for the charge defect caused by dissolution. This phenomenon is consistent with experimental observations, where Ca ion dissolution is often accompanied by an increase in solution pH. On the other hand, unlike simple crystalline minerals (e.g., NaCl), C-(A)-S-H is an amorphous mineral with a complex surface chemistry. Experimental studies have shown that the dissolution of C-(A)-S-H is not stoichiometric. The dissolution rate of Ca ions is significantly higher than that of anionic groups (e.g., [SiO₄] tetrahedra), especially when the Ca/Si ratio is greater than 1 (see **Figure R2**)^{13, 14}. As a result, the surface of C-(A)-S-H in contact with solution is often negatively charged^{16, 17}. For long time dissolution, positive ions from the solution may adsorb onto the C-(A)-S-H surface, neutralizing the surface charge over time. The final surface charge depends on the equilibrium activity of Ca ions in solution (see **Figure R3**)¹⁷. Our simulations focus on the initial, non-equilibrium dissolution stage of C-(A)-S-H. During this stage, the surface produced by Ca ion dissolution is expected to carry a negative charge, especially when the dissolved hydroxyl groups are insufficient to fully compensate for the charge defect. This behavior is consistent with the real dissolution characteristics of C-(A)-S-H.”

We understand that the surface dissolution in the case of CASH is complicated. However, comparing and averaging free energy barriers for dissolution processes that produce different end states, i.e. where the Ca ion can be coordinated with an unknown number of hydroxide ions seems a simplistic approach. Particularly if the hydroxide ions detach during the dissolution process, the metadynamics simulations will suddenly start to explore different portions of the phase space.

In fact, the dissolution rate should come from a weighted average of the rates, with the

weight being the Boltzmann factor of the dissolution barrier.

Moreover, as also pointed out by another reviewer, the Ca coordination number is an important, and probably slow, degree of freedom, which might affect the computed free energy. Although the water exchange rate is of the order of 100ps, that may not be the case for the Ca-OH coordination number. Hence, neglecting the Ca-H₂O/OH- coordination number can greatly affect the results, in unknown ways; and the results would depend on the starting configuration.

Adding a fourth CV, would make the calculations much more expensive, but now that the authors are using a cylindrical restraint, they should have removed the x and y CVs, which don't add anything to the results (fig S6-S9), and include the coordination number instead.

Authors' Reply: We thank you for these very insightful comments.

1. Consistency of the Dissolved State

We agree that different end-states would be problematic for the convergence of metadynamics. However, based on our observations and the chemical nature of the system, we argue that our simulations describe a consistent dissolution pathway. As we show in **Figure 3d**, the Ca ions on the C-(A)-S-H surface are often coordinated to one or more hydroxyl groups. Due to the strong electrostatic attraction, these OH⁻ groups act as tightly bound ligands and dissolve together with the Ca ion. The event of an OH⁻ ligand detaching from the Ca ion during dissolution is not observed in our simulations.

From a more fundamental perspective, the key event defining dissolution is the cleavage of bonds between the Ca ion and the immobile C-(A)-S-H silicate framework. Whether the Ca ion's first solvation shell in solution contains an OH⁻ (from the surface) or a H₂O (from the bulk) does not change the fact that it has transitioned from a "surface-bound" state to a "solvated" state. The critical slow process being overcome is the detachment from the surface, which our chosen CVs are designed to capture.

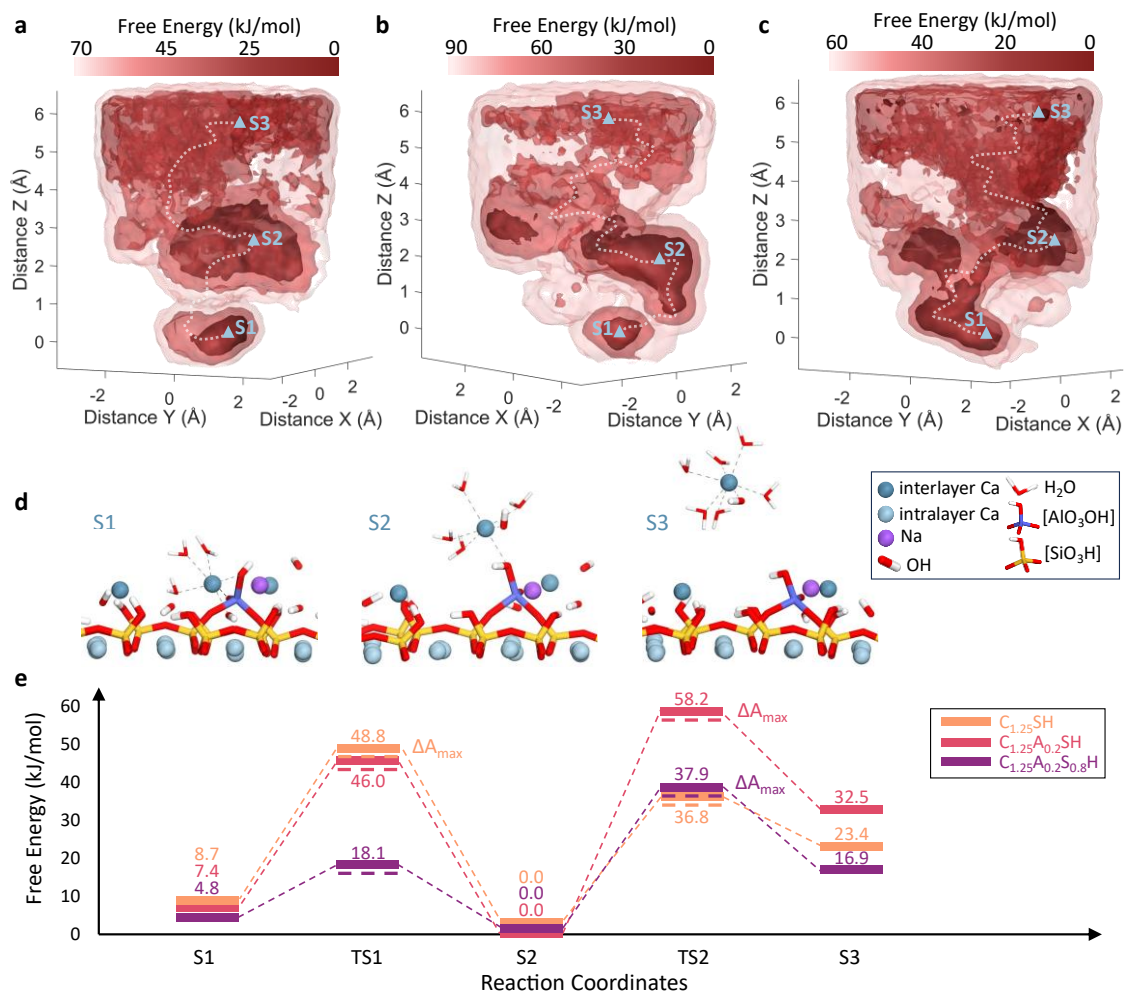


Figure 3. Atomistic mechanisms and thermodynamics of C-(A)-S-H decalcification. **a-c**, Representative three-dimensional free energy landscapes for calcium dissolution from $C_{1.25}SH$, $C_{1.25}A_{0.2}SH$, and $C_{1.25}A_{0.2}S_{0.8}H$ respectively. These landscapes depict the free energy as a function of calcium dissolution displacement along the x, y, and z axes. The origin (0, 0, 0) represents the initial state (S1) of the calcium ion. Dotted lines trace the minimum free energy pathway for calcium dissolution explored using NEB method, while wathet triangles mark key intermediate states (local free energy minima, S1-S3) along the pathway. **d**, Simulation snapshots showing calcium dissolution stages using the $C_{1.25}A_{0.2}SH$ system as a paradigm: S1 (surface-adsorbed state), S2 (inner-sphere adsorbed state), and S3 (fully dissolved state). **e**, Calcium dissolution energetics encompassing all intermediate states (S1-3) and transition states (TS1-2) obtained from . The total dissolution free energy barriers (ΔA_{max}) are the free energy differences between the lowest-energy intermediate state and the highest-energy TS along the dissolution pathway.

2. Comparing Free Energy Barriers (ΔA) vs. Calculating Absolute Rates

You are correct that, in theory, one could calculate rate constants for each energetic dissolution pathway using Transition State Theory (TST). However, we argue that for this specific system, a direct comparison of the activation free energy barrier (ΔA) with experimentally derived activation energies is a more direct and robust approach.

Firstly, calculating accurate absolute rate constants via TST is notoriously challenging, as it is highly sensitive to the full convergence of the free energy landscape, especially the product basin (dissolved states). As we acknowledged in our reply to Comment 2, achieving full convergence for the solvated state (S3) is computationally prohibitive and not the central goal of this study. Any rate constant calculated from an unconverged product state would carry a large, unquantifiable error. Even for the forward dissolution reaction only, the calculated rate constant can be quite noisy.

Secondly, experimental kinetic studies on mineral dissolution typically report macroscopic dissolution rates (rather than the dissolution rate constants) as a function of temperature. From

these temperature-dependent rates, an overall experimental activation energy can be derived via an Arrhenius analysis. This experimental activation energy is the most direct counterpart to our calculated forward free energy barrier (ΔA). Therefore, comparing ΔA across different sites provides the most meaningful link between our atomistic simulations and macroscopic experimental observations.

3. Choice of Collective Variables

The most critical point you raise is whether the Ca-OH/H₂O coordination number (CN) is a more important CV than the lateral (x, y) displacement. To definitively answer this, we followed your valuable suggestion and performed additional metadynamics simulation tests using a 2D CV set composed of: (CV1) the z-displacement and (CV2) the Ca-H₂O/OH⁻ coordination number.

As shown in **Figure S12**, the free energy barrier (ΔA) calculated using this {CN_Ow/Oh, dist.z} CV set was higher than the barrier calculated using our original {dist.x, dist.y, dist.z} CV set. This finding indicates that constraining the reaction coordinate to a specific coordination number evolution (the {CN_Ow/Oh, dist.z} path) actually forces the system over an artificially high barrier. The unconstrained 3D spatial CVs {dist.x, dist.y, dist.z} allow the system to find the true, lower-energy Minimum Energy Path. Our 3D free energy landscapes reveal that this true path is often a spiral or helical trajectory, where lateral movement is essential for the ion to navigate the complex potential energy surface of the amorphous solid. This underscores that the x and y displacements are not redundant but are, in fact, crucial degrees of freedom for describing the most favorable dissolution pathway.

Furthermore, we analyzed the evolution of the coordination numbers of the Ca ion during dissolution when using the 3D {dist.x, dist.y, dist.z} CV set. By projecting the 3D free energy landscape onto the Ca coordination numbers with aqueous oxygen (CN_Ow/Oh) and surface silicate oxygen (CN_Os), as shown in **Figure S13**, we observe a clear and physically sensible evolution. This demonstrates that while the CN is not biased, it is correctly and automatically captured as the Ca ion dissolves. This finding serves as a validation of both our CV selection and the underlying ReaxFF force field's ability to describe these complex chemical changes.

In summary, our analysis and direct comparative tests demonstrate that our chosen methodology is appropriate for capturing the essential physics of this specific system. We have added this new comparative CV analysis to the Supplementary Information and have clarified our reasoning in the main text, and we thank you for prompting this validation, which has ultimately strengthened our study.

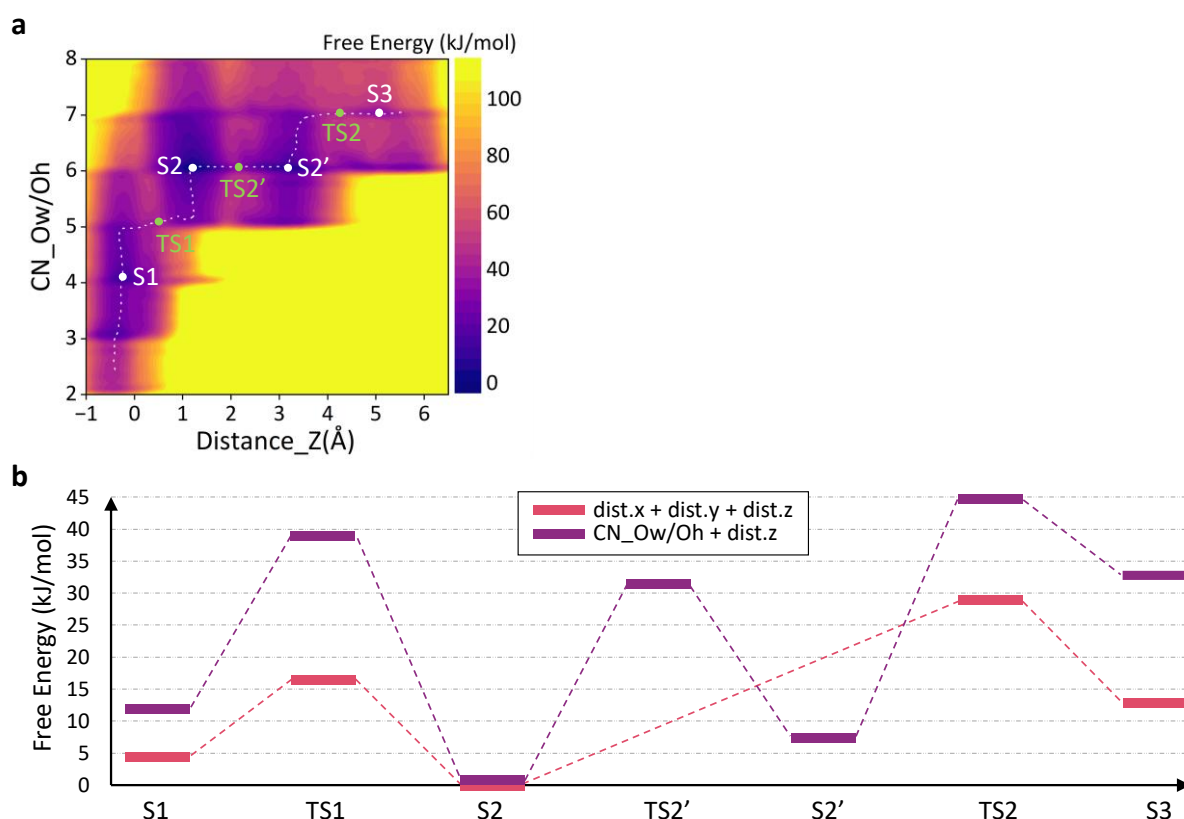


Figure S12. Tests of collective variables (CVs). **a**, Two-dimensional free energy landscape of Ca dissolution using the coordination number of aqueous oxygen (CN_Ow/Oh) and the displacement in z direction (dist.z) as two CVs. The white dashed line indicates the minimum dissolution free energy pathway and important metastable states (S1, S2, S2', S3) and transition states (TS1, TS2', TS2) are labelled. **b**, Comparison of calculated dissolution free energy barriers using the two sets of CVs: {CN_Ow/Oh, dist.z} and {dist.x, dist.y, dist.z}. The free energy barrier calculated using this {dist.z, CN_Ow/Oh} CV set was higher than the barrier calculated using our original {dist.x, dist.y, dist.z} CV set. This finding indicates that constraining the reaction coordinates to a specific coordination number evolution (the {dist.z, CN_Ow/Oh} path) actually forces the system over an artificially high barrier. The unconstrained 3D spatial CVs {dist.x, dist.y, dist.z} allow the system to find the true, lower-energy minimum energy path. For these well-tempered metadynamics tests, the width, initial height and deposition pace of Gaussian penalty potentials, and bias factor are 0.1 Å, 1.5 kJ/mol, every 600 steps, and 15 respectively.

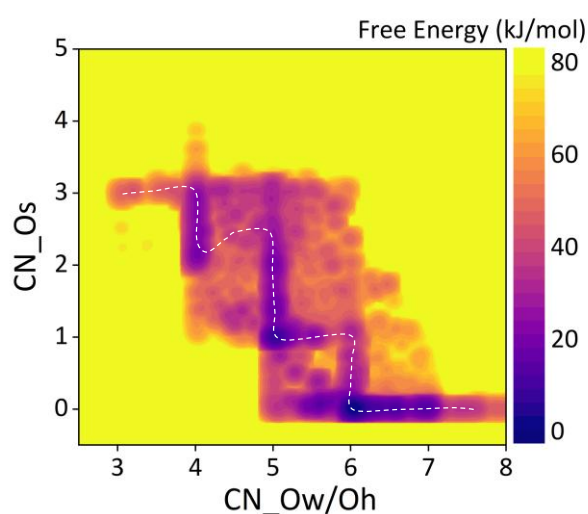


Figure S13. Two-dimensional projection of free energy landscape on the Ca coordination numbers with aqueous oxygen (CN_Ow/Oh) and surface silicate oxygen (CN_Os). The white dashed line indicates the minimum dissolution free energy pathway.

Comment 6. “We calculated the dissolution free energy for **all 32 Ca ions** on each slab model, ensuring comprehensive coverage of the surface chemical variability. The calculated dissolution free energies were subjected to statistical analysis to account for the variability in chemical environments. This approach allows us to compare the results with experimental decalcification kinetics, which capture the overall behavior of the heterogeneous C-(A)-S-H system.”

32 Ca ions, hardly seems to be representative of an experimental amorphous model. What “statistical analysis” was performed to “account for the variability in chemical environments”? How many different amorphous samples were prepared?

Authors’ Reply: Thank you for your insightful comment.

1. Representativeness of the Amorphous Models

Our study is based on three distinct amorphous C-(A)-S-H models, each with a different, experimentally relevant composition (i.e., Ca/Si and Al/Si ratios). These models were generated using well-established and widely adopted protocols for creating realistic atomistic structures of C-(A)-S-H ¹².

In principle, for any given bulk composition, multiple atomic configurations of the amorphous C-(A)-S-H could exist. The core justification for our approach rests on the principle that the macroscopic properties of C-(A)-S-H are predominantly determined by its chemical composition (e.g., Ca/Si ratio), rather than by the subtle variations between different random configurations of the same composition. This principle is strongly supported by foundational research in the field. For example, a landmark study by Pellenq et al. ¹² used grand canonical Monte Carlo simulations to generate numerous C-S-H structures. Their results (**Figure R1**) clearly showed that the formation free energies of different configurations cluster very tightly for a given Ca/Si ratio, while there are significant energy differences between structures with different Ca/Si ratios. This demonstrates that structures with the same composition are, for practical purposes, thermodynamically equivalent.

Therefore, our three models are not merely three random samples; they are chosen to be representative of three distinct thermodynamic and chemical families of C-(A)-S-H. This approach allows us to effectively and efficiently investigate how compositional differences—the most critical variable—impact the structure and dissolution properties.

[Figure Redacted]

Figure R1. Polymorphism in C-S-H. (A) Free energy as a function of Ca/Si ratio ¹².

2. Statistical Analysis and Intra-Model Sampling

Within each of these three representative models, the amorphous nature dictates a complete lack of surface symmetry. The local coordination environment of each surface Ca ion is unique. To capture the overall dissolution behavior of a single C-(A)-S-H surface, it is therefore essential to sample a large number of these non-equivalent Ca sites.

This is the context for our “statistical analysis”. For each of the three models, we calculated the dissolution free energy barrier for every accessible surface Ca ion (approximately 32 ions per model, totaling over 90 simulations). Our analysis then involves examining the distribution of these calculated energy barriers. This distribution provides a quantitative measure of the surface’s energetic heterogeneity. By comparing these distributions across the three different C-(A)-S-H models, we can draw robust conclusions about how bulk composition influences the kinetics of decalcification at the nanoscale.

Comment 7. “The average dissolution free energies for surface Ca ions in C_{1.25}SH, C_{1.25}A_{0.2}SH, and C_{1.25}A_{0.2}S_{0.8}H are approximately 41.7 kJ/mol, 47.0 kJ/mol, and 36.2 kJ/mol, respectively (Figure 5d).”

I would suspect that by reporting the 95% confidence intervals for the free energy barriers obtained from the MD simulations, the simulations number would be largely indistinguishable from each other, and that any computational value would produce a decent fit of the experiment. The solid lines in figure 5e, should be reported with the 95% confidence band.

Also, those are not “dissolution free energies”, but “activation (free) energies”. The dissolution free energy is the difference between the bulk and dissolved state.

Why 90% confidence interval? Usually, people report the 95% confidence interval.

The authors should also report all the 90 individual free energy values as a table in the SI, as well as the 1D dissolution free energy profiles projected onto the z CV.

Another useful information would be to know the variability of the Ca coordination environment in the dissolved state is. This could just be a number in a table as #H₂O/#OH-

Authors’ Reply: Thank you for these constructive suggestions.

1. 95% Confidence Interval

We agree that the 95% confidence interval is the standard for statistical reporting. The “average activation energies” have been recalculated using data with 95% confidence intervals. We have replotted **Figure 5e** to include the 95% confidence bands for the fitted lines. The revised figure is now in the manuscript. The average ΔA for surface Ca ions in C_{1.25}SH, C_{1.25}A_{0.2}SH, and C_{1.25}A_{0.2}S_{0.8}H within 95% confidence intervals are approximately 41.4 kJ/mol, 46.1 kJ/mol, and 35.2 kJ/mol, respectively, which are still distinguishable from each other.

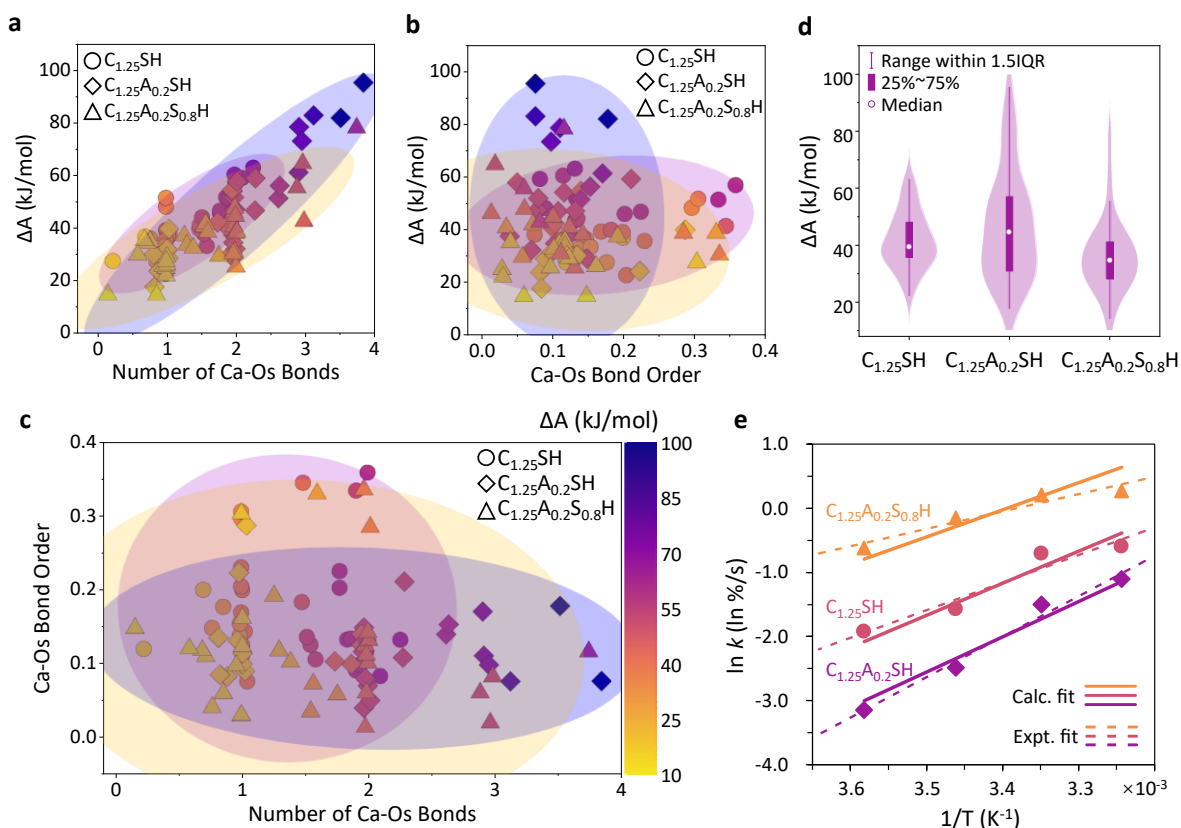


Figure 5. Activation free energy of dissolution for all calcium sites on C-(A)-S-H surfaces and comparison with experimentally measured decalcification activation energy. **a**, Activation free energy (ΔA) as a function of the initial number of Ca-Os bonds at calcium sites. Os stands for the oxygen of the aluminosilicate chains. Fractional Ca-Os bond counts rise from the use of a switching function to represent coordination numbers as continuous functions of interatomic distance. **b**, ΔA as a function of the Ca-Os bond order. For calcium sites with multiple Ca-Os bonds, the mean Ca-Os bond order is used. **c**, ΔA as a function of both the initial number of Ca-Os bonds and the Ca-Os bond order. The translucent red, purple, and yellow ellipses delineate the data ranges within the 95% confidence interval for $C_{1.25}SH$, $C_{1.25}A_{0.2}SH$, and $C_{1.25}A_{0.2}S_{0.8}H$, respectively. **d**, Distribution of ΔA for all surface Ca sites. **e**, The experimentally measured decalcification rates (k) of C-(A)-S-H at different temperatures (T) were fitted using the Arrhenius equation: $\ln k = -\frac{E_a}{R} \frac{1}{T} + \ln k_0$, where R is the gas constant, and E_a (activation energy) and $\ln k_0$ (a constant) are the fitting parameters. The dotted lines represent the experimental fits with their slopes ($-\frac{E_a}{R}$) reflecting the experimentally determined activation energy for decalcification. The solid lines represent Arrhenius-like functions defined as: $y = -\frac{A}{RT} + B$, where A is the calculated ΔA (mean values of data ranges within the 95% confidence interval), and B is an adjusted constant.

2. ΔA vs. ΔG

You are correct. Our use of “dissolution free energy” to describe the energy barrier was imprecise. The values we discuss in **Figure 5** represent the activation free energy for the dissolution process (ΔA), not the overall thermodynamic dissolution free energy (the difference between reactant and product states). We have corrected this terminology throughout the manuscript and figure captions to ensure accuracy.

3. Supplementary Information

Based on your suggestions, we have added a new table (**Table S6**) to the Supplementary Information, which lists the individual activation free energy values for all ~90 simulations performed. It also includes data on the coordination environment of the Ca ion in the fully dissolved state, reported as the average number of coordinating H_2O molecules and OH^- ions. We have also added the 1D free energy profiles (projected onto the z-coordinate) for all simulations (**Figure S14-S16**). The tabulated data are provided in the Source Data file.

Table S6. Summary of all calculated dissolution activation free energies (ΔA) of C-(A)-S-H surface Ca sites. “#Ca-Os” indicates the initial coordination number of surface Ca ions with surface oxygens (Os). “#Ca-Ow” and “#Ca-Oh” denote the coordination numbers of fully dissolved Ca ions with water oxygens (Ow) and free hydroxyl groups (Oh), respectively. To mitigate the statistical deviations of coordination calculations from thermodynamic fluctuations, for both the initial undissolved state and fully dissolved state, the calculated coordination numbers are the mean values over 100-picosecond simulation trajectories. The fractional coordination numbers arise from the use of a switching function to represent coordination numbers as continuous functions of the interatomic distance.

Ca id	C _{1.25} SH				C _{1.25} A _{0.2} SH				C _{1.25} A _{0.2} S _{0.8} H			
	#Ca-Os	#Ca-Ow	#Ca-Oh	ΔA (kJ/mol)	#Ca-Os	#Ca-Ow	#Ca-Oh	ΔA (kJ/mol)	#Ca-Os	#Ca-Ow	#Ca-Oh	ΔA (kJ/mol)
1	1.9	6.93	0	48.10	3.12	5.57	0.98	82.98	2.96	6.23	1	64.72
2	1.04	6.76	0.01	37.97	2.91	6.36	0.01	78.57	1.97	5.08	1.99	46.12
3	2.09	6.29	0.98	59.08	1.94	5.5	1	30.71	0.99	6.43	0.01	24.90
4	0.99	5.76	0.98	39.18	2.27	5.36	0.99	46.85	1.54	5.95	0.99	40.73
5	0.76	6.23	1	36.15	1.99	5.76	1.01	32.22	0.99	5.45	1	22.07
6	1.58	5.63	0.98	33.25	1.98	5.93	1.01	47.39	0.76	5.68	1	35.07
7	1.93	6.89	0.02	42.28	1.96	5.75	0.98	28.94	1.25	6.26	0.99	37.19
8	0.85	5.62	0.96	27.44	0.88	5.56	1	23.80	0.71	6.29	0.98	34.35
9	1.54	5.86	0.98	37.98	3.84	5.43	1	95.40	2.88	6.1	1.01	55.48
10	1.47	6.18	1	39.74	0.82	5.58	1	17.74	1.97	5.3	1.01	40.78
11	1	6.98	0	35.95	1.96	5.35	0.98	37.47	0.68	5.63	0.99	35.51
12	0.22	6.17	0.97	27.52	1.96	5.01	2	34.70	0.85	6.01	1	14.60
13	1.83	6.27	0.99	43.43	1.02	6.23	1	28.83	0.95	5.43	0.99	25.56
14	1.98	6.25	0.96	60.32	2.95	5.97	1	73.27	2	7.02	0	25.42
15	0.69	6.19	1	36.81	2.28	6.25	1	59.14	1.99	4.9	1.99	38.16
16	1.99	5.65	0.98	56.76	1.86	5.96	1.01	40.82	1.56	6.17	0.98	41.82
17	1	6.18	0.95	38.97	1.97	5.37	0.99	51.83	1.98	4.84	2	47.73
18	1.77	6.39	0.02	45.77	1.73	5.61	1.01	42.27	1.75	6.15	0.99	29.58
19	1.02	6.21	0.95	36.98	1	5.27	1.97	31.51	1	5.82	0.99	26.13
20	0.99	4.97	1.96	22.60	0.96	5.4	0.99	28.61	1.29	6.12	1	33.69
21	1.77	5.29	1.01	46.64	1.95	4.9	1.98	54.06	1.38	7.01	0.02	32.68
22	0.99	5.53	1.01	48.16	0.97	5.29	1.01	24.22	1.59	6	0.99	38.56
23	2.25	6.03	0.97	63.06	1	5.35	0.99	32.22	0.58	5.84	0.99	29.94
24	0.99	5.94	1	35.55	0.81	5.52	1	30.21	0.15	6.08	0.98	14.79
25	1	5.12	1.97	29.72	1.94	6.67	0	54.67	1	5.29	1.01	29.09
26	1.48	5.43	1	41.25	2.01	6.01	1	57.77	2.98	5.87	0.99	42.74
27	1.51	5.59	1	44.06	2.61	5.48	0.98	51.45	1.99	5.18	1.99	44.61
28	1.86	6.74	0	51.76	2.63	6.29	0.99	56.27	2.01	5.93	0.98	38.65
29	0.98	5.8	0.95	32.53	1.98	6.82	0.01	47.06	1.98	5.45	0.99	30.95
30	0.98	6.24	1.02	33.25	1.03	7.11	0	39.90	0.99	5.95	0.99	27.52
31	0.99	5.7	0.97	51.56	2.9	5.81	0.98	61.32	1.96	6.22	0.99	30.42
32	1.9	4.89	1.99	51.23	3.51	5.86	1.01	82.04	3.74	6.16	1	78.21

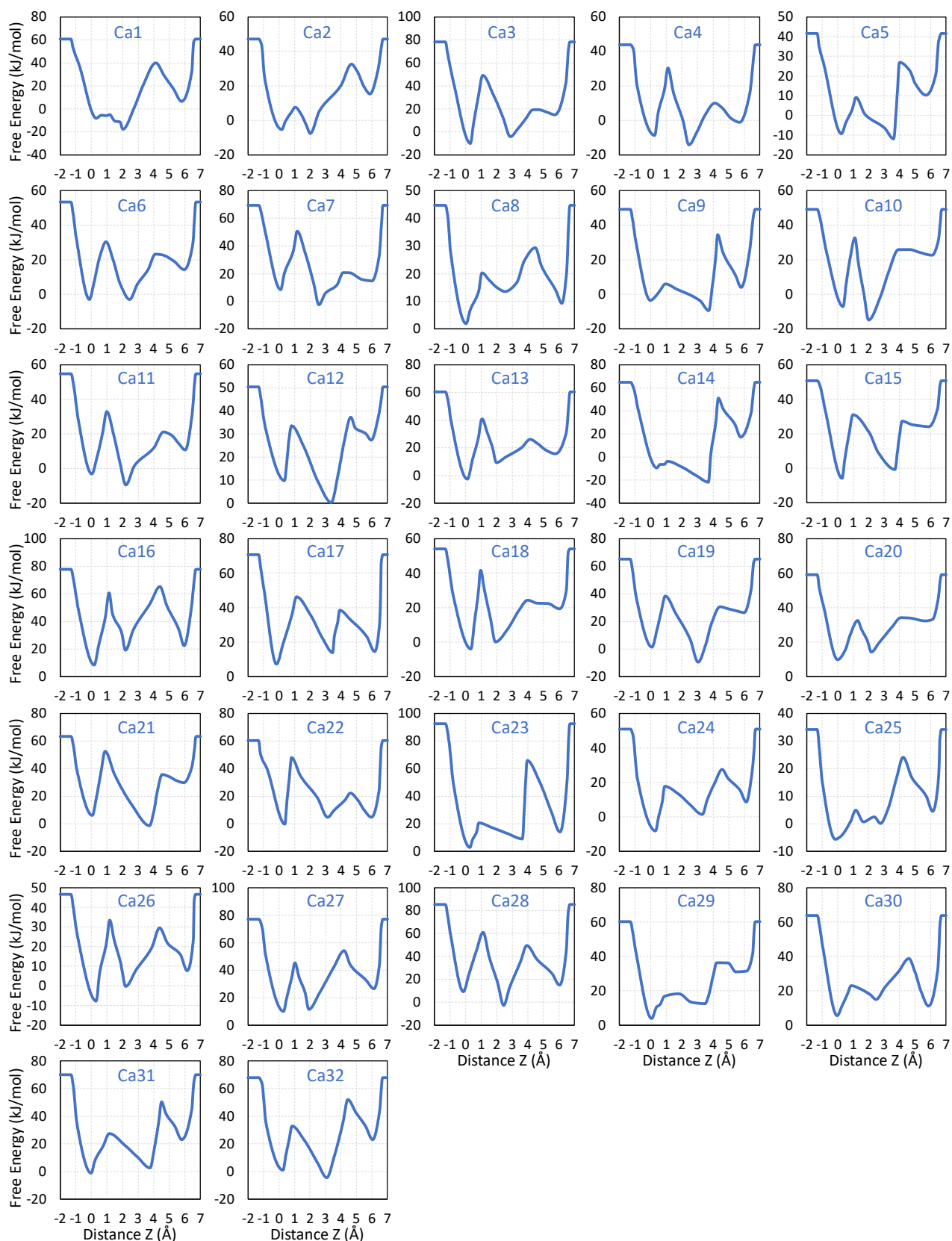


Figure S14. Dissolution free energy profiles of different surface Ca sites for C_{1.25}SH. The profiles are projections of three-dimensional free energy landscape onto the collective variable “Distance Z”.

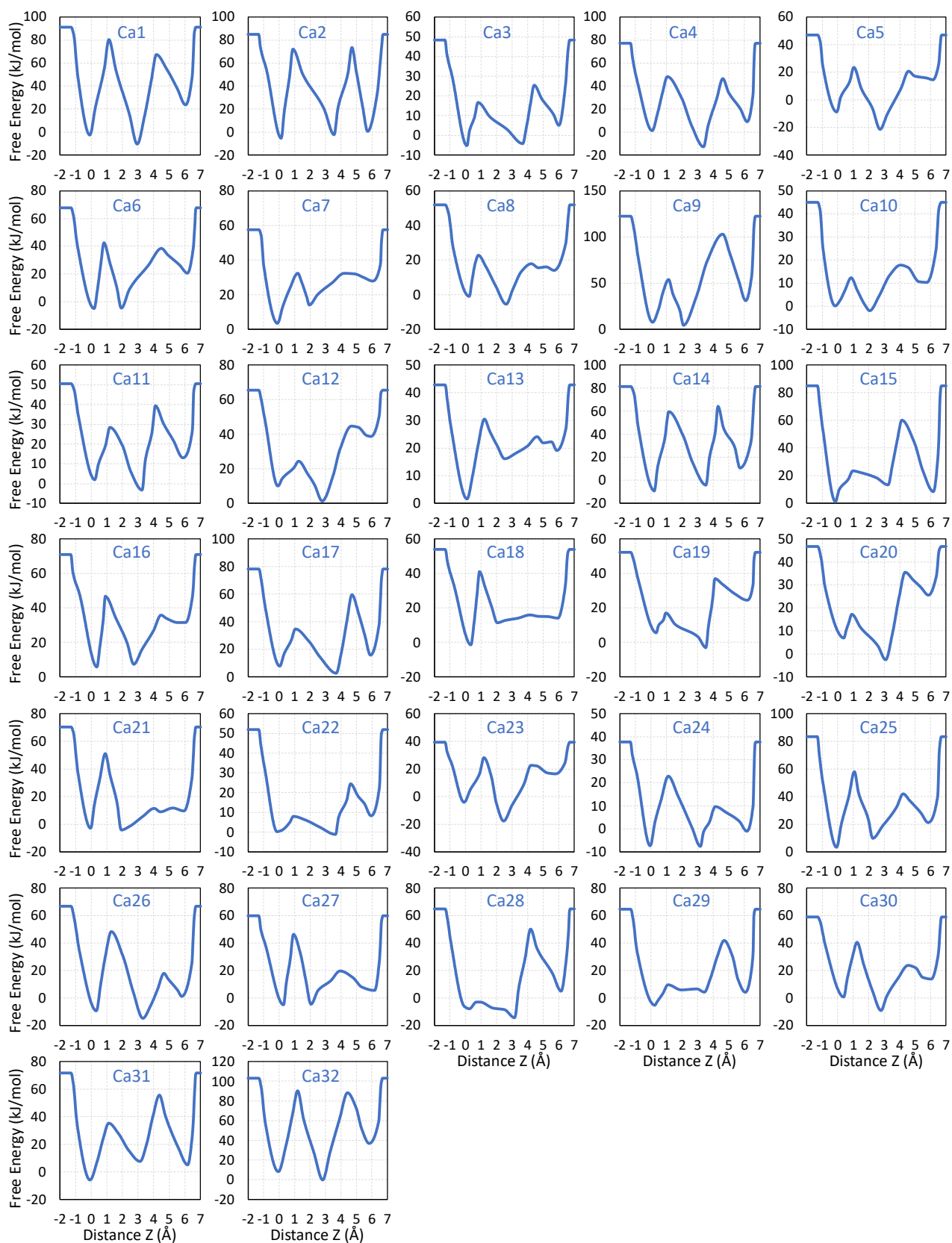


Figure S15. Dissolution free energy profiles of different surface Ca sites for $C_{1.25}A_{0.2}SH$. The profiles are projections of three-dimensional free energy landscape onto the collective variable “Distance Z”.

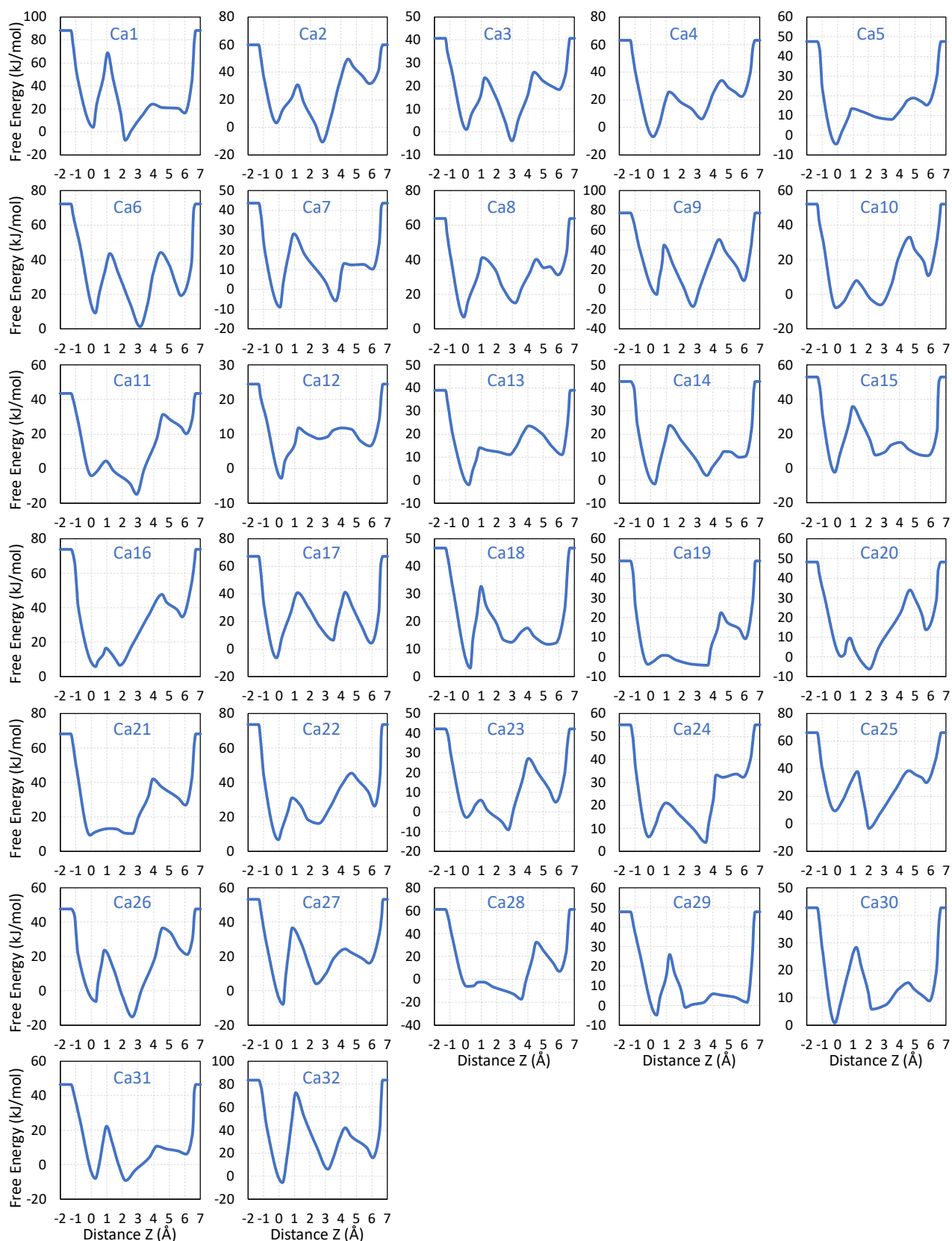


Figure S16. Dissolution free energy profiles of different surface Ca sites for $C_{1.25}A_{0.2}S_{0.8}H$. The profiles are projections of three-dimensional free energy landscape onto the collective variable “Distance Z”.

References

1. Armstrong BI, Silvestri A, De La Pierre M, Raiteri P, Gale JD. Determining the Complete Stability of Calcite Kink Sites: Real vs Ideal. *The Journal of Physical Chemistry C* **127**, 13958-13968 (2023).
2. Aufort J, Armstrong BI, Raiteri P, Gale JD. Thermodynamics of Magnesium Binding at Calcite Kink Sites and Implications for Growth inhibition. *Crystal Growth & Design* **24**, 8961-8969 (2024).
3. Silvestri A, Raiteri P, Gale JD. Obtaining consistent free energies for ion binding at surfaces from solution: Pathways versus alchemy for determining kink site stability. *Journal of chemical theory and computation* **18**, 5901-5919 (2022).
4. Shahsavari R, Pellenq RJ, Ulm FJ. Empirical force fields for complex hydrated calcio-silicate layered materials. *Physical Chemistry Chemical Physics* **13**, 1002-1011 (2011).
5. Mishra RK, *et al.* **cemff**. A force field database for cementitious materials including validations, applications and opportunities. *Cement and Concrete Research* **102**, 68-89 (2017).
6. Asgar H, *et al.* Probing Carbon Mineralization Mechanisms in Pore and Bulk Fluids by Harnessing Architected Calcium Silicates. *Energy & Fuels*, (2025).
7. Dasgupta N, Chen C, van Duin ACT. Development and application of ReaxFF methodology for understanding the chemical dynamics of metal carbonates in aqueous solutions. *Physical Chemistry Chemical Physics* **24**, 3322-3337 (2022).
8. Dupuis R, Hahn SH, van Duin ACT, Pellenq RJM, Poulesquen A. Condensation and growth of amorphous aluminosilicate nanoparticles via an aggregation process. *Physical Chemistry Chemical Physics* **24**, 9229-9235 (2022).
9. Manzano H, Pellenq RJ, Ulm FJ, Buehler MJ, van Duin AC. Hydration of calcium oxide surface predicted by reactive force field molecular dynamics. *Langmuir* **28**, 4187-4197 (2012).
10. Muraleedharan MG, Herz-Thyhsen R, Dewey JC, Kaszuba JP, van Duin ACT. Understanding the chemistry of cation leaching in illite/water interfacial system using reactive molecular dynamics simulations and hydrothermal experiments. *Acta Materialia* **186**, 564-574 (2020).
11. Stack AG, Raiteri P, Gale JD. Accurate rates of the complex mechanisms for growth and dissolution of minerals using a combination of rare-event theories. *Journal of the American Chemical Society* **134**, 11-14 (2012).
12. Abdolhosseini Qomi MJ, *et al.* Combinatorial molecular optimization of cement hydrates. *Nature communications* **5**, 4960 (2014).

Responses to Reviewers' Comments

Understanding calcium-aluminosilicate-hydrate decalcification: The aluminium paradox

Yong Tao, Yining Gao, Mohammad Javad Abdolhosseini Qomi, Roland J.-M. Pellenq, Chi Sun Poon

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First and foremost, we would like to express our thanks and appreciation for the referees' reviewing work. Their comments and constructive suggestions are very helpful to further improve the quality of our manuscript. It has now been revised in accordance with the reviewers' comments and suggestions. The revised content in manuscript is marked in red. The point-by-point responses to the reviewers' comments are as follows.

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Replies to Reviewer #4:

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Comment 1. One other possibility is to do reweighting to obtain the metal-water CN information and the associated free energy. Although using the current metadynamics data for reweighting could be tricky because the CN of metal is not directly biased. The outcome results could be used to compare with the additional simulations results shown in Fig. S12.

Authors' Reply: Thank you for this insightful suggestion. Following your recommendation, we have performed a reweighting analysis on our original metadynamics data, which used the 3D spatial coordinates {dist.x, dist.y, dist.z} as the biased CVs. The resulting free energy landscape is projected onto the unbiased {CN_Ow/Oh, dist.z} coordinates as presented in **Figure S12c**. As we anticipated, since these CVs were not directly biased, the sampling along these coordinates is not exhaustive, leading to a somewhat rugged free energy map. Nevertheless, the general dissolution pathway is observable and appears qualitatively similar to that from the biased simulation shown in **Figure S12b**.

We extended the simulation time of the biased {CN_Ow/Oh, dist.z} CV set as the previous test was not fully converged (**Figure S12a**). As shown in **Figure S12d**, both the reweighted {CN_Ow/Oh, dist.z} CVs and the biased {CN_Ow/Oh, dist.z} CVs yield relatively lower activation barriers compared to our original 3D spatial CV simulation. This indicates the {CN_Ow/Oh, dist.z} CV set is insufficient to resolve the true transition state from nearby intermediate states along the dissolution path. In this lower-dimensional projection, the transition state and certain meta-stable intermediates are effectively projected onto the same region of the CV space. This overlap leads to an averaging effect that artificially underestimates the true activation barrier. In contrast, the 3D spatial CVs {dist.x, dist.y, dist.z} provide the necessary resolution to distinguish these states, allowing the system to map out a path that identifies the more accurate, higher-energy transition state.

Figure S12b and related discussion have been revised in Supplementary Information and the

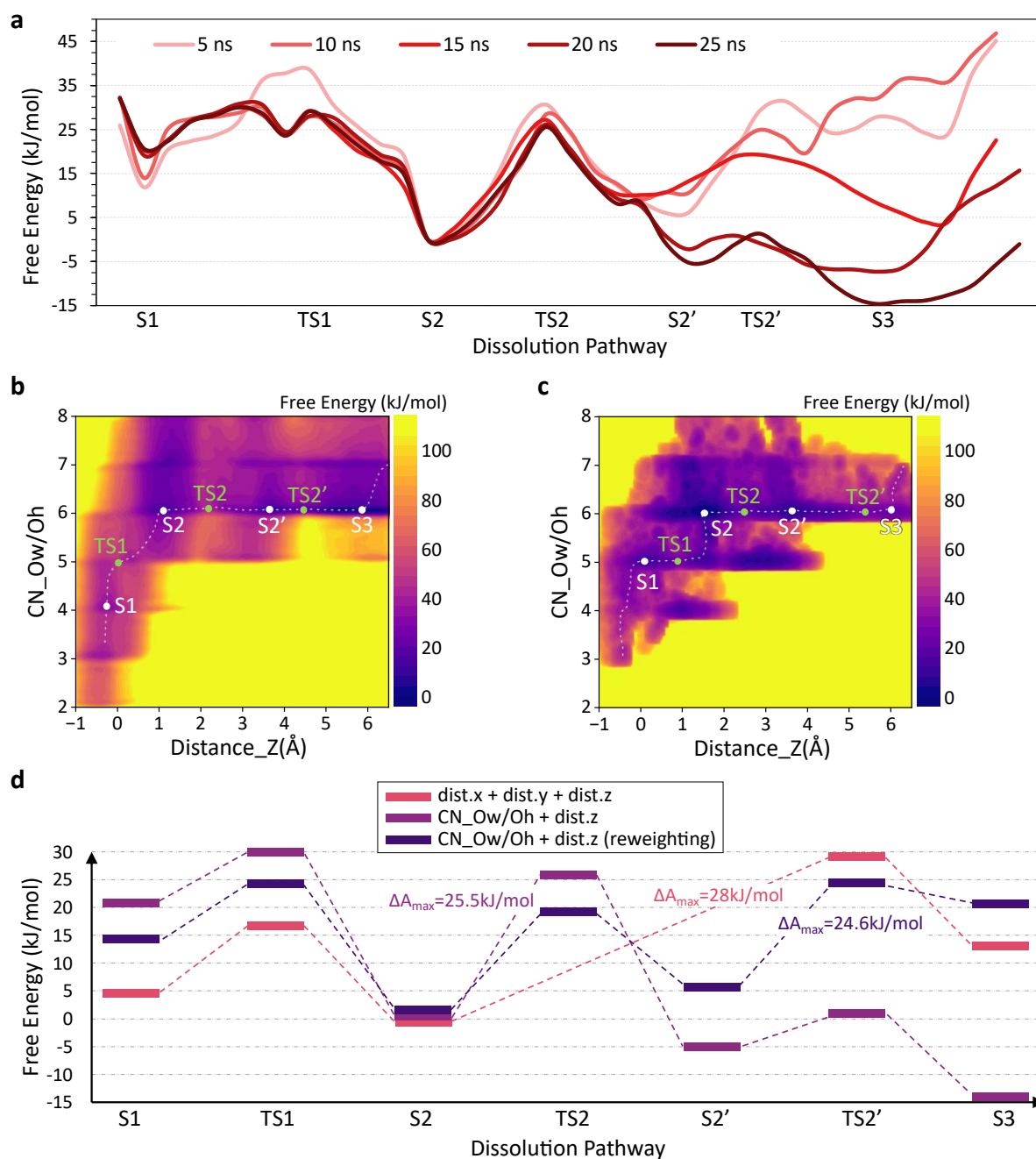


Figure S12 (renumbered as new Figure S11 in SI). Tests of collective variables (CVs). **a**, Time-dependent convergence of the free energy profiles along the minimum energy path using 2D biased {CN_Ow/Oh, dist.z} CV set. {CN_Ow/Oh, dist.z} denote the coordination number of aqueous oxygen (CN_Ow/Oh) and the displacement in z direction (dist.z) respectively. **b**, 2D free energy landscape of Ca dissolution using the biased {CN_Ow/Oh, dist.z} CV set (after 25 ns simulation). The white dashed line indicates the minimum dissolution free energy pathway and important metastable states (S1, S2, S2', S3) and transition states (TS1, TS2, TS2') are labelled. **c**, 2D free energy landscape of Ca dissolution as a function of the unbiased {CN_Ow/Oh, dist.z} CV set via reweighting of the original metadynamics using 3D biased {dist.x, dist.y, dist.z} CV set. **d**, Comparison of calculated dissolution free energy barriers using biased {dist.x, dist.y, dist.z} CV set, biased {CN_Ow/Oh, dist.z} CV set, and unbiased {CN_Ow/Oh, dist.z} CV set via reweighting. The overall free energy barrier calculated using our original {dist.x, dist.y, dist.z} CV set (28 kJ/mol) is higher than the other two cases. This indicates the {CN_Ow/Oh, dist.z} CV set is insufficient to resolve the true transition state from nearby intermediate states along the dissolution path. The overlap between the transition state and certain meta-stable intermediates leads to an averaging effect that artificially underestimates the true activation barrier. In contrast, the 3D spatial CVs {dist.x, dist.y, dist.z} provide the necessary resolution to distinguish these states, allowing the system to map out a path that identifies the more accurate, higher-energy transition state. For these well-tempered metadynamics tests, the width, initial height and deposition pace of Gaussian penalty potentials, and bias factor are 0.1 Å, 1.5 kJ/mol, every 600 steps, and 15 respectively.

Comment 2. In Figure S7, the activation energy did not change over time. Will there be less crossing of the energy barrier over time? It seems the in Fig. S7b, the fluctuation of z is not as often as that of x and y over time, especially considering z need to change from 0 to 6 multiple times. Is the crossing of barriers less frequent over time so that the barrier is not properly sampled and appear to be constant? Could you plot the evolution of the 1D free energy profiles and compare the relative energy difference between two reference status?

Authors' Reply: Thank you for this insightful question regarding the convergence of our metadynamics simulations. As you suggested, we have now plotted the evolution of the 1D free energy profile along the minimum energy path as a function of simulation time in the new **Figure S7c**.

Indeed, your observation from **Figure S7b** is correct: the frequency of barrier recrossing in the z-direction is lower than the lateral fluctuations. This is an expected physical behavior stemming from the vast difference in the phase space volume between the initial and final states. The initial state (Ca adsorbed on the surface) is a localized, well-defined basin. In contrast, the final, dissolved state represents a much larger, flatter phase space for the ion to explore in the bulk solution. Consequently, once the ion dissolves, it spends a considerable amount of time diffusing in this large region before it stochastically finds its way back to the narrow pathway leading to the initial state. The new **Figure S7c** provides a clear picture of the convergence process:

1. The free energy of the initial state (the basin on the left) converges very rapidly because its small phase space is sampled thoroughly and frequently.
2. The free energy of the dissolved state (the plateau on the right) converges more slowly, which is consistent with the extensive phase space that requires longer sampling.
3. Most importantly, the activation barrier—the relative free energy difference between the initial state and the transition state—stabilizes much earlier. As the plot demonstrates, after approximately 20 ns of simulation time, the calculated barrier height remains stable within a narrow tolerance.

Therefore, this analysis confirms that while the absolute free energy of the dissolved state takes longer to converge, the critical kinetic parameter for our study—the activation barrier—is properly sampled and well-converged within our simulation time.

Figure S7 and related discussion have been revised in Supplementary Information.

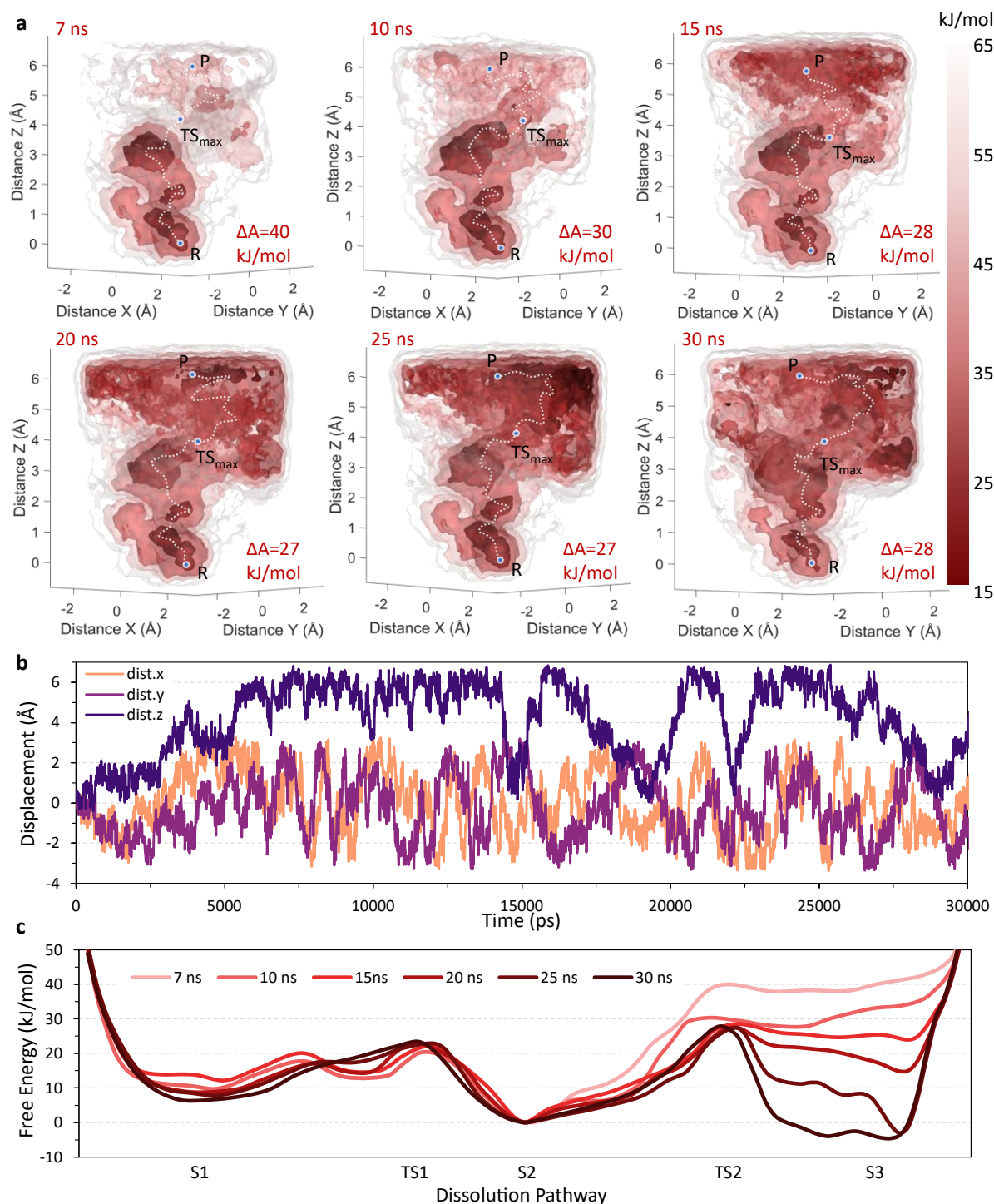


Figure S7 (renumbered as new Figure S13 in SI). Tests of simulation time for well-tempered metadynamics. a, The evolution of the three-dimensional free energy landscape of calcium dissolution with simulation time. The white dashed line indicates the Ca dissolution pathway identified via the Nudged Elastic Band method. The labels R, P, and TS_{max} represent the reactant (initial surface state), the product (fully dissolved state), and the highest-energy transition state, respectively. The overall dissolution free energy barrier (ΔA) is calculated as the energy difference between the lowest-energy state and TS_{max} along the Ca dissolution pathway. **b,** The evolution of collective variables (dissolution displacement components in x, y, and z directions: dist.x, dist.y, and dist.z) with simulation time. **c,** The one-dimensional free energy profile along the minimum energy pathway of Ca dissolution as a function of simulation time. After about 10 ns, the free energy near the surface no longer changes significantly, indicating that sampling is sufficient. Although extending the simulation time further could allow for more complete sampling of the solution space, the overall dissolution free energy barrier remains unaffected. Therefore, a simulation time of 15 ns is reasonable for the tested Ca ion site. Overall, for multiple surface Ca sites, the simulation times were determined as 15–30 ns because Ca sites with higher dissolution free energies require longer metadynamics simulations to dissolve. For these well-tempered metadynamics tests, the width, initial height and deposition pace of Gaussian penalty potentials, and bias factor are 0.1 Å, 1.5 kJ/mol, every 600 steps, and 15 respectively.

Comment 3. “As shown in Figure S12, the free energy barrier (ΔA) calculated using this {CN_Ow/Oh, dist.z} CV set was higher than the barrier calculated using our original {dist.x, dist.y, dist.z} CV set. This finding indicates that constraining the reaction coordinate to a specific coordination number evolution (the {CN_Ow/Oh, dist.z} path) actually forces the system over an artificially high barrier.”

The presence of a higher barrier by using a separate set of CV might imply the earlier energy barrier is underestimated. If the energy barrier from the previous simulation is always the highest value no matter how you change the CV, then it is more likely to conclude that the original choice of CV is appropriate.

Authors' Reply: We sincerely thank you for this critical and perceptive comment. Our previous statement was misleading. We agree completely with you that for fully converged metadynamics tests with different CVs, the optimal CV set should yield the highest free energy barrier, as it most accurately resolves the true transition state from any nearby intermediate states.

We studied the results of the previous test using {CN_Ow/Oh, dist.z} bias CV set and found that its higher energy barrier was due to the fact that the free energy did not converge completely. Therefore, we performed significantly longer simulations for the {CN_Ow/Oh, dist.z} CV set to ensure its convergence (**Figure S12a**). The converged dissolution energy barriers of the {CN_Ow/Oh, dist.z} CV set are compared with that of the original {dist.x, dist.y, dist.z} CV set in **Figure S12d**, which shows that the activation barrier from our original {dist.x, dist.y, dist.z} CV set is indeed higher. Moreover, for the 2D free energy projection on the unbiased {CN_Ow/Oh, dist.z} CV set via reweighting analysis, the resulting activation barrier is also lower than that of our original {dist.x, dist.y, dist.z} CV set as shown in **Figure S12d**. Therefore, among the widely used CV combinations for the ion dissolution simulation, the {dist.x, dist.y, dist.z} CV set we used here is a relatively more appropriate option. Other CVs besides water coordination number and dissolution distances can barely describe the state evolution of the ion dissolution, which thus are out of consideration.

Figure S12b and related discussion have been revised in Supplementary Information and the Manuscript.

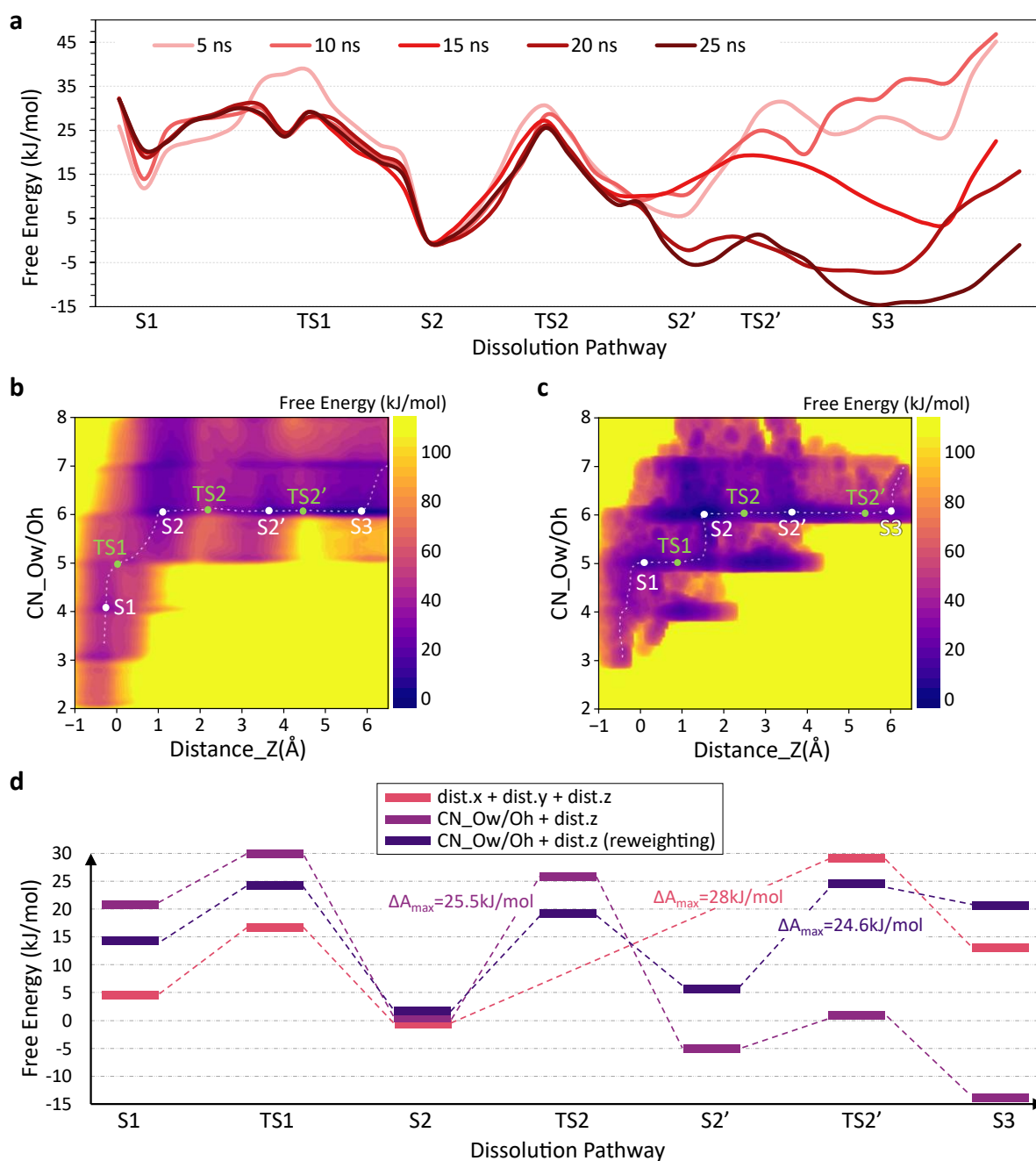


Figure S12 (renumbered as new Figure S11 in SI). Tests of collective variables (CVs). **a**, Time-dependent convergence of the free energy profiles along the minimum energy path using 2D biased $\{\text{CN_Ow/Oh}, \text{dist.z}\}$ CV set. $\{\text{CN_Ow/Oh}, \text{dist.z}\}$ denote the coordination number of aqueous oxygen (CN_Ow/Oh) and the displacement in z direction (dist.z) respectively. **b**, 2D free energy landscape of Ca dissolution using the biased $\{\text{CN_Ow/Oh}, \text{dist.z}\}$ CV set (after 25 ns simulation). The white dashed line indicates the minimum dissolution free energy pathway and important metastable states (S1, S2, S2', S3) and transition states (TS1, TS2, TS2') are labelled. **c**, 2D free energy landscape of Ca dissolution as a function of the unbiased $\{\text{CN_Ow/Oh}, \text{dist.z}\}$ CV set via reweighting of the original metadynamics using 3D biased $\{\text{dist.x}, \text{dist.y}, \text{dist.z}\}$ CV set. **d**, Comparison of calculated dissolution free energy barriers using biased $\{\text{dist.x}, \text{dist.y}, \text{dist.z}\}$ CV set, biased $\{\text{CN_Ow/Oh}, \text{dist.z}\}$ CV set, and unbiased $\{\text{CN_Ow/Oh}, \text{dist.z}\}$ CV set via reweighting. The overall free energy barrier calculated using our original $\{\text{dist.x}, \text{dist.y}, \text{dist.z}\}$ CV set (28 kJ/mol) is higher than the other two cases. This indicates the $\{\text{CN_Ow/Oh}, \text{dist.z}\}$ CV set is insufficient to resolve the true transition state from nearby intermediate states along the dissolution path. The overlap between the transition state and certain meta-stable intermediates leads to an averaging effect that artificially underestimates the true activation barrier. In contrast, the 3D spatial CVs $\{\text{dist.x}, \text{dist.y}, \text{dist.z}\}$ provide the necessary resolution to distinguish these states, allowing the system to map out a path that identifies the more accurate, higher-energy transition state. For these well-tempered metadynamics tests, the width, initial height and deposition pace of Gaussian penalty potentials, and bias factor are 0.1 Å, 1.5 kJ/mol, every 600 steps, and 15 respectively.

3. We would like to share our thoughts about the metadynamics simulations on mineral dissolution:

The total simulation time depends on the metadynamics parameters and the sampling space. While we fully agree that using highly precise parameters and long simulation times usually would yield more accurate results, computational resources often impose practical limitations (Figure R1). For instance, classical MD simulations can typically achieve hundreds of nanoseconds of sampling, while ab initio MD (AIMD) simulations are often limited to <1 ns due to their computational cost. Therefore, the parameters of AIMD-based metadynamics are rougher than those of classical MD-based metadynamics, although this will lead to the deterioration of the convergence of the former's calculation results. However, since the accuracy and universality of atomic potential adopted by AIMD is much higher than that of fitted classical force field, AIMD-based metadynamics has its advantages and existence value. In our study, we used ReaxFF-based simulations, which fall between AIMD and classical MD in terms of timescale. Therefore, the precision of our metadynamics parameters is also intermediate between those used in AIMD and classical MD.

This study primarily investigates the impact of surface structures on C-(A)-S-H decalcification thermodynamics. To achieve this, we aimed to sample a large number of surface sites to better represent the dissolution characteristics of amorphous C-(A)-S-H. While higher precision for a single Ca ion site could be achieved by focusing computational resources on one site, the decalcification characteristics of amorphous C-(A)-S-H are better captured by averaging data across a large number of Ca sites. As shown in Figure 5, the dissolution free energies for different Ca sites vary significantly, and the differences due to sampling precision for a single site are relatively negligible by comparison. Given that our three C-(A)-S-H models include over 90 surface Ca sites to consider, the refined metadynamics parameters provided in Table R1 represent the most feasible balance between accuracy and computational cost.

The atomistic mechanisms of aqueous mineral processes are largely dominated by the water dynamics and the entropy associated with the water exchange is one of the main contributions to the free energy, there is ample evidence of that, and the authors themselves discussed that the change in coordination environment of the Ca ion between the CASH, adsorbed and solution states. Therefore, having a correct sampling of the water dynamics is at least as important as having an accurate description of the interatomic interactions. Using “rough” metadynamics parameters and short simulations times, would lead to errors that can easily be larger than any gain in the accuracy of the molecular interactions that can be achieved by using an AIMD method.

One can simply test this by taking an empirical forcefield, and computing a well converged free energy, say for the ion-pairing, using proper metadynamics parameters, and then parameters typically used in AIMD (or those used in this work) and compare the results. For the short simulations, one should also test how the computed free energy depends on the starting configuration.

Moreover, no evidence is provided here that the ReaxFF model used by the authors is more accurate than a classical forcefield. In fact, see below, the authors show that the model predicts a partial charge for the solvated Ca^{2+} ion of +1, which is completely unphysical. Therefore, in my opinion, any quantitative agreement with the experimental dissolution activation energies for a gel/amorphous material is fortuitous. To the best of my knowledge, ReaxFF also doesn't use the Ewald summation method, hence the long range electrostatic effects may not be captured correctly.

We also want to emphasize that the deposition pace should be evaluated in terms of the number of simulation steps rather than absolute simulation time. This is because the timestep size determines how much the system evolves in each step. In our ReaxFF MD simulations, the timestep is 0.2 fs, meaning that each step induces only 20% of the relative perturbation caused by a classical MD step where the timestep is typically 1 fs. Consequently, the system requires less time to relax after each Gaussian deposition. Thus, the deposition pace of 600 steps in our ReaxFF MD simulations is comparable to the deposition pace commonly used in classical MD (e.g., 100-1000 steps)

This is incorrect, and it is actually the opposite of what the authors say. The system will take the same time to relax after each Gaussian deposition, this is an intrinsic time that is related to the diffusivity of the species, which need to have the time to diffuse further than the Gaussian's width. This means that with 0.2fs timestep, the system will take 5 times more MD steps to relax than if the simulation was run with a 1fs timestep. The deposition rate measured in (1/ps) should be the same, while the rate measured in (1/timesteps) should be slower for simulations with a shorter timestep, not faster. This is again easy to test with a simple model system.

Figures S6-S9

Looking at the various test that the authors have performed, it appears that the S2 state (inner-sphere adsorbed state) is always the most stable configuration, and that there is a huge variability in the relative free energy of the dissolved state, from ~5 to ~20 kJ/mol higher. This would suggest that the simulation protocol used here is extremely sensitive to the metadynamics parameters, and to the choice the initial set up.

Moreover, it's not very clear why the Ca should dissolve if the adsorbed state is the most stable configuration.

The concern you raised highlights an important point about the balance between simulation time and the stability of the studied system. While longer simulation times can improve sampling, they may also lead to undesirable changes in the system, such as significant rearrangement of the surface structure. For example, in systems with unstable initial configurations, long simulations might result in alterations to the phase space (e.g., significant surface restructuring), making the original reactant state inaccessible. Artificially constraining the initial structure (e.g., restricting the movement of atoms near the initial configuration) could prevent such rearrangements, but this would compromise the realism of the simulated reaction process. Therefore, the simulation time of metadynamics is not simply the longer the better, but must be carefully tailored to the specific system being studied.

I disagree with that statement.

A longer metadynamics simulation is always better. It ensures that the simulation explores as much as possible the configurational space, including possible slow degrees of freedom that have not been included in the CVs, which can manifest itself as hysteresis, large variability of the free energy differences, CV(s) being stuck at a given value and more.

If the surface (or the system in general) changes conformation/geometry during the simulation, then appropriate restraints need to be added to the simulation to prevent this from happening (and the corresponding free energy contributions need to be accounted for). In my view, running a short simulation, which is likely to produce a semi-random non-converged free energy value is not a better outcome.

Also, the fact that the chosen method (ReaxFF or AIMD) is slow is not a good reason to report non converged and unreliable free energy values. Given that a large fraction of the free energy contributions for aqueous processes comes from the water entropy, a more “approximate” method that allows for proper sampling the water dynamics can potentially produce more reliable results. I would indeed argue that a carefully parameterised classical forcefield that reproduces the experimental thermodynamic properties of the bulk and aqueous species can provide better results due to being able to achieve a more complete sampling of the entropic contributions.

1. Variability in the charge of Ca ions:

To validate the accuracy of the ReaxFF charge equilibration scheme, we compared the charges calculated by ReaxFF to those obtained from DFT calculations for a $\text{C}_{1.25}\text{SH}$ model (see **Figure S11a**). The results show excellent agreement between ReaxFF and DFT charges. The aqueous Ca ions (Ca_{aq}), primarily coordinated with water and hydroxyl groups, have a slightly higher charge than solid-state Ca ions (Ca_{ss}) in the interlayer. However, the difference in charge between Ca_{aq} and Ca_{ss} is small, indicating that ReaxFF provides a consistent and realistic description of the system.

In addition, we monitored the charge of the Ca ion during the dissolution process (see **Figure S11b**). When the Ca ion is fully dissolved, its charge slightly increases, consistent with the expected behavior of ions in solution. The charge changes reversibly as the Ca ion moves back and forth between the surface and solution, reflecting the dynamic nature of charge equilibration. More importantly, the Ca charge variation is small and consistent across different surface Ca sites, minimizing concerns about variability in the solvation free energy of the Ca ion in different simulations.

Since there is no experimental evidence that the Ca^{2+} solvated ion has an effective charge of around +1, these results suggest that the ReaxFF model employed here has unphysical properties. If Ca^{2+} has a charge of +1, which other part of the system has lost an electron?

The partitioning of the electronic density into atomic partial charges in DFT is an arbitrary process that requires the definition of a criterion to assign what charge belongs to each atom. The Mulliken charges are one of such methods, which is typically extremely inaccurate. One can simply compare Mulliken charges, with Bader charges, Hirshfeld charges, Wannier charges... to see how wildly the atomic partial charges can change. Hence, the fact that the ReaxFF partial charges agree with the Mulliken charges is not an indication that they are accurate, quite the contrary. What the authors are observing is an artifact of DFT which doesn't localise the charge very well with standard methods (there's no mention in the authors' reply of what DFT method they have used), and that ReaxFF suffers of the same problem.

Hybrid methods, with large fraction of exact exchange are usually required to better localise the charge, but Mulliken charges is not a good indication of where the charge is.

2. Surface charge and dipole effects:

The surface Ca ions in C-(A)-S-H are typically coordinated with free hydroxyl groups. As shown in **Figure 3d**, these hydroxyl groups often dissolve together with the Ca ion, partially compensating for the charge defect caused by dissolution. This phenomenon is consistent with experimental observations, where Ca ion dissolution is often accompanied by an increase in solution pH.

On the other hand, unlike simple crystalline minerals (e.g., NaCl), C-(A)-S-H is an amorphous mineral with a complex surface chemistry. Experimental studies have shown that the dissolution of C-(A)-S-H is not stoichiometric. The dissolution rate of Ca ions is significantly higher than that of anionic groups (e.g., [SiO₄] tetrahedra), especially when the Ca/Si ratio is greater than 1 (see **Figure R2**)^{13, 14}

. As a result, the surface of C-(A)-S-H in contact with solution is often negatively charged^{16, 17}

. For long time dissolution, positive ions from the solution may adsorb onto the C-(A)-S-H surface, neutralizing the surface charge over time.

The final surface charge depends on the equilibrium activity of Ca ions in solution (see **Figure R3**)¹⁷

. Our simulations focus on the initial, non-equilibrium dissolution stage of C-(A)-S-H.

During this stage, the surface produced by Ca ion dissolution is expected to carry a negative charge, especially when the dissolved hydroxyl groups are insufficient to fully compensate for the charge defect. This behavior is consistent with the real dissolution characteristics of C-(A)-S-H.

We understand that the surface dissolution in the case of CASH is complicated.

However, comparing and averaging free energy barriers for dissolution processes that produce different end states, i.e. where the Ca ion can be coordinated with an unknown number of hydroxide ions seems a simplistic approach. Particularly if the hydroxide ions detach during the dissolution process, the metadynamics simulations will suddenly start to explore different portions of the phase space.

In fact, the dissolution rate should come from a weighted average of the rates, with the weight being the Boltzmann factor of the dissolution barrier.

Moreover, as also pointed out by another reviewer, the Ca coordination number is an important, and probably slow, degree of freedom, which might affect the computed free energy. Although the water exchange rate is of the order of 100ps, that may not be the case for the Ca-OH coordination number. Hence, neglecting the Ca-H₂O/OH- coordination number can greatly affect the results, in unknown ways; and the results would depend on the starting configuration.

Adding a fourth CV, would make the calculations much more expensive, but now that the authors are using a cylindrical restraint, they should have removed the x and y CVs, which don't add anything to the results (fig S6-S9), and include the coordination number instead.

We calculated the dissolution free energy for **all 32 Ca ions** on each slab model, ensuring comprehensive coverage of the surface chemical variability. The calculated dissolution free energies were subjected to statistical analysis to account for the variability in chemical environments. This approach allows us to compare the results with experimental decalcification kinetics, which capture the overall behavior of the heterogeneous C-(A)-S-H system.

32 Ca ions, hardly seems to be representative of an experimental amorphous model. What “statistical analysis” was performed to “account for the variability in chemical environments”? How many different amorphous samples were prepared?

The average dissolution free energies for surface Ca ions in C1.25SH, C1.25A0.2SH, and C1.25A0.2S0.8H are approximately 41.7 kJ/mol, 47.0 kJ/mol, and 36.2 kJ/mol, respectively (Figure 5d).

I would suspect that by reporting the 95% confidence intervals for the free energy barriers obtained from the MD simulations, the simulations number would be largely indistinguishable from each other, and that any computational value would produce a decent fit of the experiment. The solid lines in figure 5e, should be reported with the 95% confidence band.

Also, those are not “dissolution free energies”, but “activation (free) energies”. The dissolution free energy is the difference between the bulk and dissolved state.

Why 90% confidence interval? Usually, people report the 95% confidence interval.

The authors should also report all the 90 individual free energy values as a table in the SI, as well as the 1D dissolution free energy profiles projected onto the z CV.

Another useful information would be to know the variability of the Ca coordination environment in the dissolved state is. This could just be a number in a table as #H₂O/#OH⁻.