

## Free Surface Dissolution of Stressed Solids

## Daniel Köhn

Physics of Geological Processes, Postbox 1048 Blindern, N-0316, Oslo, Norway; http://www.fys.uio.no/pgp Institute für Geowissenschaften, Tectonophysics, University of Mainz, Germany; http://www.uni-mainz.de/FB/Geo/Geologie/tecto

## Jochen Arnold

Institute für Geowissenschaften, Tectonophysics, University of Mainz, Germany; http://www.uni-mainz.de/FB/Geo/Geologie/tecto

## Bjørn Jamtveit

Physics of Geological Processes, Postbox 1048 Blindern, N-0316, Oslo, Norway; http://www.fys.uio.no/pgp

## Anders Malthe-Sørenssen

Physics of Geological Processes, Postbox 1048 Blindern, N-0316, Oslo, Norway; http://www.fys.uio.no/pgp

Keywords: dissolution, anti-cracks, cracks, localization, failure



Abstract: We present a new method to study the free surface dissolution of stressed solids. The model couples a thermodynamic/kinetic approach with an elastic discrete element model. In the model we mimic experiments where we stress a crystal vertically and let it dissolve. The reaction is either progressing on a free surface of the crystal in contact with fluid or from an initial hole in the crystal. Once the elastic solid is stressed it develops an instability in the form of a roughness on its free surface. This so called Asaro-Tiller-Grinfeld instability is well known in Physics from thin-film overgrowth studies. It was also recently reproduced on stressed crystals of brittle elastic salts. The simulations show that the surface roughness progresses towards cusp instabilities that can develop into grooves and into crack-like structures or anti-cracks. The roughness has a characteristic size or wavelength that depends on the elastic and surface energies in the model. A comparison with linear stability analysis, experiments and other numerical approaches shows that our model reproduces reasonable results. The localization of dissolution in anti-cracks that propagate into the crystal can introduce the growth of secondary mode I cracks along the anti-crack. These fractures show a similar characteristic scaling behavior than the structures that are produced by the Asaro-Tiller-Grinfeld instability. Combinations of anti-cracking and cracking may cause grain-size reduction and failure.





## **Table of Contents**

Introduction	5
The model	5
Dissolution of Heterogeneously Stressed Solids	6
Discrete Element Module	6
Coupling	8
Dissolution Patterns and Localization of Dissolution	9
Asaro-Tiller-Grinfeld Instability 1	11
Growth of Anti-cracks	12
Anti-cracks and cracks 1	14
Discussion	16
Conclusions 1	16
Acknowledgements	17
References 1	17

### Introduction

Dissolution precipitation creep is an important deformation mechanism in the Earth's crust. It plays a major role in the compaction of sedimentary basins and in the building of mountain chains [Weyl 1959; Rutter 1976; Spiers et al. 1990; Schwartz and Stöckert 1996]. The mechanism involves dissolution of material at sites of relatively high stresses, transport through a fluid phase and precipitation of material at sites of relatively low stresses. Most research has focused on the dissolution at confined contacts between grains [Paterson 1973; Lehner 1995; Schutjens and Spiers 1999; Dysthe et al. 2002 a, b]. However, recent experiments and theoretical considerations indicate that free surface dissolution may also be important [den Brok and Morel 2001; den Brok et al. 2002]. In the present paper we focus on free surface dissolution of stressed crystals and illustrate how concentrations of elastic energy can lead to instabilities and localization of dissolution.

The Virtual

Explorer

At the contact of a crystal to the fluid, dissolution and precipitation are driven by differences in chemical potential along the interface. On free interfaces shear-forces in the fluid can be neglected so that changes in the chemical potential can be defined as [Gibbs 1906; Kamb 1961; Paterson 1973]

 $\Delta \mu = \Delta \psi_s + V_s \Delta P_n$ 

where  $\mu$  is the chemical potential,  $_{\rm S}$  the Helmholtz free energy of the solid,  $V_{\rm S}$  the molecular volume of the solid and  $P_{\rm fl}$  the fluid pressure and the deltas represent changes in these values relative to a reference state. The Helmholtz free energy contains contributions due to surface, elastic and plastic energy. In the present study we focus on surface patterns on stressed elastic crystals in contact with fluid so that we neglect effects of plasticity. Patterns on the surface will then depend on competition between local elastic and surface energies as long as the fluid pressure does not change.

Recent experiments on brittle elastic salt crystals show the development of a roughening instability on the free solid/liquid interface [den Brok and Morel 2001; den Brok et al. 2002]. In the experiment a crystal of an elastic salt is stressed vertically while its surface is in contact with undersaturated brine. The crystal surface develops a roughness that consists of grooves oriented with their long axis perpendicular to the main compressive stress direction. The roughness on the crystal surface has a distinct spacing or wavelength that depends on the stress state of the crystal and its surface energy [Srolovitz 1989]. The grooves on the crystal surface develop because the chemical potential ( Equation 1) is higher when the crystal is stressed so that it dissolves. Stress concentrations at troughs of the roughness increase dissolution, which again has a positive feedback effect on the stress. This effect is known as the Asaro-Tiller-Grinfeld instability [ATG, Asaro and Tiller 1972; Grinfeld 1986]. Linear stability analysis of the onset of the ATG-instability [Srolovitz 1989] predicts that dissolution structures will develop with a roughness that lies within a band of stable wavelengths and thus have a characteristic spacing as observed in the experiments [den Brok and Morel 2001].

The progressive evolution of the ATG-instability and the evolution of patterns beyond this instability have been studied using numerical simulations [Yang and Srolovitz 1993; Ghoussoub and Leroy 2001; Kassner et al. 2001]. In the simulations an initial roughness develops into cusp instabilities and then evolves towards crack-like structures or anti-cracks. In the current paper we will present a new approach to model the ATG-instability and its evolution towards anti-cracks [Koehn et al. 2003] and grooves [Koehn et al. 2004]. First we introduce the numerical method. Then we show the development of the initial ATGinstability and compare the patterns with linear stability analysis and existing numerical simulations. In addition we illustrate the propagation of anti-cracks and finally present combinations of anti-crack propagation and mode I cracking (Mode I Fractures are tensile fractures that grow perpendicular to a tensile stress component, Anti-cracks are lens shaped structures that grow by dissolution or reaction at their tips perpendicular to a compressive stress).

## The model

In order to model the dissolution of stressed elastic solids we use a hybrid approach. The dissolution rate is calculated with a first order kinetic rate law from Transition State Theory. It depends on the local Gibbs chemical potential of the solid-liquid interface. The discrete element model is used to calculate the stress and elastic energy distribution in the crystal after it is being loaded. The surface energy is also determined from the elastic model and depends on the number of springs that particles have towards



The Virtual Explorer

## Dissolution of Heterogeneously Stressed Solids

we have expanded by the discrete element code "MIKE".

In order to treat the dissolution of the stressed solid we relate the change in chemical potential as defined in equation 1, which is due to a change in elastic or surface energy, which are contained within the Helmholtz free energy  $(_{\rm S})$ , to the change in local equilibrium concentration ( C) of dissolved matter in the fluid by the relation:

$$\Delta C \approx \exp\left(\frac{\Delta \psi_s}{RT}\right)$$

where R is the universal gas constant and T the temperature [Koehn et al. 2003]. The dissolution rate of the local surface can then be calculated using a linear rate law following Transition State Theory [Lasaga 1998]:

$$D = k_r V_s \left( 1 - \exp\left(-\frac{\Delta \psi_s}{RT}\right) \right)$$

where D is the velocity of dissolution perpendicular to a unit surface and  $k_r$  a rate constant depending on temperature and activation energy. We assume that the fluid volume is very large so that the concentration of dissolved matter in the fluid does not change [Koehn et al. 2003] and the dissolution rate depends only on the change in equilibrium concentration of the fluid from a system with a nonstressed crystal to a stressed crystal. This assumption is valid for the case of the den Brok and Morel (2001) experiment where the system was constantly slightly undersaturated and the fluid volume very large.

#### Discrete Element Module

#### Figure 1. Two-dimensional networks



In the two-dimensional lattice that is used for the simulations particles are arranged in a triangular network. Each particle (except for boundaries) is initially connected with six springs to six possible neighbors.

The elastic crystal in a simulation is modeled using a discrete element approach. In this model circular particles are arranged in a triangular lattice and connected by linear springs with each other (Figure 1). In a triangular configuration each particle is connected with six possible neighbors. The force on a particle from a spring is proportional to the actual length of the spring minus an equilibrium length times a spring constant so that compressive stresses in the model are by definition negative (Figure 2). The equilibrium configuration of particles and the stress field in the elastic crystal are found by a standard over-relaxation method [Allen 1954]. Particles are moved until forces that act on a single particle cancel out and an equilibrium configuration for the lattice is found. It has been shown that the triangular lattice in two-dimensions reproduces linear elasticity on a large scale [Flekkøy et al. 2002]. Therefore it can be used to model systems that behave linear elastic.

However, the model can describe the behavior of the solid beyond linear elasticity by introducing the possibility to break springs. Springs are broken once they reach a breaking-threshold defined by a maximum local tensile stress that one spring can sustain. If the tensile stress on the spring is larger than the threshold it breaks and is removed from the lattice so that the previously connected neighbors loose their cohesion. All particles have repulsive forces



between each other even if springs are removed and the particles are not really connected. Single springs can never break under pure compression. It has been found that fractures that develop in the model are very similar to fractures found in experiments [Walmann et al. 1996; Malthe-Sørenssen et al. 1998]. In order to add noise to the system to minimize lattice effects a pseudo random distribution of breaking thresholds and spring strengths can be applied to the model [Koehn and Arnold 2003, this volume].

#### Figure 2. Particles under compression



Under compression particles are pushed into each other, under tension they move away from each other. Springs can only break under tension. Particles are repulsive so that they always have a compressive force between them.

The discrete element model has three possible boundary conditions that were used in the presented simulations: Lattice boundaries, internal boundaries and three-dimensional boundaries due to deformation estimates.

Two different lattice boundaries exist in the model ( Figure 3 ). These consist either of 1. a row of particles (particle walls) along the boundary of the lattice or 2. elastic walls along the rims of the deformation box. 1. Boundary particles of particle walls are defined to be part of the lattice boundary, which means that they are moved during a deformation step and then remain stationary during the relaxation. Boundary particle springs cannot break. 2. Elastic walls are walls that act with a compressive force on the particles where the force is proportional to the distance that particles are pushed into the wall. Depending on the elastic constants of walls relative to constants of normal particles walls are either stiff (higher constant) or soft (lower constant). Elastic walls apply no friction or tension on boundaries of the model in contrast to boundary particles.

#### Figure 3. External boundaries



Two possible external boundaries are applied in the simulations. The picture on the left illustrates elastic walls. Particles have repulsive forces on walls so that the force on a particle from a wall is proportional to the distance that the particle is pushed into the wall. Particle walls are rows of particles on the boundary that are moved only during a deformation step and stationary during relaxation.

Internal boundaries of the model are grain or hole boundaries. Single grains are made up of a cluster of particles that lie within a specified area (Figure 4). Particles on the rim of the grain are defined as being part of a grain boundary. Springs that connect two grains and cross a boundary can have different spring constants and different breaking strengths than springs that lie within grains. Particles that are on the rim of grains or holes can have surface energies and can react with for example fluid in a hole. The surface

energy depends on the absolute size of a particle and on the number of springs that are part of a boundary. The number of boundary springs then defines the surface curvature.

The Virtual

Explorer

#### Figure 4. Clusters of particles



Grains A to E are defined by clusters of particles. Springs between particles of different grains can have different properties than springs within grains.

We apply deformation estimates. If a wall of the lattice is moved inwards to stress a crystal all particles are moved according to that deformation assuming that the material is homogeneous. The relaxation starts after this average is taken. Such a deformation estimate will remove boundary effects from the walls. It will also have the effect that the model is quasi three-dimensional so that even if the model has no cohesion in two dimensions (for example a throughgoing hole or crack in the center) it has a cohesion in threedimensions. Instead of applying deformation estimates one can also attach springs to particles in the third dimension and attach these to a homogeneously deforming sheet [Malthe-Sørenssen et al. 1998].

### Coupling

The discrete element code and the dissolution routines are coupled in two ways. First of all the elastic energy and surface energy of internal boundary particles in the discrete code are used as input for the dissolution routines to calculate a dissolution velocity (or reaction velocity) of a unit surface. In a second step this dissolution rate is then used to calculate a probability of how often a particle on the boundary will dissolve in a given time step according to

$$p_a = D_a dt \frac{1}{r_a} \left( 1 - \frac{N_{sp_a}}{6} \right)$$

where  $D_a$  is the dissolution rate for particle a from equation 3,  $r_a$  is the radius of particle a and  $N_{sp_a}$ the number of springs that are still attached to the particle. The last term on the right hand side of equation 4 is representative of the particles circumference that is in contact with the fluid. The 1/r term represents the size of the particle. For example, a smaller particle has a higher probability to dissolve than a large particle. A particle with 4 open springs has a higher probability to dissolve than a particle with 2 open springs because its reactive "surface" that is in contact with the fluid is larger. Particles that shrink completely within a given time step are removed from the discrete model. All other particles shrink in area depending on their probability to dissolve. The elastic model will not be influenced by the reduction of a particle's area until the particle has completely dissolved and is removed from the elastic lattice. In order to add noise to the system a pseudo random distribution can be applied to the area of the particles. This will only affect dissolution and not the effective size of the particle in the elastic model.



# Dissolution Patterns and Localization of Dissolution

#### Figure 5. Initial setup of Animation 1 and Animation 2



Initial setup of Animation 1 and Animation 2, the resolution of the lattice is 1000 x 1000 particles. The crystal is stressed vertically (with respect to the figure if it stands upright) and can dissolve from the right hand side. An initial roughness in the form of a sin-wave is applied to the fluid-solid interface.

We choose to present the dissolution patterns that develop on stressed crystal surfaces in three different sections with three different initial setups. In the first section we are concerned with the detailed development of the ATG-instability on a crystal surface with a predefined roughness that has a given wavelength and amplitude (Figure 5 and 6). We choose this setup because it is used in linear stability analysis [Srolovitz 1989; Gal et al. 1998] and in numerical simulations of Ghoussoub and Leroy (2001). Therefore we can compare the developing structures and their dynamics directly to the presented method. In the second section we are concerned with the propagation of anticracks that develop out of the ATG-instability.

We choose a setup of a vertically stressed crystal in contact with fluid on its sides and with a central elliptical hole (Figure 7). This setup is on the one hand similar to the experiment of den Brok and Morel (2001) and on the other hand we can compare the shape of the developing anti-cracks with the structures that develop in the simulations of Kassner et al. (2001). In the third section we show the interaction of anti-crack propagation and growth of mode I fractures on anti-crack walls in a stressed crystal with a small central hole (Figure 8). In the simulations stresses are applied vertically with respect to stressed crystals that stand upright.





Same setup as in Figure 5 but with a sin-wave that has a larger amplitude than that of Figure 5. Initial setup for animation 3.



#### Figure 7. Initial setup of Animation 4 and Animation 5



Initial setup for animations 4 and 5. A crystal with a central elliptical hole is stressed vertically (with respect to the figure if it stands upright). The crystal is in contact with fluid on its right and left hand side and within the hole. The resolution of the lattice is  $400 \times 461$  particles.

All the simulations were performed with kinetics for a quartz and pure water system. Relevant system parameters are (Rimstidt 1997): temperature ( $200^{\circ}$ C), rate constant for quartz dissolution at  $200^{\circ}$ C ( $1*10^{-7}$  mol sec<sup>-1</sup> m<sup>-2</sup>), Youngs modulus of pure quartz (90 GPa) and molar volume of quartz ( $22.688*10^{-6}$  m<sup>3</sup> mol<sup>-1</sup>). The amount of particles used for the simulations and their absolute size varies.

#### Figure 8. Initial setup of Animation 6 and Animation 7



Initial setup of animation 6 and 7. The crystal is stressed vertically (with respect to the figure if it stands upright). Crystal can only dissolve from the boundary of the small hole in the center. Resolution of the simulation is  $600 \times 600$  particles.



#### Journal of the Virtual Explorer, 2004 Volume 15 Paper 5

#### Asaro-Tiller-Grinfeld Instability



#### Figure 1. Dissolution of a stressed crystal

Movie shows dissolution of a stressed crystal with an initial roughness on its surface. Cusps develop but surface energy is too high for the initiation of the ATG-instability and the surface evolves to a flat shape. Color-scale represents elastic energy where blue is high and yellow low energy.

To model the initiation of the ATG-instability we choose a setup similar to the one of Gal et al. (1998) and Ghoussoub and Leroy (2001). A vertically stressed crystal is in contact with fluid on the right hand side. The surface has a predefined roughness with a wavelength that is a fourth of the height of the box with an amplitude that is 0.025 \* wavelength (Figure 5 ) and 0.25 \* wavelength (Figure 6 ). The crystal is stressed once and the dissolution patterns develop. We use resolutions of 1000000 particles per box for the three simulations presented in this section in order to attain patterns with a high resolution so that the discreteness of the model are made up of elastic walls.

Animation 1 shows a simulation with a predefined wavelength of  $3.3 \ \mu m$  and a small amplitude. The colors represent the elastic energy where blue is high and yellow low energy. The vertical stress on the crystal is 240 MPa and the fluid pressure constant at a value of 24 MPa. At this scale the ATG-instability is producing a localization and small cusps but the surface energy is dominating over

elastic energies so that the patterns disappear and the surface becomes flat. Once the surface is flat it remains flat and dissolves with a constant dissolution rate that is in accordance with the theoretically predicted dissolution rate from equation 3.

Animation 2 shows a simulation with a predefined wavelength of 3.4 µm and also a small amplitude. The color scale and the stress are the same as animation 1. Elastic energy concentrations in the valleys of the roughness drive dissolution as in animation 1. However the small change in wavelength from animation 1 to 2 of 0.1 µm is enough to stabilize the roughness. The ATG-instability develops again small cusps as in animation 1 but now the elastic energy concentration at the tips of the cusps is enough to overcome the surface energy. The cusps develop into dissolution grooves that are similar to the grooves found by den Brok and Morel (2001). Linear stability analysis [Srolovitz 1989; Gal et al. 1998] predicts that a surface roughness has to have a critical wavelength in order to develop a growing ATG-instability. This critical wavelength lies between the wavelength of the roughness in animation 1 and 2. However, whether or not the roughness survives is also dependent on its amplitude. This is normally not included in stability analysis except for the work of Ghoussoub and Leroy (2001). A larger initial amplitude has a stabilizing effect on the roughness since it produces higher elastic energy concentrations.

This effect is shown in animation 3 where the initial amplitude is 0.25\*wavelength and the wavelength 2.1 µm. Now the wavelength of 2.1 µm lies within the region of roughness growth and large-scale cusps develop out of the initial roughness. In animation 3 the cusp development is smaller than the wavelength of the roughness so that the initial localization develops within the valleys. Only later does the structure grow towards large cusps that are on the scale of the initial wavelength.



#### Figure 2. Increased wavelength



http://virtualexplorer.com.au/

Movie shows same setup as Animation 1 but with a roughness that has a slightly larger wavelength. Elastic energy can now overcome surface energy and the ATG-instability develops. Cusp instabilities evolve into grooves on the crystal surface. Color-scale represents elastic energy where blue is high and yellow low energy.

#### Figure 3. Increased amplitude



When the amplitude of the initial roughness is more pronounced smaller wavelength roughness will also develop the ATG-instability. Color-scale represents elastic energy where blue is high and yellow low energy.

#### Growth of Anti-cracks

In order to illustrate the growth of anti-cracks we use a setup where we stress a crystal with a central elliptical hole vertically (Figure 7). The crystal can dissolve from right and left hand sides and from the initial hole. We apply a strain rate on the crystal where the deformation takes place in small steps of 0.06 percent strain per 10000 years. For the simulations we use a lattice of 400 times 461 particles with particle boundaries. The fluid pressure is zero. The two simulations ( animation 4 and animation 5 ) vary in absolute size. In animation 4 the crystal has a height of 4 mm and in animation 5 a height of 0.8 mm. Colors in the movies represent differential stresses where blue is zero and red high differential stress (0-90 MPa).



#### Figure 4. Stressed crystal with a central elliptical hole

The Virtual

Explorer



Movie shows a stressed crystal with a central elliptical hole that is in contact with fluid on its right and left hand side and around the hole. A strain-rate is applied on the crystal (see text for details). Dissolution localizes and anti-cracks run into the crystal.

In animation 4 the surface energy is smaller than in animation 5 since the system is larger. However the surface energy is high enough to smoothen irregularities on the crystal surface at the beginning of the simulation. When the crystal is strained differential stresses are high at the right and left hand side of the hole and low at the top and bottom. When the crystal is strained enough that the main stress color changes to yellow small red stress concentrations can be seen at irregularities on the surface of the crystal. Elastic energy is now high enough to initiate the ATG-instability. Dissolution localizes, cusp instabilities develop and grow into anti-cracks that propagate into the crystal from its left and right hand side and from the left and right hand side of the hole. The wavelength of the structures is strongly influenced by initial irregularities on the crystal surface. At first all these irregularities develop into anti-crack structures. However at the left hand side of the hole some of the anti-cracks dominate their neighbors. This phenomenon is similar to a period doubling instability and has been also observed in numerical simulations of Kassner et al. (2001) who use a phase-field approach to model fluid-melt systems.

The period doubling produces a coarsening of the pattern [Koehn et al. 2003, 2004] since the wavelength of the roughness grows. Sudden changes of the stress field indicate additional loading steps while anti-cracks are propagating. Additional loading leads to an increase in localization of dissolution until anti-cracks from the hole in the crystal and the sides meet and merge. The effect that the crystal is not collapsing at this point is due to the deformation estimates that are taken during the straining steps and because no gravity is present in the simulations. Parts of the crystal that are now completely surrounded by fluid behave like single grains but can still be strained by minor amounts due to the deformation estimates so that anticracks can still grow. This can be seen as a three-dimensional effect so that the crystal has still a cohesion in the third dimension. Anti-cracks that propagate towards each other and are not merging by coincidence first run past each other for a short distance and then stop (Figure 9). Afterwards a small anti-crack grows from the wall of a neighboring anti-crack towards the neighbor's tip parallel to the main compressive stress direction on the crystal. Figure 9 illustrates that this unusual behavior is caused by a small stress bridge that develops from a neighbor's tip towards the anti-crack's wall. In the end the localization of dissolution produces a pattern with a distinct spacing of mostly horizontal and some minor vertical anti-cracks. Surface energies are again dominating and result in smooth edges.



#### Figure 9. Two merging anti-cracks



Figure shows the progressive sequence of two merging anti-cracks in animation 4. First the anti-cracks run past each other for a short distance that is about the same as the distance between them. Then they stop and small anti-cracks grow from anti-crack walls towards tips of neighbors. This results in rhomb-shape structures with horizontal and vertical anti-cracks.

In animation 5, surface energy is more dominant than in animation 4 since the system is smaller. The crystal dissolves from its sides and the hole for a while without producing a pronounced roughness and no real localization of dissolution. Flat cusp instabilities develop around the hole with a small amplitude. At a certain amount of strain the elastic energy is (similar to animation 4) high enough to overcome the surface energy and dissolution localizes. This transition is almost instantaneous, as long as surface energies are dominant the crystal surface almost remains a stable structure but as soon as a critical elastic energy is reached the surface becomes unstable and dissolution localizes. The system shows a period doubling instability right at the point when dissolution localizes similar to the instability seen in animation 4 . Only three of the four initial cusps on each side of the hole develop into anti-cracks. The propagation of anti-cracks is similar to the behavior in animation 4 except for the spacing of the structures in the end. Animation 5 shows less anti-cracks und thus a wider spacing than animation 4 . A larger wavelength of structures is expected since the system is smaller in animation 5 .





>Movie shows the same setup as Animation 4, but the system is smaller. Therefore surface energies are more important initially than in Animation 4, small flat cusps develop and the crystal dissolves slowly. Towards the end of the movie the ATG-instability is suddenly initiated and dissolution localizes.

#### Anti-cracks and cracks

Animation 6 and 7 show the interaction of anti-crack propagation and mode I fracturing. In these simulations a crystal with a small hole in the center is stressed vertically. The upper and lower side are confined by elastic walls whereas the right and left hand side are unconfined. The crystal is represented by 600 times 600 particles, colors in the animations represent differential stresses with the scale-bar shown on the left hand side in the movies (red is high and blue low differential stress). The crystal is strained once at the beginning of the simulations. While the anticrack grows it produces tensile stresses at its upper and lower sides. These tensile stresses result in the propagation of mode I fractures from the anti-crack walls. In the beginning of anti-crack and crack growth in animation 6 the length of mode I fractures is proportional to the length of the anti-crack. The longest fractures are the oldest in the center of the propagating anti-crack and fractures grow sub-critically with the anti-crack. After a while mode I cracks show a period doubling instability in animation 6, only every second mode I fracture continues to grow. This instability is very similar to the period doubling instability of growing anti-cracks that was discussed in the last section.

The Virtual

Explorer

If tensile stresses are not large enough for all fractures to continue growing the system goes through a period doubling instability so that only half of the fractures continue to grow. The instability is induced by stress-shielding effects of neighboring fractures. Only slight perturbations in the system are enough to induce this period doubling which results in a coarsening of the growing fracture pattern. Once the anti-crack has reached a critical length mode I fractures in the center stop to grow. However, while the anti-crack propagates towards the sides of the crystal a new cluster of mode I cracks grows on the left and right hand side of the initial cluster in the center. These new two clusters have larger mode I cracks in their center than the initial cluster in the center of the crystal. This is probably due to higher tensile stresses next to the boundaries of the crystal since the boundaries are not confined.

#### Figure 6. Propagation of an anti-crack



Movie shows the propagation of an anti-crack from an initial small hole and the development of mode I fractures along the anti-crack walls. Crystal is stressed vertically (with respect to the figure if it stands upright). Colors represent differential stresses with the scale bar shown on the left hand side in the movies (red is high and blue low differential stress.

Animation 7 shows a similar simulation with a higher breaking strength of springs, which results in a wider spacing and smaller length of mode I fractures. The wavelength of the fracture clusters does not seem to be influenced by the breaking strength of springs, the wavelength is the same for animation 6 and 7. Once the anti-crack reaches the sides of the crystal mode II shear fractures develop and the crystal fails.



The Virtual Explorer



Movie has the same setup as Animation 6 but the breaking strength of the crystal is higher. This results in less mode I fractures. When the anti-crack moves to-wards the walls of the crystal it induces failure. Colors represent differential stresses with the scale bar shown on the left hand side in the movies (red is high and blue low differential stress).

### Discussion

The presented simulations show that free surface dissolution of stressed crystals can initiate instabilities that may lead to brittle failure and grain size reduction. The simulation results are in accordance with predictions of linear stability analysis of previous studies [Srolovitz 1989; Gal et al. 1998]. The wavelength of the structures depends on the elastic energy, which is a function of the strain on the system, the elastic properties of the crystal and the free surface energy. The surface energy is dependent on the size of the system. For the ATG-instability the surface energy mainly plays a role in the absolute size and shape of small perturbations on the crystal surface that can trigger the instability. This parameter is hard to quantify. If the crystal surface is too smooth no instability will develop. However if a strain rate is applied on the system the instability will eventually be initiated in order to accommodate the strain as long as no other mechanism takes over. If the breaking strength of the crystal is reached before the instability develops the crystal will simply fracture. If dissolution at confined contacts is faster, strain will be released and the instability will not develop. How important free surface dissolution is in comparison with other mechanisms during deformation has to be established. Recent experiments however indicate that free surface dissolution can play a major role in dissolution precipitation creep [Koehn et al. 2004].

The simulations shed light on a previously known discrepancy between numerical models of the ATG-instability and the experiments of den Brok and Morel (2001). Numerical simulations by Ghoussoub and Leroy (2001) produce cusp instabilities but no quasi-stable dissolution grooves like the experiments of den Brok and Morel (2001). Animation 2 that was presented in section 3.1 shows clearly that the cusp instability is not necessarily stable but can develop into groove like structures. How stable these grooves are is not yet clear and needs to be studied in a numerical model that includes dissolution as well as growth and diffusion of mater in the fluid.

The question remains how fast systems will develop anti-cracks that may initiate failure and under what conditions grooves develop. This is not a straight-forward question. Anti-cracks like the ones shown in section 2.2 that develop out of rough surfaces have yet to be established in experiments. There are however similarities to lens like structures that develop at the olivine to spinel phase transition in the mantle of the Earth [Green and Burnley 1989]. However, the pressure maybe more important in the spinel anti-crack structures than the elastic energy that drives the ATG at free surfaces.

The discreteness of the model has to be treated with care. If the particles are too large the dissolution of a particle by itself will trigger the instability. However the size of the simulations presented in this paper should be sufficiently large so that surface energies of single particles are very high and the removal of a particle by itself does not induce the ATG. This is definitely true for the simulation shown in animation 1 where a rough surface is smoothened by surface energies. In this simulation the particles are small enough so that a wavelength on the surface has to be quite pronounced in order to let the roughness grow.

## Conclusions

We present a method to model the dissolution of free surfaces of stressed crystals in contact with a fluid. The simulations are in accordance with linear stability analysis, other numerical approaches to the problem and show similarities to experiments. Free surface dissolution of a



stressed crystal can lead to instabilities (ATG-instability), which strongly localize dissolution. The localization is transient and evolves from initial cusp instabilities to grooves or anti-cracks. Anti-cracks propagating into crystals may lead to brittle failure. Propagating anti-cracks show a secondary instability, a period doubling that leads to a coarsening of the structures. Anti-crack associated mode I fractures grow sub-critically and develop the same period doubling instability as anti-cracks. The simulations suggest that there is a strong physical similarity between cracks and anti-cracks. This is a further indication that anticracks may be associated with earthquakes as are cracks.

The Virtual

### Acknowledgements

Part of this project was funded by a grant from the Center of Advanced Studies of the Norwegian Academy of Sciences and by the EU-Network "Precip-Dissolution" contract number HPRN-CT-2000-00058. JA acknowledges funding by the DFG-Graduiertenkolleg "Composition and Evolution of Crust and Mantle". Discussions with Francois Renard, Renault Toussaint, Jens Feder and Dag Dysthe are gratefully acknowledged.



## References

Allen, D.M.d.G. 1954. Relaxation Methods. McGraw Hill, New York.

- Asaro, R., Tiller, W. 1972. Interface morphology development during stress corrosion cracking: Part I, via surface diffusion. Metall. Trans. 3, 1789-1796.
- den Brok, S.W.J., Morel, J. 2000. The effect of elastic strain on the microstructure of free surfaces of stressed minerals in contact with an aquaeous Solution. Geophys. Res. Ltrs., 28, 603-606.
- den Brok, S.W.J., Morel, J., Zahid, M. 2002. In situ experimental study of roughness development at a stressed solid/fluid interface. In: Deformation Mechanisms, Rheology and Tectonics: Current Status and Future Perspectives, Vol. 200 Geological Society Special Publication, 73-83.
- Dysthe, D.K., Podladchikov, Y., Renard, F., Feder, J., Jamtveit, B. 2002a. Universal scaling in pressure solution creep. Physical Review Letters 89, p. 6102.
- Dysthe, D.K., Renard, F., Porcheron, F., Rousseau, B. 2002b. Fluid in mineral interfaces - molecular simulations of structure and diffusion. Geophysical Research Letters 29, 7, 13.
- Flekkøy, E.G., Malthe-Sørenssen, A., Jamtveit, B. 2002. Modeling hydro-fracture, Journal of Geophysical Research, 107, B8, ECV 1, 1-11.
- Gal, D., Nur, A., Aharonov, E. 1998. Stability analysis of a pressure-solution surface. Geophysical Research Letters, 25, 1237-1240.
- Ghoussoub, J., Leroy, Y.M. 2001. Solid-fluid phase transformation within grain boundaries during compaction by pressure solution. J. of the Mech. and Phys. of Solids 49, 2385 - 2430.
- Gibbs, J.W. 1906. On the equilibrium of heterogeneous substances. The Scientific Papers of J. Willard Gibbs, Vol. 1, Longmans Green, Toronto, Ont., pp. 55-349.
- Green, H.W., Burnley, P.C. 1989. A new self-organizing mechanism for deep-focus earthquakes. Nature, 341, 733-737.
- Grinfeld, M.A. 1986. Instability of the separation boundary between a non-hydrostatically stressed solid and a melt. Sov. Phys. Dokl. 31, 831.
- Jessell, M., Bons, P.D., Evans, L., Barr, T., Stuewe, K. 2001. Elle: the numerical simulation of metamorphic and deformation microstructures, Computers And Geosciences 27, 17-30.
- Kamb, W.B. 1961. The thermodynamic theory of nonhydrostatically stressed solids. J. Geophys. Res. 66: 259-271.

- Kassner, K., Misbah, C., Mueller, J., Kappey, J., Kohlert, P. 2001. Phase-field modelling of stress-induced instabilities. Physical Review E. 63.
- Koehn, D., Arnold, J., Jamtveit, B., Malthe-Sørenssen, A. 2003. Instabilities in stress corrosion and the transition to brittle failure. American Journal of Science 303, 956-971.
- Koehn, D., Dysthe, D.K., Jamtveit, B., 2004 (in press) Transient dissolution patterns on stressed crystal surfaces. Geochimica Cosmochimica Acta.
- Lasaga, A.C. 1998. Kinetic theory in the earth sciences, Princeton University Press, Princeton
- Lehner, F.K. 1995. A model for intergranular pressure solution in open systems. Tectonophysics 245, p. 153-170.
- Malthe-Sørenssen, A., Walmann, T., Feder, J., Jøssang, T., Meakin, P. 1998. Simulation of extensional clay fractures. Physical Review E, 58, 5548-5564.
- Paterson, M.S. 1973. Nonhydrostatic thermodynamics and its geologic applications. Rev. Geophys. Space Phys. 11: 355-389.
- Rimstidt, J.D. 1997. Quartz solubility at low temperature. Geochimica et Cosmochimica Acta 61, 2553-2558.
- Rutter, E.H. 1976. The kinetics of rock deformation by pressure solution. Philos. Trans. R. Soc. London 283, 203-219.
- Spiers, C.J. Schutjens, P.M.T.M., Brzesowsky, R.H., Peach, C.J., Liezenberg, J.L., Zwart, H.J. 1990. Experimental determination of constitutive parameters governing creep of rocksalt by pressure solution. In: R.J. Knipe, E.H. Rutter, (Eds), Deformation Mechanisms, Rheology and Tectonics. Geol. Soc. Spec. Publ. 54, 215-227.
- Schutjens, P.M. and C.S. Spiers, 1999. Intergranular pressure solution in NaCI: Grain-to-grain contact experiments under the optical microscope. Oil and Gas Science and Technology 54, p. 729-750.
- Schwartz, S., and B. Stöckert, 1996. Pressure solution in siliciclastic HP-LT metamorphic rocks constraints on the state of stress in deep levels of accretionary complexes, Tectonophysics 255, p. 203-209.
- Srolovitz, D.J. 1989. On the stability of surfaces of stressed solids: Acta Metall. 37, 621-625.
- Walmann, T., Malthe-Sørenssen, A., Feder, J., Jøssang, T., Meakin, P., Hardy, H.H. 1996. Scaling relations for the lengths and widths of fractures, Phys. Rev. Lett., 77, 5292-5296.
- Weyl, P.K. 1959. Pressure solution and the force of crystallization - a phenomenological theory. J. Geophys. Res. 69, 2001-2025.
- Yang, W.H., Srolovitz, D.J. 1993. Cracklike surface instabilities in stressed solids. Phys. Rev. Ltrs. 71, 1593-1596.