Supplementary Materials for

X-ray–driven reaction front dynamics at calcite-water interfaces
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Materials and Methods

Materials

A calcite-saturated solution was prepared by adding pre-washed calcite powder (<90 µm particle size) to deionized water, and was equilibrated on a shaker table in contact with atmosphere for more than 48 hours. The solution was then filtered using a 0.45 µm polypropylene filter, and a calcite crystal (10 mm × 10 mm × 3 mm) was added to the reservoir to maintain its equilibrium with calcite.

An optically clear natural calcite crystal (Bolivia) was cleaved along the (104) direction with a razor blade and was mounted using marine epoxy on a fluid cell, which was immediately filled with calcite-saturated solution through external fluid feed-through ports. A grid-like pattern was scribed manually on the sample, creating nine distinct areas on the calcite surface.

Methods

The sample was imaged in situ using an Asylum Research MFP-3D Atomic Force Microscope (AFM) operating in AC mode (figure S1A), and with pyramidal probes mounted on Si₃N₄ cantilevers (Bruker; nominal resonant frequency, 19 kHz; nominal spring constant, 0.1 N/m). The scan rate was set at 0.5 – 1 Hz. Sample areas with minimal surface topography were identified and marked with the use of the scribed grid. The sample was then transferred to a sealed thin film cell filled with the calcite-saturated solution (about 2 µm thick) that is held in place by a Kapton membrane (7.5 µm thick) for X-ray imaging. AFM was also performed after one of the irradiation runs to characterize the overall dissolution of calcite (figure S1B).

An X-ray beam with a flux density of 10¹² photons/(14 µm)²/s and an incident photon energy of 10 keV was focused on a surface of calcite (see schematic in Figure 1). Imaging was performed at a scattering condition \( Q = 4\pi / \lambda \sin(\alpha) = 2.1 \AA^{-1} \), where \( \lambda \) is the wavelength and \( \alpha = 11.82 \text{ deg.} \) is the angle of incidence of the X-ray beam. At this angle of incidence, the illuminated area of the sample is 14 × 68 µm². A Fresnel Zone Plate with an outermost zone width of 60 nm and an outer diameter of 100 µm, placed after the sample, forms an image using X-rays that are specularly reflected by the calcite surface with an effective pixel size of 23 × 92 nm² on the sample surface, and projects the image on a CMOS camera (Andor Neo). Additional instrumental details were described previously in (10).

The dissolution process at the calcite-water interface was initiated and imaged by irradiation with: (1) X-ray square-wave pulse (3 s on, 10 s off). Images were recorded during the 3s exposure with a peak absorbed radiation dose of 4 × 10⁵ Gy/s (~ 10⁵ Gy/s time-averaged) (fig. 2), (2) Continuous irradiation (fig. 4). See Supplementary Text for absorbed radiation dose calculations.

Supplementary Text

Image Analysis:

a) Contrast Mechanisms:

Contrast mechanisms for imaging of surface topography by XRIM depend on the mode by which X-rays are reflected from particular structures as illustrated in figures S2-S3. For instance, a featureless crystal surface would produce a flat-field bright image, as all scattered rays satisfy the specular reflection condition (Figure 1B). In the case of steps, a geometric phase shift between scattered X-rays on either side of a step, leads to destructive interference at the step.
location, producing negative (dark) contrast in the image relative to the surface of calcite (Figure 1a and figure S2) (11, 22). Imaging of pits, relies on the walls of etch pits to reflect X-rays at a different angle than the angle of detection of the microscope’s camera (equal to the angle of X-ray beam incidence. Consequently, pits also exhibit dark contrast (figure S3A), but with a nominal contrast of ~100% from the pit walls. In instances when the etch pit bottoms flatten out, forming an interior surface parallel to the crystal surface, a secondary reflected signal (R) is superimposed on the reflection from the top calcite surface (R). The spatial location of the 2R intensity with respect to the center of the pit, δ, is simply related to the depth of the pit, by $d = \delta \tan(\alpha)$ (figure S3B).

b) Average calcite dissolution rate:

The depth distribution of two homogeneously nucleated pits (site 3 and site 3’) are extracted by the method of subsection (a) and shown in figure S3C. To calculate the calcite dissolution rate time-averaged over the entire experimental run ($t = 0$ s to $t = 1900$ s), the difference between the initial depth $d(t=0) = 0$ (as evidenced from the image in figure 2A) and the final depth is divided by the time period where dissolution is observed, i.e. rate = $\Delta d/\Delta t$. For instance, for site 3, $\Delta d=1\mu m$ and $\Delta t=1440$ s, giving a rate = 2.29 calcite monolayers/sec. Site 3’ gives a rate = 2.18 monolayers/sec. We report the average of these two values as the experimental area-normalized rate in the main text.

The kinetic model presented in the next section predicts the time-dependent calcite surface concentration (see Eq. S5). By taking the time derivative of the latter, we find the instantaneous calcite dissolution rate as presented in Figure 3E. Time-averaging of the instantaneous rate, from the beginning of the dissolution process ($t = 0$ s), until the system reaches steady state ($t \sim 1000$ s) gives the average calcite dissolution rate that is quoted in the text and is readily comparable to the experimental dissolution rate that is estimated from the X-ray imaging at similar time scales.

c) Image Processing:

The raw X-ray images were corrected for the extrinsic background of the camera by subtraction of the “read” signal and “dark” counts scaled by the exposure time of the raw image. To correct for the uneven illumination across the field of view of the image, a flat-field normalization is performed using a procedure described previously that does not affect the local contrast in the image (10). Briefly, the X-ray beam illumination function is extracted from the raw image and then used to divide out a raw image that has been previously corrected for the extrinsic backgrounds of the camera. The above procedure was applied to all X-ray images presented here and in the manuscript.

In addition to flat-field correction, the images were spatially scaled vertically by an amount equal to $1/\sin \alpha (\alpha = 11.82^\circ)$ to correct for the projection angle of the lens with respect to the surface (see figure 1). The scaling was performed with a bi-cubic interpolation and a median filter of 1-2 pixels in size.

d) Dissolution Pit Area Measurements:

Measurement of the time-dependent areas of the dissolution pits are performed using the ImageJ (v 1.49m) plugin “Analyze Particles…” (23). A preprocessing step consists of segmenting the image series to identify the dissolution pits. Initially, a median filter with a size of 5 pixels is applied to smooth out intensity fluctuations due to noise. This operation is followed by thresholding the 16-bit image using the Rényi entropy. The combination of the above two operations systematically singles out the dissolution pits from the rest of the image, allowing their areas to be measured as a function of time.
e) Dissolution Front Flows:

To extract the spatial distribution and velocity of the dissolution front as it propagates across the calcite surface we employ a technique known as Particle Image Velocimetry (PIV). The Reaction front velocities of a dislocation etch pit (site 4 in figure 2a) using PIV is shown in figure S4.

PIV is commonly used to monitor the flow of particles suspended in a medium, but here we adapt it to extract dissolution front flows. Given a series of images that have been segmented, as described in the preceding subsection, PIV is applied to a pair of images that are ordered chronologically (see figure S5). Using cross-correlation between the intensity distributions in the two images, a displacement vector of the dissolution front is computed at each pixel position of the first image (in time). Given that the time interval between the two images is known the velocity of the dissolution front is thereby determined.

The PIV ImageJ plugin (24) was used in determining the dissolution front flows presented here and in the manuscript. A few parameters must be set appropriately in the algorithm to ensure that the velocities measured are accurate. These include the size of the interrogation window (typically set at 16 pixels) and the size of the search window (varied between 32-60 pixels). To determine appropriate values for the previous two parameters, we time differentiate the area measurements (figure 2B) or more precisely the radius of the dissolution pit. The latter procedure gives an average dissolution front velocity that constrains the choice of the values of the interrogation window and the search window.

Chemical Kinetics Model:

a) Chemical Reactions:

To predict the effect of irradiation on the calcite/water interface and the magnitude by which it occurs, we use a chemical kinetics model. This model is comprised of a network of interdependent chemical reactions that can be categorized in five classes: 1) Carbonate Radical, 2) Carbonate Equilibria, 3) Calcite surface reactions, 4) Carbon dioxide (de)-hydration, 5) Water Dissociation and Radiolysis. (see Table S1 for a list of chemical reactions, kinetic constants, and rates). A summary of the master equations that define the model is given here and further expanded on in subsections III.b-d. Roughly, the equations that define the model belong to three main classes:

\[ \frac{dc_X(t)}{dt} = R_X^{\text{bulk}}(k_1,\ldots,k_m,c_1(t),\ldots,c_n(t),c_y(t)) + g(E,X)J(E,t) \]  
(Eq. S1)

\[ \frac{dc_y(t)}{dt} = R_y^{\text{bulk}}(k_1,\ldots,k_m,c_1(t),\ldots,c_n(t),c_y(t)) + A_R R_y^{\text{surface}}(r_1,\ldots,r_{14},a_1(t),\ldots,a_9(t),a_y(t)) \]  
(Eq. S2)

\[ \frac{dc_{\text{calcite}}(t)}{dt} = R_{\text{surface}}^{\text{calcite}}(r_1,\ldots,r_{14},a_1(t),\ldots,a_9(t)) \]  
(Eq. S3)

The time-dependent concentration of aqueous radical species, \( c_y(t) \), is described by Eq. (S1), where \( R^{\text{bulk}}(\ldots) \) is a reaction term associated with homogeneous reactions in the bulk solution that describes the time dependence of the concentration of component \( X \) participating in \( m \) chemical reactions that involve \( n \) chemical species as reactants/products; each chemical reaction
is characterized by a kinetic bulk constant $k_i$. Radical production is described within the spur diffusion model (9, 15, 16), whereby the generation of component $X$ (eg. OH$^\bullet$) by irradiation is given by $g(E,X)J(E,t)$, where $g$ is the primary yield (25), and $J$ is the absorbed radiation dose by the system through X-ray absorption. Both of these terms depend on the energy $E$ of the generated photoelectrons (subsection III.d). Note that $R_{\text{bulk}}$ could also depend on powers of $c_i(t)$ depending on the order of the specific reaction (not indicated in Eq. (S1-S3) for notational simplicity).

The evolution of the concentration of the carbonate species is predicted by an equation of the form of Eq. (S2), where $A_R$ is the reactive surface area of calcite and $R_{\text{surface}}(...)$ is the reaction term that encapsulates the role that component $Y$ plays in the surface reactions of calcite characterized by dissolution (precipitation) rates $r_i (r_p)$. Terms involving $A_R$ effectively “couple” bulk reactions ($R_{\text{bulk}}$) to surface reactions ($R_{\text{surface}}$) in which component $Y$ participates and are functions of ionic activities $a_i(t)$. Finally, Eq. (S3) describes the dissolution/precipitation of calcite using the classic model of Plummer (17) (see Table S1). Also see subsection III.b.

A total of 99 Reactions enter the chemical kinetics model and are classified in the following five categories: 1) Carbonate Radical, 2) Carbonate Equilibria, 3) Calcite Dissolution, 4) Carbon dioxide (de)-hydration, 5) Water Dissociation and Radiolysis. Here, we outline in detail the reactions and corresponding kinetic constants present in the first 4 categories and refer the reader to these references (9, 16) for a list of the water radiolysis reactions (5) as well as corresponding kinetic constants.

b) Carbonate Species and Calcite Surface Master Equations:

To calculate the temporal evolution of each chemical species in the calcite saturated solution upon irradiation, a kinetic reaction model is used. For instance, the differential equation for the carbonate ion is given by:

$$
\frac{dc_i(t)}{dt} = -k_i c_i(t) c_{O_2}(t) - k_{i,0} c_i(t) c_{O_2}(t) - k_{i,0} c_i(t) c_{O_2}(t) - k_{i,0} c_i(t) c_{O_2}(t) + k_{i,0} c_{i,0}(t) + r_i A_R - r_p A_R a_i(t) a_j(t)
$$

(S4)

where $c_i(t)$ is the time-dependent concentration (M, molar) of chemical component $i$, the activity $a_i(t) = \gamma_i c_i(t)/c^\circ$, where $\gamma$ is the activity coefficient and $c^\circ$ is the standard concentration (1 M). Activity coefficients for all species are calculated with the Geochemist’s Workbench® (26). The kinetic bulk constants ($k_i$) characterize the chemical reaction $i$. Experimental values for the kinetic constants were taken from the literature as indicated by the references in Table (S1).

The rates of calcite dissolution (precipitation), $r_i (r_p)$ in Eq.(S4) characterize surface reactions (Equations 9-15 in Table S1). These rates dictate how many carbonate ions are released (consumed) during the dissolution (precipitation) of calcite but depends on $a$ priori knowledge of the available amount of calcite that reacts during the experimental run, characterized by the reactive surface area of the mineral $A_R$ (27) in units of area per volume. Our approximation of $A_R$ is minimalistic, based purely on quantities that are specified by the x-ray measurement and AFM characterization, and is given by $A_R = A_{\text{beam}} N_d/V$, where $A_{\text{beam}}$ is the beam footprint (subsection I.b), $N_d$ is the number of calcium carbonate monolayers that are dissolved.
given by \( N_d = \frac{d}{c} \). \( d \) is the relative depth of the irradiated spot due to dissolution characterized by AFM (subsection I.b, figure S1), and \( c \) is the lattice constant of the mineral along the surface normal. Furthermore, this change in the quantity of available carbonate ions must be related to the rest of the bulk system through a volume term \( V_R \), where reactions driven by irradiation occur (Table S1). This “reactive” volume, given by \( V_R = A_{\text{beam}} R_e \), is naturally set by the properties of the X-ray beam \( A_{\text{beam}} \) and the associated photoelectrons through a property known as the range \( R_e \). The latter is defined as the path length over which an electron undergoes collisions in the aqueous solution, triggering reactions until its kinetic energy is reduced to 0 eV. The value for the range is specified in subsection (e). Terms involving \( r_i A_R \) in Eq.S4 and other similar equations couple bulk reactions and concentrations to the calcite surface reaction.

To model the surface reaction of calcite, we use the calcite dissolution reaction model put forth by (17). The differential rate equation that determines the temporal evolution of calcite dissolution is given by:

\[
\frac{dc_{\text{calc}}(s)}{dt} = -r_1 a_{\text{calc}}(t) - r_3 a_{\text{calc}}(t) a_{\text{calc}}(t) - r_4 a_{\text{calc}}(t) a_{\text{calc}}(t) - r_5 a_{\text{calc}}(t) a_{\text{calc}}(t) a_{\text{calc}}(t)
\]

(S5)

where \( c_{\text{calc}}(s) \) has units of mol cm\(^{-2}\), both dissolution (forward rates, \( r_1 \)) and precipitation (backward rates, \( r_5 \)) are included in the model. Equation (S5) models the change that calcite undergoes and is controlled by the time-dependent concentrations of the different species that enter (S5).

c) Numerical and benchmarking procedures:

Differential equations are derived for each chemical species that are initially present in the calcite-saturated solution \( \{ CO_3^{2-}, HCO_3^-, H^+, CO_2, Ca^{2+}, CO_3^{2-}, OH^-, H^+, CaCO_3(s) \} \) as well as for those species that are produced by radiolysis \( \{ CO_3^{2-}, CO_4^-, e_{\text{aq}}, H, H^+, H_2O, H_2O_2, H_2O_2, HO_2, HO_2, HO_2, O_2, O_2, O_2, OH, O^2 \} \). For consistency, the concentration of water is also allowed to vary with time, although it varies negligibly from the initial bulk concentration (~55 M).

The resulting 25 coupled differential equations are solved numerically, as an initial value problem, by the backward differentiation formula with a variable step (28) as implemented in the software package Mathematica (29). The initial conditions of the system are specified by the initial equilibrium concentrations (discussed below). The differential equations are solved from the initial irradiation at \( t=0 \) s until the concentrations reach a steady state at time \( t \), typically on the order of a few thousands of seconds.

Two benchmark tests are performed to assess the ability of the kinetic model: 1) to properly predict the dissolution of calcite at varying solution conditions, 2) to produce the proper equilibrium state of the calcite saturated aqueous solution. Both benchmarks are performed in the absence of irradiation.

The dissolution rates of calcite are calculated as a function of varying pH conditions and compared to experimental data. This is performed by setting the initial value of solution pH \( (t=0) \) to some value then solving the kinetic model as a function of time until the calcite saturation index reaches a value of 0. The procedure is repeated for a range of pH initial conditions in the range of pH = 4 – 10 (in steps of 0.1). The dissolution rate of calcite is
calculated from $\frac{dc(t)}{dt}$ evaluated at $t=0$. Calculating the rate in this manner is conceptually identical to an experimental measurement known as the initial rate method (30). Comparison between the simulated calcite dissolution rate and the measured rate by Chou et al. (13) is shown in Figure S4. Good agreement between the simulation and the data indicates that the model properly captures the interdependency of calcite dissolution rate on the solution conditions. Note that the behavior of the predicted dissolution rate at pH > 9 does not follow the trend of the data. However, the predicted pH-dependent dissolution rate is more in line with the general trend of calcite dissolution observed in various other experiments (2).

The second benchmark consists of testing the kinetic model against the thermodynamic predictions of the widely used software, the Geochemist’s Workbench (GW) (26). The equilibrium solution concentrations of 100 g of calcite in contact with 1 kg of aqueous solution are predicted in GW using thermodynamic equilibrium (see Table S2). To simulate the dissolution of calcite in contact with de-ionized water to produce a calcite-saturated solution: 1) the initial concentrations of $\text{CO}_3^{2-}$, $\text{HCO}_3^-$, $\text{Ca}^{2+}$, $\text{CaCO}_3$ are set to 0 in the kinetic model, 2) the initial concentration of $\text{H}^+$ and $\text{OH}^-$ are calculated at a pH = 5.65, 3) the concentration of dissolved $\text{CO}_2(\text{aq})$ is kept fixed at $10^{-5}$ M. The latter is needed to reproduce the fact that the system is open, i.e. in contact with an infinite reservoir of $\text{CO}_2(\text{g})$ during equilibration. Moreover, the concentration of $\text{CO}_2(\text{aq})$ is reset to $10^{-5}$ M if it drops below this value at anytime during the course of solving the kinetic model from $t=0$ s to $t=10^5$ s. The time evolution of the concentrations is plotted in figure S7.

As shown in Table S2, the steady-state values of the concentrations, $c(t=10^5 \text{s})$, of all chemical species present in the final calcite-saturated solution are in excellent agreement with the thermodynamic values predicted by GW. These equilibrium concentrations define the initial conditions used in all subsequent modeling of the system when subjected to irradiation.

d) Modeling equations for radicals:

The primary effect of irradiation on the system is to produce radicals in the aqueous solution. To predict the time evolution of the amount of radicals produced and their respective reactions with the calcite-saturated solution, differential equations in the form of Equation S1 are derived for each radical species. These equations incorporate the 100-eV primary yields, $g(X)$, that quantify the amount of species $X$ produced per 100 eV of absorbed radiation in the system. The general form of the equation that dictates the temporal evolution of the concentration of some radical $X$ is reproduced here for convenience (see Eq. S1)

$$\frac{dc_X(t)}{dt} = R(c_1(t),\ldots,c_m(t),c_X(t)) + g(X)J(t) \quad (S6)$$

The reaction term $R(\ldots)$ is comprised of $n$ chemical reactions described by kinetic constants $k_i$, between $X$ and $m$ chemical species present in the system. The reaction term, for instance, includes reactions that generate primary radiation products ($e_h$, $\text{OH}$, ...) as well as any relevant reactions in water radiolysis and reactions with the calcite saturated solution (see Table S1).

The second term in (4) depends on the primary yield, $g(X)$, and the absorbed radiation dose per unit time, $J(t)$. The values we used for the (mass balanced) primary yields of the primary radical products valid for electron energies ranging from ($10^4$ – $10^6$ eV) were calculated...
in (3I) and are listed in Table S2 of Ref. (9). The rate of absorbed radiation by the system during X-ray imaging is evaluated next.

c) Absorbed Radiation Dose:

The dose absorbed by the system due to irradiation by X-rays is determined almost entirely by the photoelectric cross-section at 10 keV. The current density of produced photoelectrons upon incidence on the sample, \( J^e \) (number of electrons per unit time per unit area) is given by

\[
J^e = J^{ph} N^d \sigma f(\theta) \quad (S7)
\]

where \( J^{ph} \) is the X-ray flux density (number of photons per unit time per unit area), \( N^d \) is the number of molecules per unit area illuminated by the X-ray beam, \( \sigma \) is the photoelectron cross-section, and \( f(\theta) \) is a solid-angle correction (discussed below). The flux density in the experiment is measured to be \( J^{ph} = 10^{12} \) photons / (sec \( \times \) \( A_{beam} \)), where \( A_{beam} = (14 \ \mu m)^2 / \sin(\alpha) \) is the beam footprint on the surface of calcite at an angle of incidence \( \alpha = 11.82^\circ \).

The X-ray beam illuminates both water molecules and calcite molecules, however, at 10 keV the photoelectric cross-section of calcite \( \sigma = 39.92 \text{ cm}^2/\text{g} \) is much larger than that of water \( \sigma = 4.94 \text{ cm}^2/\text{g} \) calculated from the XCOM NIST database (32). Consequently, we ignore photoelectrons generated by water, and use \( N \) to refer to the number of calcite molecules illuminated by the X-ray beam. The number of CaCO₃ molecules illuminated per unit area is

\[
N^a = \frac{n}{A_{uc}} \frac{R^e}{c} \quad (S8)
\]

where \( n/A_{uc} \) is the number of molecules per area of the calcite unit cell (\( = 1 \text{ CaCO}_3 / 20.2 \text{ Å}^2 \)), \( R^e \) is the range of a 10 keV photoelectron (\( = 1.2 \mu m \)) from the continuous slowing down approximation (25), and \( c (= 3.0355 \text{ Å}) \) is the lattice constant of calcite along the surface normal. In essence, the expression for \( N^d \) (Eq. S8) takes into account the production of photoelectrons down to a depth of \( R^e \) in the calcite crystal.

The value used for the photoelectron cross-section in (S7) is over the entire solid angle (4\( \pi \)), but since photoelectrons have a finite path length before thermalizing and capture, only a fraction of them can emanate from the surface of calcite to cause radiolysis. The factor \( f(\theta) = (1 - \cos \theta) / 2\pi \), that multiplies \( \sigma \) performs this correction where, \( \theta \) is the angle subtended by the path of an electron along the surface normal and the maximum path for electron escape from the calcite crystal. We estimate \( \cos \theta = R^e / 2R^e \). Note that we have ignored the dependence of the cross-section on the polarization of x-ray photons (orthogonal to the surface normal). Such a correction should also enter in \( f(\theta) \), and further reduces the value of the cross-section, yet by a negligible amount compared to the other prefactors in (S7).

Under the conditions of our experiments, we find from the above considerations that X-rays induce the calcite crystal to generate a photoelectron current density \( J^e = 1.7 \times 10^{-2} \) electrons s⁻¹ Å⁻².

Finally, the absorbed dose per unit time is related to the electron current density by

\[
J(E,t) = S(E) J^e(t) \quad (S9)
\]
where \( S(E) \) is the stopping power of water at an electron energy \( E \). For simplicity in modeling the radiolysis of the calcite saturated solution, we assume that the energy of photoelectron current density \( J \) is due entirely to electrons with an energy of 10 keV and is given by the value calculated above (this approximation is further discussed in subsection g). This entails that 

\[
J(t) = J(10\text{keV}) \bigg|_{E=10\text{keV}}
\]

in (Eq. S1 and S6) and therefore the values of the primary yields \( g \) are also chosen for this energy. Given that the stopping power of water at an electron energy of 10 keV is known (= 22.56 MeV cm\(^2\)/g, ESTAR NIST database), we find an absorbed radiation rate of 3.9 \times 10^5 Gy/s. This value is nearly 3 orders of magnitude smaller than the radiation dose that the same system would be subjected to in a typical transmission electron microscope experiment (\( \approx 10^8 \) Gy/s) \( ^{(9)} \).

f) Radiolysis of the Calcite Saturated Solution:

Given the value of absorbed dose, the kinetic model is fully defined and was used to simulate the behavior of calcite system as shown in the main text. Here, we reproduce the temporal evolution of all the chemical species in solution as obtained from solutions to the model. The initial concentrations were taken from Table S2 for a calcite saturated solution, \( c_X = 0 \) for all radiation products \( X \), \( c_{\text{water}} = 55.56 \text{ M} \), and \( c_{\text{calcite}} = 1 \text{ mol cm}^{-2} \).

g) Model Sensitivity Analysis:

In calculating the amount of photoelectrons generated by calcite, we made the assumption that CaCO\(_3\) molecules that are approximately 1 \( \mu \)m (i.e. \( R^e \)) deep into the calcite crystal contribute to the \( J \) that is generated at the calcite/water interface. While this represents a good estimate of the amount of photoelectrons generated, \( J \) is no longer mainly constituted of electrons with a kinetic energy of 10 keV. In fact, the inelastic mean free path of a 10 keV electron in calcite is \( \sim 15 \) nm, hence only the first 15 nm of calcite contribute photoelectrons with an energy that is exactly 10 keV. Electrons that are produced at distances larger than 15 nm will lose energy due to collisions with the crystal lattice. A better approximation would have been to consider that both the absorbed dose in (Eq. S9) and the primary yields \( g \) are energy dependent terms. However, this would require using the entire spectrum of photoelectron energies in the kinetic model (Eq. S1), adding further complexity to a model that is already quite involved. To estimate the dependence of our predictions on the above assumption, we carried out two simulations of the central physical quantity that is predicted by the model and used to interpret the experimental results, i.e. the calcite saturation index. As shown in Figure S9, the use of a current density that comes only from the first 15 nm of calcite (\( J = 2 \times 10^4 \)) has minimal effect on the quantitative character of the solutions over the time scales we probe 10’s – 100’s of seconds. In addition, note that the qualitative behavior of the saturation index is identical in either case. Given that photoelectrons of energies ranging from 0.1 keV – 10 keV all contribute to generating radicals, we choose to use the current density of \( J = 1.7 \times 10^2 \text{ electrons s}^{-1} \text{Å}^{-2} \) (as derived in subsection (e)) in all calculations presented in the main text, as it provides a closer approximation to the irradiation effects that occurred in the actual experiments.

Calculations of the sensitivity of the predicted calcite dissolution to the photoelectron current density are shown in Figure S10.
Fig. S1.
In situ AFM characterization of the sample, A) Amplitude image of the pristine cleaved calcite surface, B) height image after radiation driven dissolution. Line profile is taken across a large region to characterize the global dissolution of calcite.
Fig. S2
Step retreat during calcite dissolution. Steps appear in an XRIM image with dark contrast. Diminishing contrast and subtle changes in step locations are signatures of step retreat. Images taken under constant X-ray irradiation (see main text). Experimental time is denoted by t. Scale bar is 3 μm.
Fig. S3

X-ray reflection contrast mechanisms of etch pits. (A) A pit on the calcite surface, with the geometrical shape of a cone is imaged with dark contrast, since X-rays reflected from its walls (red) are not detected by the camera, which is held fixed to satisfy the specular reflection. (B) Pits that form a flat bottom with a shape of a conical frustum, generate a secondary reflected signal that adds up to the reflected beam from the top surface and appear bright in the image with twice the reflected intensity ($2R$). (C) The depth of etch pits shown in fig. 2A are extracted and
shown as a function of time. Time and statistical averaging of the depth distributions gives a calcite dissolution rate of 2.24 calcite monolayers/sec. Scale bar 1 µm.

**Fig. S4**

Reaction front velocities of a dislocation etch pit (site 4) of figure 2a in the main text. The outlines indicate the shapes of the pit at various times. The dashed circle indicates the presumed location of a dislocation. The reaction fronts during initial times propagate outwards from the position of the dislocation. At later times the lateral shape of the pit becomes rectangular, but is largely unchanged near the presumed location of a dislocation.
Fig. S5
Dissolution Front Velocity Measurements. A) X-ray images that were flat-field corrected, scale bar is 1µm. B) Image segmentation by the Rényi Entropy. C) Particle Image Velocimetry applied to the pair of segmented images shown in (B).
Fig. S6
Comparison of the pH-dependent rate of calcite dissolution predicted by the kinetic model and the data of Chou et al (13). The data was extracted from a digital copy of (13).
Fig. S7
Temporal evolution of the concentrations, predicted by the theoretical model, due to dissolution of calcite in contact with deionized water at $t=0$ s, producing a calcite-saturated aqueous solution at $t > 10^3$ sec.
**Fig. S8**
Temporal evolution of the concentrations of chemical species in the calcite saturated solution due to constant irradiation by x-rays starting at $t=0$ s. A) Chemical species initially present in the solution, except for CO$_3^-$ and OH radicals. B) Additional chemical species produced by radiolysis.
Dependence of the calcite saturation index on the photoelectron current density generated by the calcite crystal due to the constant irradiation of X-rays beginning at time $t = 0$ s. Units of the current density, $J_e$, are electrons s$^{-1}$ Å$^{-2}$.

**Fig. S9**
Fig. S9
Sensitivity analysis of the calcite dissolution rate on the photoelectron current density generated when the system is subject to an X-ray square-wave pulse (fig. 3 in the main text). $J_0$ is the photoelectron density used in all calculations presented in the main text, $J_0 = 1.7 \times 10^{-2} \text{ electrons s}^{-1} \text{ Å}^{-2}$. The dissolution rate predicted in the text is marked by a dashed ellipse. The experimental bounds (dashed lines) give the range of measured calcite dissolution rates at a pH=5. Bounds were estimated from Fig. 5.4, p. 157 of Ref. (2).
Reactions and corresponding kinetic, equilibrium, and rate constants involving chemical species present in the calcite saturated solution and the calcite crystal. By convention, H$_2$CO$_3$* = CO$_2$(aq) + H$_2$CO$_3$.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Kinetic Constants ($k$), Equilibrium constants ($K$) and dissolution rates ($r$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I.</strong> Carbonate Radical:</td>
<td></td>
</tr>
<tr>
<td>1. OH + CO$_3^{2-}$ → CO$_3^{-}$ + OH$^-$</td>
<td>$k_1 = 4.2 \times 10^8$ M$^{-1}$ s$^{-1}$ (33)</td>
</tr>
<tr>
<td>2. CO$_3^{-}$ + CO$_3^{-}$ → CO$_2$(aq) + CO$_4^{2-}$</td>
<td>$2k_2 = 8.2 \times 10^3$ s$^{-1}$ (34)</td>
</tr>
<tr>
<td>3. OH + HCO$_3^{-}$ → CO$_3^{-}$ + H$_2$O</td>
<td>$k_3 = 8.5 \times 10^6$ M$^{-1}$ s$^{-1}$ (35)</td>
</tr>
<tr>
<td>4. O$^-$ + CO$_3^{2-}$ + H$_2$O → CO$_3^{-}$ + 2 OH$^-$</td>
<td>$k_4 = 10^7 / c_{H_2O}$ M$^{-1}$ s$^{-1}$ (33)</td>
</tr>
<tr>
<td><strong>II.</strong> Carbonate Equilibrium:</td>
<td></td>
</tr>
<tr>
<td>5. CO$_3^{2-}$ + H$^+$ → HCO$_3^{-}$</td>
<td>$k_5 = 5 \times 10^{10}$ M$^{-1}$ s$^{-1}$ (36)</td>
</tr>
<tr>
<td>6. HCO$_3^{-}$ → CO$_3^{2-}$ + H$^+$</td>
<td>$k_6 = k_5 K_{II}^1, K_{II}^1 = 10^{-10.33}$</td>
</tr>
<tr>
<td>7. H$^+$ + HCO$_3^{-}$ → H$_2$CO$_3$</td>
<td>$k_7 = 5 \times 10^{10}$ M$^{-1}$ s$^{-1}$ (36)</td>
</tr>
<tr>
<td>8. H$_2$CO$_3$ → H$^+$ + HCO$_3^{-}$</td>
<td>$k_8 = k_7 K_{II}^2, K_{II}^2 = 10^{-3.45}$</td>
</tr>
<tr>
<td><strong>III.</strong> Calcite dissolution and precipitation:</td>
<td></td>
</tr>
<tr>
<td>9. CaCO$_3$(s) + H$^+$ → Ca$^{2+}$ + HCO$_3^{-}$</td>
<td>$r_1 = 8.9 \times 10^{-5}$ mol cm$^{-2}$ s$^{-1}$ (13)</td>
</tr>
<tr>
<td>10. Ca$^{2+}$ + HCO$_3^{-}$ → CaCO$_3$ + H$^+$</td>
<td>$r_{-1} = r_1 / K_{III}^1, K_{III}^1 = 10^{1.83}$</td>
</tr>
<tr>
<td>11. CaCO$_3$(s) + H$_2$CO$_3$* → Ca$^{2+}$ + 2HCO$_3^{-}$</td>
<td>$r_2 = 5.0 \times 10^{-8}$ mol cm$^{-2}$ s$^{-1}$ (13)</td>
</tr>
<tr>
<td>12. Ca$^{2+}$ + 2 HCO$_3^{-}$ → CaCO$_3$(s) + H$_2$CO$_3$*</td>
<td>$r_{-2} = r_2 / K_{III}^2, K_{III}^2 = 10^{-8.5}$</td>
</tr>
<tr>
<td>13. CaCO$_3$(s) → Ca$^{2+}$ + CO$_3^{2-}$</td>
<td>$r_3 = 6.5 \times 10^{-11}$ mol cm$^{-2}$ s$^{-1}$ (13)</td>
</tr>
<tr>
<td>14. Ca$^{2+}$ + CO$_3^{2-}$ → CaCO$_3$(s)</td>
<td>$r_{-3} = r_3 / K_{III}^3, K_{III}^3 = 10^{-8.46}$</td>
</tr>
<tr>
<td>15. CaCO$_3$(aq) → Ca$^{2+}$ + CO$_3^{2-}$</td>
<td>$k_{15} = 10^{-2}$ s$^{-1}$ (36)</td>
</tr>
<tr>
<td>16. Ca$^{2+}$ + CO$_3^{2-}$ → CaCO$_3$(aq)</td>
<td>$k_{16} = 2$ M$^{-1}$ s$^{-1}$ (36)</td>
</tr>
<tr>
<td><strong>IV.</strong> Carbon dioxide (de)-hydration:</td>
<td></td>
</tr>
<tr>
<td>17. CO$_2$(aq) + H$_2$O → H$_2$CO$_3$</td>
<td></td>
</tr>
<tr>
<td>18. H$_2$CO$_3$ → CO$_2$(aq) + H$_2$O</td>
<td></td>
</tr>
<tr>
<td>19. CO$_2$(aq) + OH$^-$ → HCO$_3^{-}$</td>
<td>$k_{17} = 6.6 \times 10^{-4}$ M$^{-1}$ s$^{-1}$ (36)</td>
</tr>
<tr>
<td>20. HCO$_3^{-}$ → CO$_2$(aq) + OH$^-$</td>
<td>$k_{18} = 24.8$ s$^{-1}$ (37)</td>
</tr>
</tbody>
</table>

**Table S1.**
Table S2.
Comparison between the equilibrium concentrations predicted by the Geochemist’s Workbench® (GW) and the steady-state values ($t=10^5$ s) predicted by the kinetic model (KM) for a calcite saturated aqueous solution.

<table>
<thead>
<tr>
<th></th>
<th>HCO$_3$</th>
<th>Ca$^{2+}$</th>
<th>CO$_3^{2-}$</th>
<th>H$_2$CO$_3$</th>
<th>CaCO$_3$(aq)</th>
<th>OH$^-$</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW, c[M]</td>
<td>9.5×10$^{-4}$</td>
<td>4.8×10$^{-4}$</td>
<td>9.7×10$^{-6}$</td>
<td>–</td>
<td>1.0×10$^{-6}$</td>
<td>2.0×10$^{-6}$</td>
<td>8.28</td>
</tr>
<tr>
<td>KM, c[M]</td>
<td>1.2×10$^{-5}$</td>
<td>4.3×10$^{-4}$</td>
<td>1.1×10$^{-5}$</td>
<td>1.7×10$^{-8}$</td>
<td>9.8×10$^{-7}$</td>
<td>2.0×10$^{-6}$</td>
<td>8.30</td>
</tr>
</tbody>
</table>
**Movie S1**
Mineral dissolution under pulsed irradiation. The movie represents the entire data sequence that is presented in figure 2 of the main text. Scale bar is 3 µm and time stamp is the experimental time.

**Movie S2**
Mineral dissolution under constant irradiation. The movie represents the entire data sequence that is presented in figure 4 of the main text. Scale bar is 3 µm and time stamp is the experimental time.

**Movies S3-S5**
Dependence of Mineral dissolution processes on the time-dependence of the under-saturation of the solution, controlled by varying the x-ray square wave pulse off-time from 10s (Movie S3), 1s (Movie S4), 0.3s (Movie S5). When the x-ray pulse off-time is more or equal to 1s, the surface dissolves by the formation of dislocation etch pits (Movies S3, S4). When the pulse off-time is less than 1s and prolonged undersaturation (see main text), reaction front instabilities emerge and are shown in Movie S5 to annihilate pre-existing dislocation etch pits by surface retreat.

**Movie S6.** Close-up of Movie S2, scale bar is 2 µm and the time stamp is the experimental time. False color scale: blue indicates a dissolution pit, red: calcite surface, white: reaction front.