Simulation of surface dynamics during dissolution as a function of the surface orientation: Implications for non-constant dissolution rates

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Abstract

An important problem in geochemistry is the understanding of how changes occurring on a surface during dissolution affect the variability of measured dissolution rates. In this study a new approach to study the effect of surface dynamics on dissolution rates is tested by coupling experimental data with a numerical model that simulates the retreat of surface profiles during dissolution. We present specific results from the simulation of dissolution of fluorite surfaces. The equations that determine the retreat of a surface are based on experimentally obtained equations that relate the retreat rate of a surface to a single variable, the crystallographic orientation of the surface.

Our results show that depending on the starting orientation, different types of topography are developed similar to those observed experimentally. During the initial dissolution phase, changes of topography are rapid and associated with fast dissolution rates. The progressively slower dissolution rates are coupled with the development of surface segments with orientations that dissolve at a slower rate. Consequently, the overall retreat rate of a profile decreases during the simulation, and tends to a near constant value. The results show a close relationship between dissolution rates, surface orientation and surface dynamics, which suggests that the dissolution rate of a specific mineral phase is not constant but varies with dissolution time and surface structure. This variability needs to be considered in the evaluation of experimentally derived dissolution rates, future dissolution experiments, and predictive kinetic models of dissolution.

Keywords: modeling; kinetics; rate constant; topography; dissolution; surface

1. Introduction

Predictive dissolution models and an in-depth understanding of dissolution processes are needed in many areas of geochemistry such as, the nuclear waste disposal industry (e.g. Grambow et al., 2011), weathering (e.g. Brantley et al., 2008), mineral replacement reactions

(e.g. Putnis and Austrheim, 2010) and environmental remediation (e.g. Putnis and Ruiz-Agudo, 2013). In general, dissolution is a process characterized by the breaking of bonds between atoms or clusters of atoms on a surface and the atoms in the bulk of the crystal. This is followed by the release of the surface atoms or clusters into solution, and consequent change of the surface structure where the atoms were released. The preferential dissolution of kink sites relative to steps and of steps relative to terraces makes dissolution a dynamic process that continuously changes the surface in terms of area and reactivity (Fischer et al., 2012; Godinho et al., 2012; Godinho et al., 2014a; Lasaga and Lüttge, 2001; Lüttge, 2005). This suggests that the traditional method of calculating dissolution rates normalised to an overall surface area (Brantley et al., 2008; Lasaga, 1981; Oelkers and Schott, 2009) should result in a variation of dissolution rates with dissolution time. Furthermore, the stochastic nature of dissolution, i.e. each surface site has some probability to be released into solution, and the existence of different surface sites characteristic of each surface orientation suggest that dissolution rates are not a constant for a single crystal phase (e.g. Arvidson et al., 2003; Fischer et al., 2012; Godinho et al., 2014a; Lüttge et al., 2013).

The dissolution processes of minerals have been extensively studied using different approaches. For example, direct observations of dissolution using atomic force microscopy or optical profilometry frequently focus on the study of cleavage surfaces with low density of defects (e.g. Cama et al., 2010; Ruiz-Agudo and Putnis, 2012). In classical dissolution experiments, powders with a high surface area / volume ratio and a high density of high energy sites are dissolved and the dissolution rate is monitored through the fluid chemistry. In contrast to such experiments, surfaces found in nature commonly present irregular topographies either as stepped surfaces, pores or grain boundaries (Anbeek, 1992; White and Brantley, 2003; Yanina et al., 2006). The variety of surfaces present on the starting material used in each study has been suggested to contribute to the discrepancies of several orders of magnitude of measured dissolution rates for the same mineral phase (e.g. Emmanuel and Ague, 2011; Moore et al., 2012; Yoo and Mudd, 2008).

Numerical modelling has been used to improve our ability to predict dissolution rates and study dissolution mechanisms (Lüttge et al., 2013; Stack et al., 2013 and references therein). Ideally the simulations should account for the atomic interactions between surface atoms and of these atoms with atoms in the fluid phase. This is possible using for example molecular dynamics (Stack et al., 2012; Stack et al., 2013). However, due to computational time restrictions, this technique is limited with regard to finite duration of dissolution and size of the modelled system. To simulate dissolution of areas that can be related to macroscopic systems simpler algorithms need to be used. This can be achieved by using a theoretical simplification relative to the atomic scale, as used in kinetic Monte Carlo methods. For example, using an algorithm in which the detachment of a surface site has a specific probability based on the number of near neighbour sites or the energy of the site (Cama et al., 2010; Kurganskaya and Lüttge, 2013; Lasaga and Lüttge, 2001). Alternatively, the equations governing the numerical model can be set based on experimental results. Different models have been developed to simulate the development of etch pits or the macroscopic shapes of crystals caused by dissolution (Alekseev et al., 2002; Lüttge et al., 2005; Smereka et al., 2005; Snyder and Doherty, 2007).

In this contribution, we test whether a simple conceptual model that relates dissolution rates to the surface orientation, which has been shown to be directly related to the atomic structure of the surface (Godinho et al., 2014a), is sufficient to explain the experimental observations that show (a) dissolution rates are not constant though time, and (b) the structure of the initial surface determines the time dependent development of topography. To do this we use a simple numerical model to investigate the coupling between dissolution rates, surface orientation and surface topography during dissolution. Other environmental factors, such as solution composition or temperature are not considered, i.e. are assumed to remain constant in comparable experiments. In the presented model, we simulate the development of topography on a two dimensional profile over fluorite surfaces with different orientations and test its validity by comparison with experimental results. The novelty of this simulation approach is that the governing equations used to calculate the local dissolution rates were determined experimentally (Godinho et al., 2012) and only dependent on the orientation of a surface. Our results show that the dissolution rate of a mineral phase cannot be a single value for a specific dissolution condition (e.g. temperature, fluid composition). Instead, dissolution rates vary due to the continuous change of the surface structure during dissolution.

2. Conceptual model

The numerical model described here is based conceptually on the general model for dissolution of polycrystalline materials presented in Godinho et al. (2012) and Godinho et al. (2014a). This model is based on experimental results which showed that, during dissolution of fluorite, stable surfaces tend to persist, and high energy sites, such as steps, are progressively removed (Godinho et al., 2012). The preferential release of atoms from less stable sites exposes more stable surfaces, causing systematic changes of topography and the progressive stabilization of the surface. The topography developed is dependent on the initial density and type of steps and the inclination of the surface relative to its closest stable plane (Godinho et al., 2011; Godinho et al., 2012; Godinho et al., 2014a, 2014b). Both factors are directly related to the surface orientation (Maldonado et al., 2013). Experiments show that after an initial very dynamic stage during which a high increase of roughness and fast decrease of dissolution rates occur, the surfaces tend to an approximately constant topography that is specific for each initial orientation. The continuously smaller changes of topography are caused by a progressively less dynamic surface. Furthermore, experiments showed that the progressive variation of topography is associated with an increase in surface area. Contrary to classic dissolution theory (Brantley et al., 2008; Lasaga, 1981; Schott et al., 2009), it was shown that the increase in surface area can result in the decrease of the overall dissolution rate (Godinho et al., 2014a).

To understand the dynamics of dissolution it is important to distinguish between two types of steps, here referred to as “atomic scale steps” and “macro scale steps” (Godinho et al., 2014a; Maldonado et al., 2013). Atomic scale steps are formed by the interception of two stable planes {001} and/or {111}. The atoms at the steps have a lower coordination number, thus are more likely to dissolve. When one atomic scale step is removed by dissolution a larger area of the terrace is exposed. As dissolution progresses, the density of this type of steps decreases and consequently the dissolution rate also decreases. The so-called macro scale steps are also formed by the intercept between the stable planes, thus preferential dissolution also occurs at

these sites. Larger terraces exist on both sides of a macro scale step, forming a persistent source of instability from where atomic scale steps emanate to the terraces (Godinho et al., 2014a; Lasaga et al., 2001). Examples of this type of step are the top of a topographic peak formed during dissolution, the edge of a pore and a grain boundary.

3. Numerical implementation

3.1. Model set-up

We have implemented our model using the open-source modelling platform Elle (Bons et al., 2008; Jessell et al., 2001; Piazzolo et al., 2010, <http://microstructure.info/elle>). Elle was originally designed to simulate the evolution of a 2D microstructure, which is defined in a XY coordinate system according to the given governing equations. Elle is based on a data structure that can describe a polycrystalline material using a two dimensional network of nodes (Fig. 1). Grains are represented by closed polygons defined by nodes connected by straight segments. Each polygon can have independent attributes that may determine the behaviour of the nodes during the simulation. For example, a polygon can be defined as representing a crystal of predefined crystallographic orientation (polygons II-III), while an adjacent polygon may be defined as a fluid (polygon I) (Fig. 1). If two adjacent polygons have different orientation, then the dividing nodes represent a grain boundary (dashed lines) and can be given a specific distinct behaviour. The model has horizontal wrapping meaning that a node on the $X = 1$ boundary (right side in Fig. 1) is connected to a node on the $X=0$ boundary (left side in Fig.1). Elle has been used to study the macro scale topographical developments during stylolite formation resulting from liquid – solid interactions (Ebner et al., 2009; Koehn et al., 2004; Koehn et al., 2007).

Dissolution of a surface is simulated by the retreat of the solid-liquid interface specified in the model. During the simulation, the nodes at the solid-liquid interface (solid line, Fig. 1), which define the surface profile, move in the Y direction (e.g. Fig. 2) at a rate determined by the controlling equations (Fig. 3). For each iteration all nodes are displaced once in a random order. Consequently, a node may move before its neighbours in one iteration and after them in the next iteration. The displacement of a node is calculated based on its position relative to the position of its two neighbour nodes. After each iteration the roughness average (Ra) and average retreat rate (R) of the profile are calculated using equations 1 and 2, respectively, where n is the number of moving nodes, $|Y_i - Y_a|$ is the absolute vertical distance between node i and the average vertical position of all nodes (Y_a), and R_i is the retreat rate of node i . It should be noted that the distances between nodes are not directly related to atomic distances but are chosen to ensure numerical stability and feasibility. The straight segment between two nodes does not necessarily represent an atomic flat surface but a surface with a density of atomic scale steps corresponding to the local orientation of the segment. In the model, the user defines the time (t) of an iteration, which represents a dissolution interval.

$$Ra = \frac{1}{n} \sum_{i=1}^n |Y_i - Y_a| \quad \text{eq. (1)}$$

$$R = \frac{1}{n} \sum_{i=1}^n R_i \quad \text{eq. (2)}$$

3.2. Governing equations

During an iteration the displacement of a node in the Y direction (ΔY) is calculated as a function of the absolute orientation (θ) of the segments connecting a moving node to its neighbours. θ is defined as the angle between the local segment of a surface and the {001} plane. At each iteration, θ is the sum of the initial crystallographic orientation (φ) of the corresponding polygon and the angle (α) between the segment and a horizontal line (Fig. 2 and Eq. 3). φ is defined as the angle between surface (001) and the studied initial surface (hhl).

$$\theta = |\varphi + \alpha| \quad \text{eq. (3)}$$

The absolute orientation of each segment on either side of a node can be used to calculate the relative retreat rate (Rs) of the node using three empirical equations $f(\theta)$ (Eq. 4 - 6) relevant for three θ ranges (Godinho et al., 2012). Note that the empirically derived value of Rs implicitly accounts for the density of atomic scale steps of a surface with specific orientation; i.e. a faster retreat rate implies higher density of steps (Godinho et al., 2012).

$$f_1(\theta): 0^\circ \leq \theta \leq 35,5^\circ$$

$$Rs = 0,0019.\theta^2 + 0,021.\theta + 0,282 \quad \text{Eq. (4)}$$

$$f_2(\theta): 35,5^\circ < \theta \leq 55^\circ$$

$$Rs = 0,0048.\theta^2 + 0,607.\theta + 18,879 \quad \text{Eq. (5)}$$

$$f_3(\theta): 55^\circ < \theta \leq 90^\circ$$

$$Rs = -0,0016.\theta^2 + 0,306.\theta - 12,034 \quad \text{Eq. (6)}$$

These equations are only valid for θ angles between 0° and 90° . The crystal symmetry of (hhl) surfaces within the fluorite structure (Fig. A.1) allows a recalculation of angles higher than 90° to an angle corresponding to a surface with equivalent structure between 0° and 90° by using the appropriate symmetry operation (Eq. 7).

$$\theta = 180 - \theta \quad \text{Eq. (7)}$$

Finally the displacement of each node ΔY is calculated using equation 8 where the total retreat rate ($Rs + Re$) is multiplied by the input time step (t). Re is an input parameter optimized for each starting orientation to approach numerical and experimental results (see discussion for details). Re represents the additional instability of macro scale steps, as explained in the conceptual model. Such a macro scale step only occurs at topographic highs, thus the Re contribution is only applicable to the nodes with both neighbours in a lower Y position (e.g. node 2 at the first iteration (t_1) in Fig. 2).

$$\Delta Y = (Rs + Re) . t \quad \text{Eq. (8)}$$

Each moving node is bound by two interface segments and consequently two rates are possible. The slowest rate is chosen based on the experimental observation that surfaces that dissolve more slowly are progressively exposed during dissolution.

3.3. Simulation details

We chose to investigate the retreat behaviour of surfaces (115), (334) and (110) as for these surfaces a) experimental dissolution data exists (Godinho et al., 2012; Godinho et al., 2014a, 2014b), and b) each of these surfaces is defined by a different retreat rate equation (Eq. 4 – 6). For the corresponding initial orientations the modelling parameters were optimized such that the simulated profiles develop a topography similar to the topography developed experimentally (Fig. 4) during dissolution in a 0,05 M NaClO₄ solution with pH 3,6 (see Godinho et al., 2014a for experimental details).

The results presented here were obtained with the initial moving boundary constituted by 1168 moving nodes and a time per iteration of 5×10^{-7} . It should be noted that the absolute displacement of a node is directly proportional to the time step (Eq. 8), and the distance between nodes affects the variation of orientation of a segment (α) when a node is moved in the Y direction. In order to compare simulation results with dissolution experiments, different *Re* values were tested for each initial orientation. Details about the optimization and calibration procedures are detailed in the appendix.

4. Results

Starting with a flat profile, simulation results show the development of a specific topography, which is characteristic for each initial orientation (Fig. 5). For all starting orientations tested, segments with an inclination matching the stable orientations (001) and/or (111) tend to form during the simulation (Fig. 5). Surface (115) develops small topography with peaks composed mainly by one or two segments. The segments are a mixture of (001) and (111) surfaces. Surface (334) develops larger terraces corresponding to the (111) surface connected by (001) steps. Surface (110) develops the highest topography with symmetric peaks composed by segments corresponding to two (111) type surfaces.

The resulting profiles (Fig. 5) are similar to those seen in equivalent dissolution experiments (Fig. 4). Based on the observation that the inclinations of the peaks that constitute both modelled and experimental profiles are the same (Fig. 4 and 5), either (001) or (111) surfaces, the roughness parameters from experimental profiles can be used to calibrate the modelled profiles with real units and optimize the input parameters (see details in appendix). Examples of profiles obtained using different *Re* values can be seen in figure 6. Generally, an increase in *Re* causes an increase in topography, which means a decrease in the number of peaks and an increase in the overall peak height. However, over some threshold value that is characteristic of each initial orientation, the profile remains flat (Fig. 6b and 6c). The roughness parameters obtained after calibration with the *Re* value for which the developed topography is most concordant with experimental observations (Tab. A.1) are presented in table 1.

The Ra of the three profiles increases during the initial iterations of the simulations and tends asymptotically to a plateau at later iterations (Fig. 7). Inversely, the retreat rates decrease with simulation time but also tend to a plateau value (Fig. 7). The more pronounced decrease of retreat rates occurs simultaneously with the more pronounced increase of Ra. The different surfaces start exhibiting a near constant Ra at different iteration steps, (110) reaches this regime at a lower number of iterations, then (334) and finally (115) at a higher number (Fig. 7). The most pronounced change in Ra and retreat rates occur at the beginning of the simulation and progressively decrease during the simulation for surfaces (334) and (115). Surface (110) has a delay of approximately 0,1 million iterations until significant changes in Ra occur. The factor of retreat rate decrease (RRD), defined as the ratio between the initial retreat rate and the retreat rate at the near-constant regime, is highest for surface (110), and lowest for surface (115) (Tab. 1). While the initial retreat rates of the modelled surfaces diverge by a factor of up to 25, the final retreat rate of the three surfaces diverges only by a factor of 2. In other words, independently of the topography developed on each surface, the dissolution rates converge to a similar constant value for the three surfaces (Fig. 7).

The variation of experimental Ra and modelled Ra with time follows similar trends (Fig. 8). In general, the modelled Ra values (circle points, Fig. 8) are higher than the experimental Ra values (triangle points, Fig. 8). The modelled Ra of surface (110) increases significantly faster than the experimental Ra (solid lines, Fig. 8). However, both quantities tend to a similar constant value.

5. Discussion

5.1. Model behavior

The equations governing the simulation that determine the movement of the nodes and consequent development of topography depend mainly on the orientation of the segments that constitute the profile. Therefore, the specific topography developed for each initial orientation (Figs. 5 and 6) can be attributed to equations 4 - 6 that relate the segment orientation to a dissolution rate (Fig. 9). Generally, the development of topography is driven by the progressive stabilization of surface segments. That is, the slower the retreat rate of a node the smaller is its displacement, and consequently the smaller is the change in orientation (α) of the segment per time step. In other words, segments corresponding to surfaces with a slower retreat rate tend to form and persist during the simulation. In practice, this effect is directly related to the assumption that the slowest of the two retreat rates calculated for each node limits its local dissolution. For example, the orientations of all segments of a profile ideally tend to orientations corresponding to points 1, 5 or 7 in figure 9, depending on the initial orientation of the surface (φ). Experimentally, a change in the inclination of a segment along a simulation path corresponds to an average tendency of a surface to reduce the density of atomic scale steps through dissolution (Godinho et al., 2012). The retreat rate of segments with orientations at the middle of the paths, such as those corresponding to the (115) and (334) points, need to increase (for example between surface (115) and point 4) before the rate reaches the most stable points for which the displacement is minimum. This increase requires an additional effect

that forces the node to retreat faster resulting in a significant change in the orientation of the surface segment. Three possible node configurations can contribute to this behavior:

Stable neighbor: Assuming that the segment between nodes 1 and 2, in figure 2, has a slow retreat rate, then node 2 moves in small steps. In this case, if the segment between nodes 2 and 3 defines the movement of node 3 and has a retreat rate higher than the rate of node 2, angle β will continuously increase as node 3 moves faster than node 2. This happens even if it leads to a destabilization of the segment between nodes 2 and 3 and/or the segment between node 3 and the other neighbor. In other words, the retreat rate of a segment is influenced by its neighbor nodes, which results in the propagation of stable areas. This is concordant with experimental observations.

Macro scale step effect: The additional instability of macro scale steps, which is modeled by incorporating R_e in equation 8, can cause the destabilization of the adjacent segments. For each initial orientation there is a range of values that can cause the development of a range of topographies (Fig. 6). Above some R_e value, the effect of R_s is negligible and topography is not developed. For R_e values below that range, the retreat of a node per iteration is too small to destabilize a segment, e.g. surfaces close to (001) such as (115).

Random order: For each iteration, each node can move before or after its neighbors. This can cause a change in the inclination of a segment to an orientation with a faster retreat rate, or cause the formation or disappearance of peaks. This introduces into the simulation a stochastic factor corresponding to the statistical probability of less likely events occurring in natural systems (e.g. Stack et al., 2012). This factor is more likely to affect the topography developed during the initial iterations of a simulation, i.e. when the nodes are approximately aligned. This causes the formation of randomly distributed peaks with diverse heights. Such distribution is consistent with a similar random distribution of roughness parameters, within some range, observed experimentally (Tab. A.1). Physically, this is directly related to the random opening of etch pits on terraces or the stochastic nature of dissolution (Fischer et al., 2012).

5.2. Effect of surface orientation on topography development

In the following, the behavior of each surface tested is discussed in relation to the simulation paths exemplified in figure 9 and the three effects explained in the previous section. For a starting orientation of $\theta = 90^\circ$ (diamond symbol), which corresponds to surface (110), two symmetric paths defined by equation 7 determine the movement of the nodes (paths 6 - 5 and 6 - 7). During the simulation the inclination of the profile segments (α) continuously vary from 0° to 35° . The resulting profile (Fig. 5) reflects the symmetry of the paths with peaks composed of two sides with 35° inclination that correspond to two (111) surfaces (points 5 and 7). Once a segment reaches an inclination corresponding to points 5 or 7 its nodes enter a continuous regime of constant orientation and R_s (Fig. 7).

If the starting orientation has an angle close to a stable orientation (e.g. point 3 close to (115) and point 5 close to (334)), the nodes have a starting R_s that is lower than R_s at point 6 and consequent low mobility. In these cases the “stable neighbor” effect dominates (if $R_e = 0$), resulting in a profile with small topography and peaks separated by only a few nodes (Fig. 6). If

the starting orientation is $\theta = 16^\circ$ (square point in Fig. 9), which corresponds to surface (115), the closest stable orientation is point 3 (surface (001)) (Fig. 9). The final profile exhibits alternating segments corresponding to point 3 and point 5, i.e. surfaces (001) and (111), respectively (Fig. 9). If the starting orientation is $\theta = 47^\circ$, which corresponds to surface (334) and no macro scale step effect is allowed, the topography developed is similar to that developed for surface (115) (Fig. 6a and 6c). In this case the (111) orientation (point 5) is the closest stable orientation (Fig. 9).

5.3. Changes in dissolution rates with surface orientation

In this section we discuss the relative variation of retreat rates as a function of surface orientation during a simulation, as this factor was shown experimentally to be related to the variation of dissolution rates with dissolution time (Godinho et al., 2012; Godinho et al., 2014a). The development of topography in all profiles is accompanied by a progressive decrease in retreat rate for each individual node. Consequently the overall retreat rate of the profile also decreases (Fig. 7). This decrease is more pronounced during the iterations in which Ra increases faster. These results are concordant with experimental observations (Godinho et al., 2014a). The final plateau value of retreat rates of the different profiles is similar regardless of the initial surface orientation and final topography. This is an important result, which suggests that after an initially fast dissolution period that depends on the density of atomic steps of a surface, the overall dissolution rate tends to the dissolution rate of the most stable surface of a mineral phase. In the modelled case of fluorite, the overall dissolution rate tends to the dissolution rate of the (111) or (001) surfaces. In the cases of surfaces (110) and (334), because persistent topography is developed the additional instability of macro scale steps is added to the overall dissolution rate.

The number of iterations necessary for a profile to reach a stable topography with most segments at an orientation close to the stable surfaces, is directly related to equations 4 - 6. For example, changes in the profile of surface (110) only start to be significant after 0,1 million iterations, which differs from the other profiles (Fig. 5) and from what was observed experimentally (Fig. 8), where changes of Ra are more significant at early stages of dissolution. This behaviour results from equation 6 for which the variation of retreat rate for angles close to 90° is smaller than the variation when the angles are below 80° (Fig. 9). In contrast, the movement of nodes in segments with inclinations 16° and 47° are defined by equations with a steep slope (Fig. 9), resulting in faster variations from the beginning of the simulation. The strong dependence of the profile variation on the equations used can cause discrepancies between experimental and modelled values. For example, equation 6 has an associated experimental error that is higher than the error associated with equations 4 and 5 (Godinho et al., 2012). This may be the cause of the differences between the variation of experimental and modelled Ra (Fig. 8 and Tab. 1). The plateau values of the simulated Ra are higher than the experimental Ra (Fig. 8). This may be due to the approximations done for the model calibration. When counting the number of peaks a threshold value has to be set to exclude small peaks from the calibration. This corresponds to a flattening of experimental surfaces equivalent to an increase of a peak height in the simulated peak and consequent general increase of Ra values of the overall profile.

5.4. Numerical model: final remarks

The numerical model presented here differs from previous approaches to simulate dissolution (e.g. Cama et al., 2010; Lasaga and Lüttge, 2001; Stack et al., 2013). For the first time the governing equations of the simulation are set as a function of the surface orientation alone. This allows the simulation of the time dependent changes of topography occurring on surfaces with different initial orientations. Nevertheless, the usefulness of this model to quantify absolute dissolution rates is limited because the model does not include the effect of planes existing in three dimensions. However, we demonstrate that the presented model is a reliable tool to study the variability and coupling between surface properties that change during dissolution, including: a) topography, which is related to surface area; b) retreat rate, which is related to the overall dissolution rate; c) surface orientation, which is related to the local structure of a surface.

It should be noted that equations 4 - 6 were obtained based on the assumption that dissolution rates are constant through time (Godinho et al., 2012). Therefore, an additional experimental error is expected. Nevertheless, by using these equations in our numerical model it is possible to evaluate the changes of dissolution rates with time in accordance with experimental values (Godinho et al., 2014a). This model corroborates our previously proposed model (Godinho et al., 2012) by suggesting that the decrease of high energy sites that are removed during dissolution, is associated with the development of topography, which causes a decrease in dissolution rates even if the total surface area increases.

The governing equations are valid only to simulate dissolution on surfaces with miller indices (hhl) under the specific experimental conditions used to obtain them, thus independent of environmental conditions. Nevertheless, the model and the principle that step sites are dissolved preferentially causing the exposure of more stable surfaces, can be generalised to interpret dissolution data of fluorite surfaces with orientations different from the ones studied here, and also of other materials exhibiting surfaces with different orientations, e.g. spent nuclear fuel. It should be noted that the model is not directly related to the probability of dissolution at each atomic site and does not account for more complex factors originating from structures developed in three dimensions. The limitations of the developed program come from the simplicity of the algorithm used. At the same time, this simplicity is the basis for the strength and beauty of this study where surface orientation alone can be used to simulate the changes in topography and dissolution rate of a surface. Our results suggest that, in principle, macro scale steps are developed during dissolution of surfaces with a high density of atomic scale high energy sites. The observed changes occurring on the surface have a direct effect on the variability of dissolution rates. We suggest that the dynamic nature of dissolution that continuously alters the dissolving surface contributes to the non-constant dissolution rate of mineral surfaces.

6. Conclusions

A simple model that simulates the retreat of fluorite surfaces during dissolution, only depending on the surface orientation, was shown to reproduce the development of topography observed experimentally. A simple algorithm was used in which the displacement of each point is calculated using empirical equations. These equations relate the stability of each segment, by

means of the density of atomic scale steps of the segment, to its orientation. The dynamic nature of dissolution and the strong relation between surface orientation, retreat rate and topography development suggests a) dissolution rates are not directly proportional to surface area if the stability and structure of the surface changes significantly during dissolution; b) future models to simulate dissolution need to include structural parameters that account for the stability of each surface site; c) further studies of surface orientations different from the cleavage planes and with a high density of defects are necessary to understand dissolution kinetics; d) independently of the initial orientation of a surface, its overall dissolution rate approaches the dissolution rate of the most stable surface (111) plus a contribution from persistent macro scale steps if topography is developed.

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References

- Alekseev, Y.V., Alekseev, G.Y., Bityurin, V.A., 2002. Atomic-Topological and Statistical Background for a Correct Dissolution Theory of Crystal Substances. *Protection of Metals* 38, 517-529.
- Anbeek, C., 1992. Surface roughness of minerals and implications for dissolution studies. *Geochim. Cosmochim. Acta* 56, 3957-3970.
- Arvidson, R.S., Ertan, I.E., Amonette, J.E., Lüttge, A., 2003. Variation in calcite dissolution rates: A fundamental problem? *Geochim. Cosmochim. Acta* 67, 1623-1634.
- Bons, P.D.D., Koehn, D., Jessell, M.W., 2008. (Eds.), *Microdynamics simulation. Lecture Notes in Earth Sciences*. vol. 106 Springer, Berlin.
- Brantley, S.L., Kubicki, J., White, A.F., 2008. *Kinetics of water-rock interaction*. Springer, New York.
- Cama, J., Zhang, L., Soler, J.M., Giudici, G., Arvidson, R.S., Lüttge, A., 2010. Fluorite dissolution at acidic pH: In situ AFM and ex situ VSI experiments and Monte Carlo simulations. *Geochim. Cosmochim. Acta* 74, 4298–4311.
- Emmanuel, S., Ague, J.J., 2011. Impact of nano-size weathering products on the dissolution rates of primary minerals. *Chem. Geol.* 282, 11–18.
- Ebner, M., Koehn, D., Toussaint, R., Renard, F., 2009. The influence of rock heterogeneity on the scaling properties of simulated and natural stylolites. *J. Struct. Geol.* 31, 72–82.
- Fischer, C., Arvidson, R.S., Lüttge, A., 2012. How predictable are dissolution rates of crystalline material? *Geochim. Cosmochim. Acta* 98, 177-185.

430 Godinho, J.R.A., Piazzolo, S., Stennett, M.C., Hyatt, N.C., 2011. Sintering of CaF_2 pellets as nuclear fuel
 431 analogue for surface stability experiments. *J. Nucl. Mater.* 419, 46-51.

432 Godinho, J.R.A., Piazzolo, S., Evins, L.Z., 2012. Effect of surface orientation on dissolution rates and
 433 topography of CaF_2 . *Geochim. Cosmochim. Acta* 86, 392-403.

434 Godinho, J.R.A.; Piazzolo, S., Balic-Zunic, T., 2014a. Importance of surface structure on dissolution of
 435 fluorite: implications for surface dynamics and dissolution rates. *Geochim. Cosmochim. Acta* 126, 398-
 436 410.

437 Godinho, J.R.A.; Piazzolo, S., Putnis, C.V., 2014b. Direct observations of the dissolution of fluorite surfaces
 438 with different orientations. *Cryst. Growth Des.* 14, 69-77.

439 Gambrow, B., Ferry, C., Casas, I., Bruno, J., Quinones, J., Johnson, L., 2011. Spent fuel waste disposal:
 440 analyses of model uncertainty in the MICADO project. *Energy Proc.* 7, 487 – 494.

441 Jessell, M. W., Bons, P., Evans, L., Barr, T., Stüwe, K., 2001. *Elle*: the numerical simulation of
 442 metamorphic and deformation microstructures. *Comp. and Geosc.* 27, 17-30.

443 Koehn, D., Renard, F., Toussaint, R., Passchier, C.W., 2007. Growth of stylolite teeth patterns depending
 444 on normal stress and finite compaction. *Earth Plan. Sci. Let.* 257, 582–595.

445 Koehn, D., Dysthe, K., Jamtveit, B., 2004. Transient dissolution patterns on stressed crystal surfaces.
 446 *Geochim. Cosmochim. Acta* 68, 3317–3325.

447 Kurganskaya, I., Lüttge, A., 2013. Kinetic Monte Carlo simulations of silicate dissolution: Model
 448 complexity and parameterization. *J. Phys. Chem. C* 117, 24894-24906.

449 Lasaga, A., 1981, Transition state theory, *Rev. Min.* 8, 135 – 170.

450 Lasaga, A., Lüttge, A., 2001. Variation of crystal dissolution rate based on a dissolution step-wave model.
 451 *Science* 291, 2400-2404.

452 Lüttge, A., 2005. Etch pit coalescence, surface area, and overall mineral dissolution rates. *Am. Miner.* 90,
 453 1776-1783.

454 Lüttge, A., Arvidson, R.S., Fischer, C., 2013. A stochastic treatment of crystal dissolution kinetics.
 455 *Elements* 9, 183–188.

456 Maldonado, P., Godinho, J.R.A., Evins, L.Z., Oppeneer, P.M., 2013. Ab Initio prediction of surface stability
 457 of fluorite materials and experimental verification. *J. Phys. Chem. C* 117, 6639-6650.

458 Moore, J., Lichtner, P.C., White, A.F., Brantley, S.L., 2012. Using a reactive transport model to elucidate
 459 differences between laboratory and field dissolution rates in regolith. *Geochim. Cosmochim. Acta* 93, 235-
 460 261.

461 Oelkers, E.H., Schott, J., 2009. Thermodynamics and kinetics of water-rock interaction. *Rev. Min. &*
 462 *Geochem.* Vol. 70.

463 Piazzolo, S., Jessell, M. W., Bons, P. D., Evans, L., Becker, J. K., 2010. Numerical simulations of
 464 microstructures using the *Elle* platform: A modern research and teaching tool. *J. Geol. Soc. of India* 75,
 465 110-127.

- 466 Putnis, A., Austrheim, H., 2010. Fluid-induced processes: metasomatism and metamorphism. *Geofluids*
467 10, 254-269.
- 468 Putnis, C.V., Ruiz-Agudo, E., 2013. The mineral-water interface: Where minerals react with the
469 environment, *Elements* 9, 177-182.
- 470 Ruiz-Agudo, E., Putnis, C.V., 2012. Direct observations of mineral-fluid reactions using atomic force
471 microscopy: the specific example of calcite. *Min. Mag.* 76, 227–253.
- 472 Schott, J., Pokrovsky, O.S., Oelkers, E.H., 2009. The link between mineral dissolution/precipitation
473 kinetics and solution chemistry (in thermodynamics and kinetics of water–rock interaction). *Rev. Mineral.*
474 *Geochem.* 70, 207–258.
- 475 Smereka, P., Li, X., Russo, G., Srolovitz, D.J., 2005. Simulation of faceted film growth in three dimensions:
476 microstructure, morphology and texture. *Acta Materialia* 53, 1191–1204.
- 477 Snyder, R.C., Doherty, M.F., 2007. Facet crystal shape evolution during dissolution or growth. *AIChE J.*
478 53, 1337-1348.
- 479 Stack, A.G., Gale, J.D., Raiteri, P., 2013. Virtual probes of mineral-water interfaces: The more flops, the
480 better! *Elements* 9, 211–216.
- 481 Stack, A.G., Raiteri, P., Gale, J.D., 2012. Accurate rates of the complex mechanisms for growth and
482 dissolution of minerals using a combination of rare-event theories. *J. Am. Chem. Soc.* 134, 11–14.
- 483 White, A.F, Brantley, S.L., 2003. The effect of time on the weathering of silicate minerals: why do
484 weathering rates differ in the laboratory and field? *Chem. Geol.* 202, 479-506.
- 485 Yanina, S.V., Rosso, K.M., Meakin, P., 2006. Defect distribution and dissolution morphologies on low-
486 index surfaces of α -quartz. *Geochim. Cosmochim. Acta* 70, 1113–1127.
- 487 Yoo, K., Mudd, S.M., 2008. Discrepancy between mineral residence time and soil age: Implications for the
488 interpretation of chemical weathering rates. *Geology* 36, 35–38.

489 **Captions**

490 **Fig. 1:** Schematic representation of the initial graphic display composed of 3 polygons identified by roman
491 numbers (I-III). Dashed lines with black circles represent grain boundaries separating solid polygons that
492 can have different properties, e.g. orientation. The solid line with white circles represents the interface
493 between liquid (polygon I) and solid (polygons II and III) phases, which is constituted by the moving
494 nodes. X and Y identify the horizontal and vertical axes, respectively.

495 **Fig. 2:** Example of a hypothetical displacement of 3 nodes (identified n1 - n3) representing the interface
496 liquid-solid. The nodes are initially aligned with the horizontal. The angles between node 2 and its
497 neighbours (α) are represented for iteration 1 (t_1) and 2 (t_2). Assuming node 1 moves first, its
498 displacement is calculated using the initial surface orientation (φ). To calculate the displacement of node
499 2, angle α_1 is add to the initial orientation, resulting in a displacement different from node 1. At iteration 2
500 the Re contribution is add to node 2 as it is a topographic high.

501 **Fig. 3:** Schematic representation of the sequence of operations performed during one iteration. Equation
502 numbers correspond to those in the text.

Fig. 4: AFM height images and profiles of representative (110), (334) and (115) surfaces after 1600 hrs of dissolution. Note the different maximum height values for each surface. The orientation of the stable surfaces is indicated except for surface (115) as the developing surfaces and noise are indistinguishable.

Fig. 5: Modelled profiles of surfaces (115), (334) and (110) after the stable surfaces are developed and a near constant topography is reached. The final orientations of surfaces constituting the profile are indicated. Inset shows a zoom-in area of the profile of surface (115).

Fig. 6: Comparison between the profiles modelled using different Re values for each of the starting orientations studied: **a)** (115); **b)** (110); **c)** (334).

Fig. 7: Variation of the modelled normalized Ra (left axis) and normalized retreat rates (right axis) as a function of the number of iterations, for the 3 example surfaces. Line shapes identify the same surface. Marks identify Ra curves and unmarked lines identify retreat rate curves. The shorter modelled time for surface (110) is given by the limit of the numerical box. For higher average retreat rates, $Y = 0$ is reached earlier than at low average retreat rates.

Fig. 8: Experimental variation of Ra (triangle points) and modelled variation of Ra normalized to real units (circle points) of the 3 example surfaces. Line shapes identify the same surface. Experimental values are plotted versus dissolution time in hours (lower axis) and modelled values are plotted versus simulation time in millions of iterations (top axis).

Fig. 9: Variation of retreat rate as a function of θ , using equations 4 – 6. i.e. dissolution trends that define the simulation paths. Trends defined by each equation are represented by different lines. $f_1(\theta)$, equation 4 (dotted lines); $f_2(\theta)$, equation 5 (dashed lines); $f_3(\theta)$, equation 6 (continuous line). The orientations studied are marked: (115) square, (334) circle, (110) diamond. The limit of each path is identified as points 1 - 7. The orientations corresponding to the slowest retreat rate (001) and (111) are identified.

Tab. 1: Comparison between experimental and modelled normalized Ra values at the plateau regime of profiles corresponding to the studied surfaces. The initial input angle of the polygons for each of the studied surfaces (φ in eq. 3), and optimized Re parameter are indicated. Ranges of Ra values are indicated when the plateau is not obvious. The factor of retreat rate decrease (RRD), defined as the ration between the initial and final retreat rate is indicated.

Surface	φ (°)	Re parameter	Experimental Ra (nm)	Modelled Ra (nm)	RRD
(115)	16	0	3	7	4
(334)	47	0,01	22	33-37	12
(110)	90	0,0015	94-112	120	22

Figure 1

Figure 2

(a) Iteration1 (t_1)

(b) Iteration2 (t_2)

Figure 3

Figure 4

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure A.1