Supplementary Material

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Setting of a dissolution rate criterion at nanoscale

A macroscopic mineral dissolving under constant conditions does not have a constant dissolution rate over time due to the evolution of the surface topography[1–3]. The experimental methodology in that case is to wait until the system reaches a stationary state and the net dissolution over a time interval is constant. In simulations this is not possible due to size and time limitations. Therefore, it is important to set a clear reproducible and representative criterion in shorter time and spatial scales to calculate the dissolution rate.

The dissolution rate is defined as the amount of dissolved material in a certain period of time $\Delta t$. In simulations the crucial point is to choose that $\Delta t$. As the step retreat triggered by the presence of dislocations is going to lead the dissolution rate, it is logical to use them as a reference point. In these simulations the final time $t_f$ is set as the double of the time needed for a dislocation atom to be dissolved at far from equilibrium conditions. The choice is explicitly shown for a given simulation in Figure S1. The initial zone at the very beginning of the curve with a strong slope corresponds to adatoms dissolution. The second zone presents a continuously rising dissolution rate due to terraces. In the third region, after $t_f/2$, the time for a dislocation atom to dissolve has been reached, and dissolution rate increases considerably due to the rise of exposed kink atoms. When the plane is completely detached, the rate decreases again until $t_f$, at which time the next
Figure 1: **Criterion to calculate the dissolution rate.** Dissolving simulation of a mineral with $E_D = 7.0$ and $E_P = 1.0 \ k_B T$ at $\Delta G = -54.72 \ kcal \ mol^{-1}$. A Typical curve at far from equilibrium conditions is shown. A very first zone contains the fast dissolution of adatoms. Following zone before $t_f/2$ contains a rising rate due to the terraces dissolution. Once $t_f/2$ is reached, deeper layers start also to dissolve due to dislocation opening. Final time considered is $t_f$. From this moment the behaviour is repeated producing a pulsating dissolution. $m$ represents the slope to the coloured points in $t_f$, $2t_f$ and $3t_f$. In this particular case, the three mechanisms are appreciated.

dislocation atom dissolves.

A pulsating frequency due to step retreat plane by plane leads the dissolution as described recently by Fischer and Luttge$[^3]$. At macroscopic scale, different domains and planes overlap and hide this frequency, and very accurate experiments and monocrystals are necessary to observe it. The chosen $t_f$ represents a whole pulse and the obtained slope is representative of longer times except for the dissolution of adatoms, which is negligible. The higher the dissolution energy $E_D$ of the mineral is, the more differentiated and sharper are the regions, while for low cohesive minerals, atom neighbourhood loses importance, and dissolution rate is essentially linear.
Methodology for accelerating simulations close to equilibrium

One of the technical difficulties to compute dissolution rates at close to equilibrium conditions, when microscopic reversibility is taken into account, is the huge simulation time consumed in irrelevant backward and forward reactions without actual net dissolution. The algorithm used to overcome this problem is explained below.

1) First of all, and as other KMC codes, a list of possible events is built based on the dissolving rate term in Equation 2 in the article. The sum of all dissolving rate events is $R_D$. An event $E_C$ is then randomly selected thanks to a random number $u_1 \in [0, R_D]$, $u_1 \cdot R_D \rightarrow E_C$. With other random number $u_2 \in (0,1]$ the simulation time step $t_{\text{step}}$ is calculated as follows:

$$t_{\text{step}} = \frac{1}{R_D} \cdot \ln \left( \frac{1}{u_2} \right)$$

From the chosen event $E_C$, its dissolution rate $r_D^{EC}$ and its dissolution characteristic time $t_D^{EC} = 1/r_D^{EC}$ is stored.

2) Second, using Equation 3 in the article, the precipitation rate $r_P^{EC}$ and the precipitation characteristic time $t_P^{EC} = 1/r_P^{EC}$ are calculated.

3) Knowing that the dissolution and precipitation events are Poissons processes, the effective time $t_{\text{D,eff}}^{EC}$ needed for the atom to leave with certain probability is:

$$t_{\text{D,eff}}^{EC} = -\ln(1 - P) \cdot t_D^{EC}$$

where P is the probability of the event to happen. To ensure that the $t_{\text{D,eff}}^{EC}$ is captured, a P threshold value of 99.9% was used.
4) Once the effective dissolution time $t_{EC}^{D_{eff}}$ and the characteristic precipitation time $t_{EC}^{P}$ have been determined, the effective probability $P'$ for an atom to truly dissolve can be estimated. With a third random number $u_3 \in [0, 1]$, the event is accepted or not.

$$P' = \exp \left( - \frac{t_{EC}^{D_{eff}}}{t_{EC}^{P}} \right)$$  \hspace{1cm} (1)

- if accepted, the simulation time is increased by $t_{step}$ and the system and event list are updated for the next simulation step.
- if rejected, it is considered that the atom has left and has returned back, so the simulation time increment is $t_{step} + t_{return}$. The system and event list do not need to be updated, and only simulation time changes. $t_{return}$ is calculated as follows using another random number $u_4 \in (0, 1)$:

$$t_{return} = \frac{1}{R_D - r_{EC}^{D} + r_{EC}^{P}} \cdot \ln \left( \frac{1}{u_4} \right)$$

**Calculation of the relationship between $\Delta G_{crit}$, $E_D$ and $E_P$**

From the expression to determine the effective probability for an atom to dissolve $P'$, Equation 1 above, it is possible to derive an approximated expression to relate $E_D$, $E_P$ and $\Delta G_{crit}^*$ for a dislocation opening. If $P'$ is calculated for an atom close to a dislocation:

$$P' = \exp \left( - \ln \left( \frac{f_l \cdot \exp \left( -N_{nD} \cdot E_D \right)}{f_l \cdot \exp \left( -N_{nD} \cdot E_P + \Delta G_{crit}^* \right)} \right) \right)$$  \hspace{1cm} (2)

And if this is related to the macroscopic $\Delta G_{crit}$ by the Equations 5 and 7 in the article, this can be simplified to the expression:

$$\Delta G_{crit}(k_B T \text{ units}) \approx (\alpha - b - N_{nD} \cdot (E_D - E_P)) \cdot N_{nK}$$  \hspace{1cm} (3)
Figure 2: Dispersion in $\alpha$ depending on $P'$.

where $\alpha$ reads as:

$$\alpha = \ln \left( \frac{\ln P'}{\ln(1 - P)} \right)$$  \hspace{1cm} (4)

$P$ is the previously selected threshold of 0.999. Note that for finer simulations this threshold could set to be higher. The only remaining term is $P'$, the effective probability for an atom to dissolve. It is an unknown value that must be set ad-hoc. To consider a low $P'$ value implies that a small proportion of the dislocations attempting to open finally manage it, and therefore, the expression reports the beginning of the $\Delta G_{\text{crit}}$ onset. Nevertheless, a cleared choice is to obtain the medium height value for a better sighting. For that, it has been considered that half of the dislocations are able to open, meaning $P' = 0.5$. Figure S2 shows the $\alpha$ value dispersion which allows to report an error of such an approximation. In this work the final value considered is $\alpha = -2.3 \pm 0.9 \text{ } k_B T$ corresponding to $P' = 0.5$ and $P = 0.999$.

**Dissolution rate dependence with dislocation density**

Simulations with different dislocation densities have been used to check their dependence with dissolution rate at far from equilibrium conditions where mechanisms III and/or
Figure 3: Relative dissolution rate versus the number of dislocations. 2 dislocation case has been chosen as reference point. This value equates to a dislocation density of $\sim 5.5 \times 10^{10}$ cm$^{-2}$. Each point is the mean of 8 values. Error bars are smaller than the point except of the $E_D = 12.0 \ k_B T$ case.

II dominate. Simulations with 0, 2, 4, 10, 20, 50, 100 and 200 dislocations randomly distributed have been done for minerals of $E_D = 4.0, 7.0, 9.0, 12.0 \ k_B T$ units. In Figure S3, the dissolution rates of all the systems are compared, taking as reference the system with two dislocations.

At far from equilibrium conditions, in low cohesive minerals ($E_D = 4.0, 7.0 \ k_B T$ units) the dissolution rate exhibits a small linear dependence with the number of dislocations. In this conditions, corresponding to the mechanism III region, perfect planes are opened spontaneously, so the dislocations hardly affect dissolution. On the opposite side, for highly cohesive minerals ($E_D = 9.0, 12.0 \ k_B T$ units) the rate is more sensitive to dislocations since they represent the only dissolution source. The increase is not lineal, approaching a limit value at high dislocation density due to the coalescence of dissolution fronts.
Dissolution rate dependence with surface roughness

Surface topography of a mineral may have an important effect on the dissolution rate. Figure S4 shows the difference on the dissolution rate for a Kossel crystal with different initial topography. Taking into consideration that initial irregularities are important in mechanism I, and initial step atoms and vacancies are important in mechanisms II/III, both quantities are recorded per nm$^2$. The system considered in this work presents a density of 1.7436 nm$^{-2}$ of atoms forming terraces or adatoms and 0.0969 nm$^{-2}$ step atoms (see Figure 1 in the article). A more regular system presents a density of 0.225 nm$^{-2}$ and 0.0411 nm$^{-2}$ respectively. Both systems have $E_D = 7.0$ and $E_P = 1.0 \ k_B T$. A difference in dissolution rate is appreciated for the whole $\Delta G$ range, although is smaller than one order of magnitude.
Extended Arrhenius equation

The activation energy in the Arrhenius equation compiles the contribution from many terms and not just the energy barrier of the elementary reactions. It must be considered that generally experimental fits for determining $E_a$ do not consider a temperature dependence on the fundamental frequency\[1\]. Sort temperature ranges, and taking logarithms for the fitting camouflages such dependency which some fine experiments have demonstrated\[1,4,5\]. This dependence should always overestimate the value of $E_a$ comparing to $N_n k \cdot E_D$. To deal with such an overestimation, lineal dependence on the temperature is taken, which only considers vibrational contribution to the fundamental frequency\[1,2,6\]:

$$R = A' \cdot T \cdot \exp \left( -\frac{E_a}{k_B \cdot T} \right)$$

(5)

It is important to point that in reality exists rotational and translational contribution to fundamental frequency whose dependence with $T$ is not lineal ($T^{3/2}$ and $T^{1/2}$)\[1\]. The data reported with Equation 5 for Figure 3 in the article is shown in Table S1. The obtained activation energy values by this equation are just $\sim 3 \text{ kJ mol}^{-1}$ lower than those computed with an Arrhenius fit. This indicates that the temperature de-

Table 1: Activation energy and fitting parameters. Reported values in Figure 3 in the article using Equation 5.

<table>
<thead>
<tr>
<th></th>
<th>Kossel crystal</th>
<th>Diamond like system</th>
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<tbody>
<tr>
<td>mech. III / f.e.</td>
<td>ln $A'$ 20.99 ± 0.16</td>
<td>13.78 ± 0.03</td>
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<tr>
<td></td>
<td>$E_a$ 3.9</td>
<td>2.0</td>
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<tr>
<td></td>
<td>$E_D$ 67.5 ± 0.5 kJ mol$^{-1}$</td>
<td>35.17 ± 0.08 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>mech. I / c.e.</td>
<td>ln $A'$ 17.15 ± 0.06</td>
<td>6.88 ± 0.28</td>
</tr>
<tr>
<td></td>
<td>$E_a$ 2.9</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>$E_D$ 50.70 ± 0.19 kJ mol$^{-1}$</td>
<td>35.3 ± 0.9 kJ mol$^{-1}$</td>
</tr>
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dependence of the fundamental frequency could be non-negligible for materials with low dissolution activation energy\textsuperscript{[1]}.

**Four coordinated systems**

Coordination number, as can be shown from the mechanisms described in the article, plays an important role in the dissolution. This section looks for checking the extension of the proposed model to a four coordinated mineral. For that, a diamond like structure system was used to simulate same cases as the Kossel crystal study. The results in the Figure S5 show a TST behaviour whatever the value of $E_D$ or $E_P$. Only one mechanism governs the dissolution characterized by a random detachment of atoms in the surface without dislocation opening for any $E_D$ or $E_P$ value. The further from the equilibrium, the more dissolution until a plateau is reached. In this sense, the study done by Kurganskaya and Luttge for the quartz\textsuperscript{[7]} meets this dissolution mechanism at far from equilibrium conditions when only the first neighbours are considered.
Besides, from Figure 3 in the article $E_a \approx 2 \cdot E_D$ either at far from equilibrium conditions or close to it. This agrees with the fact that kink atoms, with coordination two, are the only source of dissolution without dislocation opening assistance.

These results highlight the importance of mineral structure in dissolution mechanisms.

References


