

# *In situ* experimental study of roughness development at a stressed solid/fluid interface

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**Abstract:** Theory and experiments have demonstrated that the initially flat surface of an elastically strained solid is morphologically unstable. The elastic strain energy of a rough, corrugated surface is lower than that of a flat one. Hence, stress forces the surface into a rough structure, but the associated increase in surface energy counteracts this roughening. In this way an equilibrium surface roughness consisting of  $\mu\text{m}$ -scale grooves and ridges can develop if the solid is transported, e.g. by diffusion through an aqueous solution, from sites of high stress to sites of low stress. We report *in situ* experimental observations of the surface of elastically strained potassium (K-) alum single crystals held in K-alum solution. The observations confirm earlier reports of the development of stress-induced  $\mu\text{m}$ -scale grooves on the surface of this material. The *in situ* observations show, however, that the stress-induced surface morphology is not a static, but a dynamic structure. The grooves are mobile, and may for example propagate or increase or decrease in length. They may move upwards, downwards, or remain where they are. Others rotate and undulate. It is suggested that if stress is high enough, grain boundaries in (wet) rocks could possess a similar structure of channels, continuously changing position and orientation, in line with the so-called 'dynamically stable' island-channel grain boundary structure that is essential to several pressure solution models.

The mechanical behaviour of the Earth's crust is strongly affected by the presence of small amounts of interstitial water at grain boundaries and in micropores and fractures (e.g. Fyfe *et al.* 1976). Under the influence of stress gradients, the mineral grains may locally dissolve in the interstitial water and the dissolved material diffuse through – or flow with – the water to other locations, where it may precipitate again. This material transport may lead to deformation of the rocks, a mechanism commonly referred to as 'pressure solution' (PS) (e.g. Lehner 1990, Paterson 1995 and references therein). PS is widely regarded as a very important ductile deformation mechanism in the continental crust, at least up to low- to medium-grade metamorphic conditions. Yet, how precisely PS works, notably at the microscopical scale, is poorly understood. Reliable PS constitutive flow laws are therefore lacking for most rocks and rock-forming minerals (rocksalt forms a noticeable exception: Spiers & Schutjens 1990; Spiers & Carter 1998). For this reason PS is generally not taken into consideration in crustal strength profiles or deformation mechanism maps (e.g. Carter & Tsenn 1987; Ranalli 1987; Twiss & Moores 1992).

One of the major problems in defining a PS flow law is that the microstructure of grain boundaries during deformation by PS is not well understood. This is an important problem. It can be shown that different, but reasonable, assumptions made on the grain boundary structure may lead to up to 10 orders of magnitude difference in the predicted strain rate (den Brok 1998). A point of major uncertainty is whether or not grain boundaries can maintain a *rough* microstructure while PS is in progress. It is held by some (e.g. Raj 1982; Spiers & Schutjens 1990; Lehner 1990; Ghoussoub & Leroy 2001) that water at grain boundaries is present in some kind of 'island-channel' structure which provides easy access for water to enter the boundary and for dissolved material to diffuse out of it. Schutjens & Spiers (1999) recently reported *in situ* observations of such grain boundary roughening phenomena, and there are numerous 'post-mortem' observations of rough grain boundaries reported by various groups (e.g. Spiers & Schutjens 1990; Cox & Paterson 1991; Dewers & Hajash 1995). However, until recently, the idea of a rough grain boundary consisting of islands and channels could not be explained as a predicted feature of any model (Lehner 1995).

In the present paper we present experimental support for a model proposed by Leroy & Heidug (1994) and further developed by Ghousoub & Leroy (2001) that, at least qualitatively, offers an explanation for the development of a rough boundary structure during deformation by PS. The model is based on recent theories and experimental observations on the effect of elastic strain on the stability of solid–fluid interfaces. The initially straight surface of an elastically strained solid is morphologically unstable. It turns into a rough structure if a local material transport is possible, e.g. by diffusional mass transfer through an aqueous solution. The elastic energy is responsible for the instability, while interfacial energy is the stabilising influence. Thus, an equilibrium structure is formed, consisting of  $\mu\text{m}$ -scale valleys and ridges. We have performed an *in situ* experimental study of such roughness development on free crystal faces held under stress in a slightly undersaturated aqueous solution.

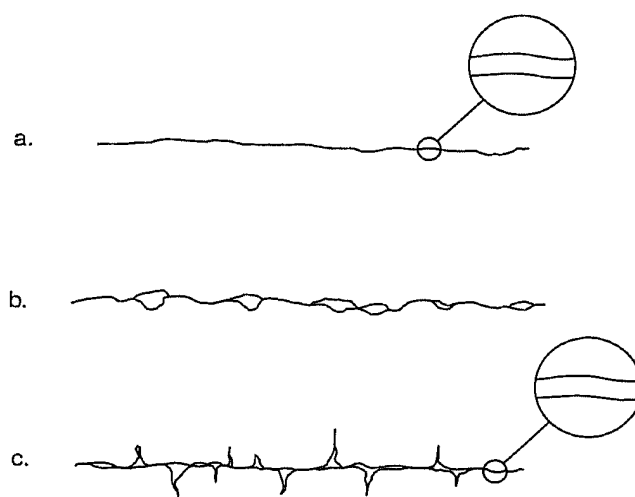
Before presenting our results we will first discuss the different grain boundary models proposed in the literature to illustrate where the problems lie.

### Grain boundary models

Basically, three different grain boundary models have been proposed in the PS literature (Fig. 1): (i) the thin film model; (ii) the island–channel model; and (iii) the island–crack model.

#### *Thin film model*

In the thin film model (Fig. 1a) it is assumed that water is present at grain boundaries in the form of a strongly adsorbed, very thin, continuous fluid film capable of transmitting shear stresses (e.g. Weyl 1959; Rutter 1976). The molecular structure of such films remains obscure to date. Originally it was thought that they would typically be 1 or 2 nm thick (e.g. Rutter 1976) or possibly even thicker (e.g. 1–30 nm: Hickman & Evans 1991). Surface force measurements by Peschel *et al.* (1982), Israelachvili (1986, 1992, 1997) and Horn *et al.* (1988, 1989) have shown, however, that such films must be much thinner. At NPT-conditions, a 1–2 nm aqueous solution film squeezed between silica plates is able to resist an effective shear stress of  $\sim 0.1$  MPa only. About 1 MPa was needed to squeeze out such a water film completely. According to Zhu & Granick (2001) water films more than about three monolayers thick (i.e.  $\geq 6$  Å) possess an



**Fig. 1.** Cartoon illustrating grain boundary models. The grain boundaries are depicted in cross section. (a) Thin film model (Weyl 1959; Rutter 1976). The thin aqueous film is assumed to be only a few nm wide. (b) Island–channel model (Raj 1982; Spiers *et al.* 1990; Lehner 1990). The boundary is commonly assumed to be effectively a few hundreds of nm wide. (c) Island–crack model (Gratz 1991; den Brok 1998). The boundary at the crack-bound islands is assumed to consist of a thin film (cf. Fig. 1a). Crack spacing several  $\mu\text{m}$ 's.

intrinsic liquid structure. Hence, thin films capable of resisting geologically realistic stresses can only be expected to be at most one or two atomic layers thick. The diffusivity in such molecularly thin aqueous films is not well known. Originally, it was assumed that the diffusivity is several orders of magnitude lower than in the bulk fluid, because of electro-viscous effects (e.g. Rutter 1976). More recently it has appeared, however, that the viscosity increase due to the electro-viscous effect in thin solution films is very small (considerably less than a factor 10 according to, e.g. Rubie 1986). Moreover, molecular dynamics based computer simulations have predicted that the self-diffusivity in molecularly thin films is decreased only by a factor  $\leq 2$  (Magda *et al.* 1985; Vanderlick & Davis 1987; Schoen *et al.* 1988; Bitsanis *et al.* 1990).

#### *Island–channel grain boundary model*

It may be argued on the basis of the work of e.g. Israelachvili (1997) that at stresses higher than a few Mpa, thin films will be squeezed out from between the mineral grains leading to solid–solid contacts. In the island–channel model (Fig. 1b) it is assumed that the grain boundary has a microscopically *rough* structure, consisting

of solid–solid contact ‘islands’ (or pillars) across which the stress is transmitted, and water-filled ‘channels’ containing free liquid at a uniform pressure equal to the macroscopic pore fluid pressure (e.g. Raj 1982; Lehner 1990; Spiers & Schutjens 1990, Ghoussoub & Leroy 2001). The channels form an interconnected network through which dissolved material can be transported away, out of the grain boundary. This island–channel structure is assumed to be dynamically stable, i.e. it is assumed to be a time-statistically constant, non-equilibrium structure. During continuous dissolution, islands and channels are assumed to change position continuously, while on average the structure remains the same. The island–channel structure may typically be up to a few hundred nm thick (Schutjens & Spiers 1999; 100–250 nm at the halite–glass contact following de Meer *et al.* 2001).

The island–channel model assumes that grain boundaries can maintain a rough structure during the PS process. Whether this is possible may be questioned. A rough structure may very well be unstable and smooth out with ongoing PS. The islands supporting the stress could be preferentially dissolved and the fluid mechanically expelled or trapped in inclusions by surface energy driven healing of the grain boundaries (e.g. Hickman & Evans 1991). In support of the island–channel model it was suggested that the roughness may smooth out for conditions approaching equilibrium, but not necessarily so for the non-equilibrium conditions corresponding to PS (Spiers & Schutjens 1990; Lehner 1990, 1995). A rough structure may possibly be treated as a quasi-stationary, non-equilibrium structure, because of: (1) local crystal plastic deformation; (2) the presence of defects in the solid; (3) heterogeneities in solid deformation; or (4) crystallographically controlled interface kinetics (Spiers & Schutjens 1990). All of this could continuously perturb the rate of dissolution and precipitation along the phase boundary. In this way, a rough surface with some average, dynamically stable non-equilibrium structure could, in principle, be maintained during deformation by PS. However, whether or not this is actually the case remains unclear (e.g. Lehner 1995). Moreover, different solids may be capable of supporting different rough structures maintained by different mechanisms.

#### *Island–crack model (Gratz 1991)*

Gratz (1991) studied the surface of quartz grains from sandstones compacted by PS in the nature.

He observed that the surface consisted of numerous  $\mu\text{m}$ -scale islands, separated by crack-like features. On the basis of his observations he proposed a grain boundary model consisting of static islands supporting the stress, separated by microfracture-controlled fluid channels (Fig. 1c). He assumed that the grain-to-grain contacts at the fracture-bound islands contained a thin fluid film of the type assumed by Weyl (1959) and Rutter (1976), and that the diffusivity in the film on the islands was several orders of magnitude lower than the diffusivity in the channels. Thus, the rate of mass removal would be controlled by the diffusion in the fluid film at the island–island contacts. Compared to the thin film model, the overall diffusivity would be significantly increased due to the presence of the microfractures.

Compared to the dynamically stable island–channel grain boundary structure, the island–crack grain boundary structure proposed by Gratz is a static structure. Channels remain where they are at fixed positions. The roughness is maintained due to the growth of the fractures. With ongoing dissolution the roughness is not expected to be smoothed out.

#### *Relationship between the models*

It is important to note that the three different grain boundary models do not exclude each other. The dominance of either one of the grain boundary structures may depend on several factors, such as, e.g. the type of solid(s) involved, the  $P$ – $T$  conditions prevailing, the amount of water present, or the intensity of the stress. At very low stresses, thin film diffusion could very well dominate the PS process, whereas at intermediate stresses, islands and channels could develop. At the highest stresses, microfractures could start to dominate the PS process.

#### **Morphological (in-)stability of elastically strained surfaces**

The question we wish to examine is whether or not a rough, dynamically stable island–channel type grain boundary structure can exist, while PS is going on, even in the absence of perturbing influences such as defects, plastic deformation and so on. Would the roughness not tend to be smoothed out? In this paper we will argue that this is not the case. It has been observed recently in experiments on various solids (e.g. Kim *et al.* 1999 and references therein) that a non-hydrostatically stressed, elastically strained

solid, which is in contact with its own melt or vapor, can partially release its elastic strain energy by a morphological instability at the interface. This strain relief mechanism gives rise to what appears to be a roughening of the surface into grooves and ridges of a particular spacing. A corrugated surface has a lower elastic energy than a flat one. This phenomenon was first predicted by Asaro & Tiller (1972), but since the independent rediscovery of the instability by Grinfeld (1986) and Srolovitz (1989) it is often referred to as 'Grinfeld instability'.

Following Srolovitz (1989) the nominally flat surface of an elastically stressed solid is unstable with respect to the growth of perturbations with wavelengths ( $\lambda$ ) greater than a critical wavelength ( $\lambda_c$ ). For  $\lambda > \lambda_c$  the energy of the system may be lowered by the formation of a rough surface of high-stress valleys and low-stress ridges, thus providing a driving force for material transport, e.g. by diffusion through an aqueous solution from the valley to the ridge (Fig. 2). The equilibrium geometry of the surface is then controlled by a balance between the elastic strain energy driving an increase in the amplitude of the valley-and-ridge structure, and the surface energy driving a decrease in the amplitude, i.e. a smoothing of the valley-and-ridge structure. According to Srolovitz (1989) the change in free energy ( $\Delta F$ ) in going from a flat surface to a surface consisting of valleys and ridges with an amplitude  $c$  and a wavelength  $\lambda$  (Fig. 2) may

be approximated by:

$$\Delta F = \frac{-c\lambda\sigma^2}{4E} + 2c\gamma \quad (1)$$

where  $\sigma$  is the differential stress in the bulk,  $\gamma$  is the surface energy, and  $E$  is Young's modulus. The critical wavelength (i.e. the wave length at  $\Delta F = 0$ ) is then equal to

$$\lambda_c = 8\gamma E/\sigma^2. \quad (2)$$

For a typical rock-forming mineral such as quartz, with  $\gamma \approx 0.5 \text{ J/m}^2$  and  $E \approx 50 \text{ GPa}$ ,  $\lambda_c$  would be of the order of  $20 \mu\text{m}$  for  $\sigma = 100 \text{ MPa}$  and  $5 \mu\text{m}$  for  $\sigma = 200 \text{ MPa}$ . Hence, provided that dissolution and precipitation can take place, a microstructurally significant surface roughness could be developed by stressing the rocks within the elastic deformation regime.

Leroy & Heidug (1994) were the first to realise that Grinfeld-type instabilities could be relevant to PS phenomena. They used linear stability analysis to numerically study the interface evolution of a fluid-filled tubular pore embedded in a stressed solid matrix. They superposed small disturbances on a known equilibrium shape and then analysed their evolution in time, using kinetic laws to describe the relevant transport mechanisms. They investigated the alteration in pore geometry caused by a dissolution-precipitation reaction and showed that large fluid-filled pores in a stressed solid matrix are morphologically unstable and should break up into smaller pores. Ghossoub (2000) and Ghossoub & Leroy (2001) applied the theory to the evolution of grain boundary structure in aggregates deforming by PS. They numerically showed how the instability would lead to localized dissolution and penetration of water into the grain boundary by marginal dissolution. They suggested that the newly formed fluid layer would be highly instable, leading to a repeated reorganization or dynamic evolution of the grain boundary internal structure during the action of PS.

Experimental evidence for the development of Grinfeld-type instabilities at the surface of elastically strained, soluble solid in contact with an aqueous solution was first provided by Morel (2000) and den Brok & Morel (2001). These authors performed experiments on potassium (K-) alum ( $\text{K Al} [\text{SO}_4]_2 \cdot 12\text{H}_2\text{O}$ ), which was used as a rock analogue material. Rectangular single crystals of this material were put in a vessel at room P-T conditions and elastically strained with a dead weight in a slightly under-saturated K-alum solution. Grooves developed in the initially flat surface of the crystals, oriented dominantly perpendicular to the maximum

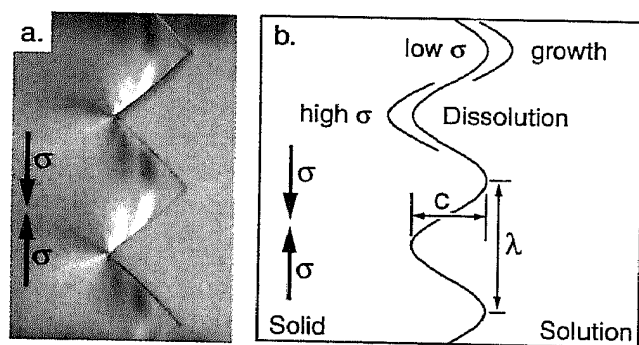


Fig. 2. (a) Plexiglass model under stress (plexiglass left, air right) seen through crossed polarizers and illustrating the concentration of stress at concavities. Crests between the grooves are almost free of stress. Grooves are about 0.5 mm apart. (b) Free face of a solid stressed with a bulk stress  $\sigma$  in contact with a solution and with a sinusoidal surface profile. The profile has wavelength  $\lambda$  and amplitude  $c$ . The stress in the valleys is higher than the stress on the ridges, thus providing a driving force for further increase in amplitude of the valley-and-ridge structure, e.g. by dissolution at the high-stress valleys and growth at the low-stress ridges (after den Brok & Morel 2001).

compressive stress. The grooves disappeared soon after the stress was taken off. The grooves were typically 20–40  $\mu\text{m}$  wide and 10–20  $\mu\text{m}$  deep, and their size was broadly in agreement with the above theory.

In this paper we report on *in situ* observations made on K-alum single crystals stressed in aqueous solution under conditions similar to those reported by den Brok & Morel (2001). From the experiments it appears that stress-induced surface roughness is not a static structure, but dynamic, with grooves constantly changing position and orientation.

### *In situ* experiments: procedure

The experiments were carried out *in situ*, in a see-through vessel mounted under an optical microscope (Fig. 3; cf. den Brok *et al.* 1998). This vessel consists of two 50  $\times$  50 mm glass slides of 1.6 mm thick, separated by a 1.1 mm thick U-shaped Ertalon spacer. The glass slides and the spacer were glued together with UV-activated loctite ('Loctite 350'). The slot-shaped vessel thus obtained measures about 10  $\times$  20  $\times$  1.2 mm in size. Samples used were rectangular platelets of about 6  $\times$  8  $\times$  1 mm, cut with a diamond blade (Buehler) saw from solution-grown potassium

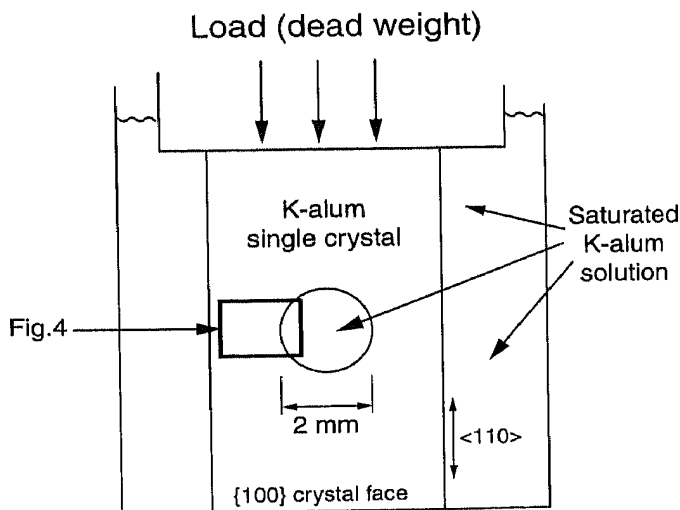
alum single crystals. Volitaile oil ('Shell S4919') was used as a lubricant. A  $2 \pm 0.05$  mm diameter hole was drilled in the middle of each samples with a twist drill, again using volatile oil as a lubricant. This hole was drilled in order to obtain a geometrically well-defined stress concentration in the centre of the sample, as in experiments by Sprunt & Nur (1977) and Bosworth (1981). Without a hole, the surface phenomena of interest would develop dominantly at the stress concentrations at the corner of the contact between the sample and the piston, where it is difficult to make good observations.

After the hole was drilled, the sides of the samples were polished using polishing paper (mesh size up to 1200), again using volatile oil as a lubricant. Finally, the samples were cleaned in distilled water and dried with tissue paper.

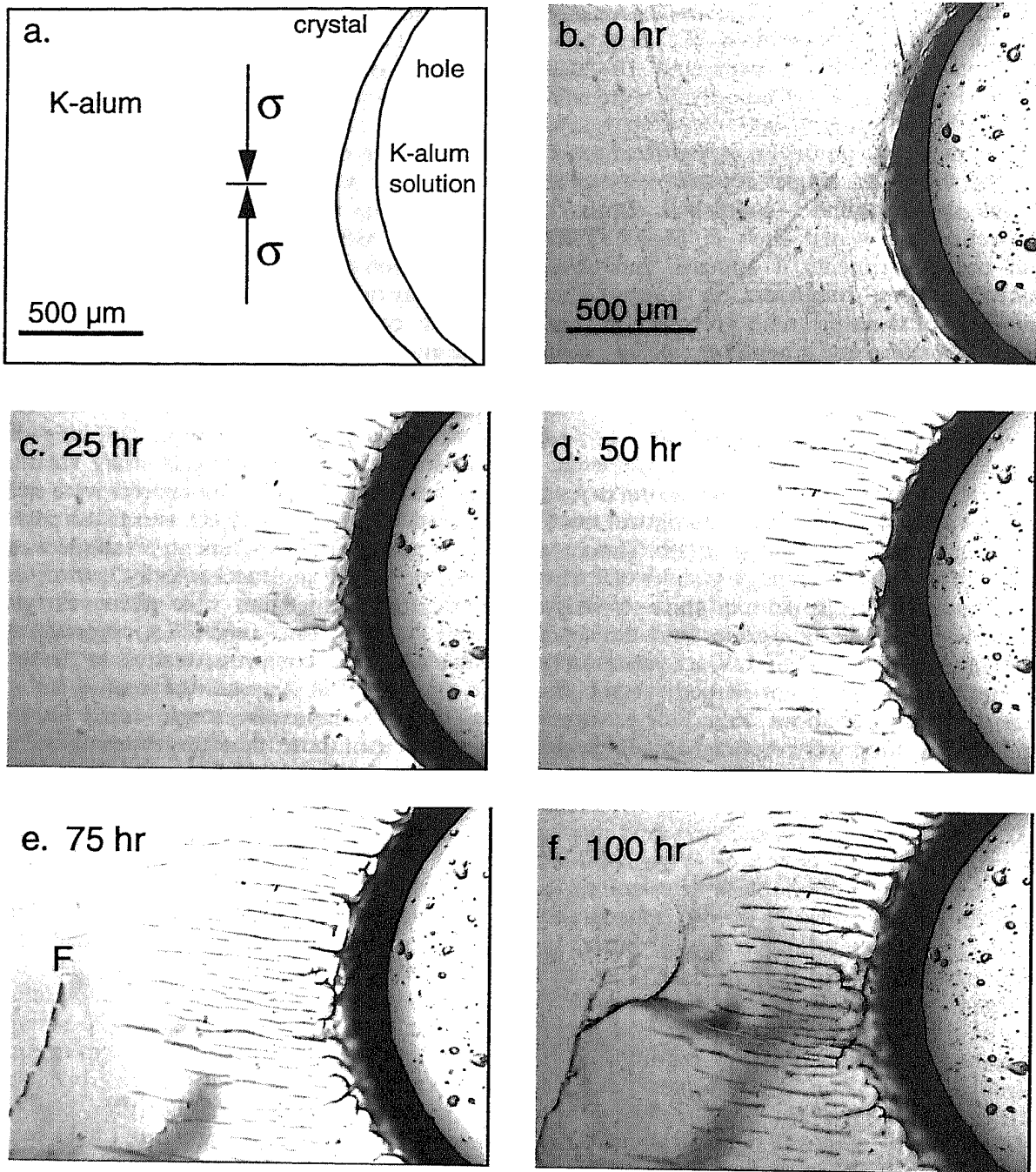
To perform an experiment, a sample was slid into the vessel and mechanically loaded with a 1 mm thick and 8 mm wide piston carrying a dead weight. The weight corresponded to a calculated bulk compressive stress in the sample of 2 to 3 MPa. Around the central hole, the maximum compressive stress would be 4 to 5 times higher (note that the compressive stress would be 3 times higher in case of a hole in an infinitely large crystal, but 4 to 5 times higher in case of our samples actually measuring 6  $\times$  8  $\times$  1 mm in size; Morel 2000).

The piston was made of Vanadium steel, because alum solutions are weakly acid (due to  $\text{Al}^{3+}$  in solution) and would corrode ordinary steel. After loading, the vessel was filled with a slightly undersaturated potassium alum solution, injected from above with the help of a syringe. A layer of silicon oil was added on top to prevent evaporization of the solution. Experiments were carried out at 'room' temperature, in a small room in which the temperature could be controlled sufficiently accurately to keep the temperature in the solution to within  $\pm 0.2$   $^{\circ}\text{C}$ .

The optical microscope was coupled to a TK-1070E JVC digital colour video camera connected to a personal computer running 'NIH-image', a public domain image processing and analysis software available at <http://rsb.info.nih.gov/nih-image/>. Thus, images of part of the sample, with a spatial resolution of 2–3  $\mu\text{m}$ /pixel, were automatically captured at regular intervals during the entire experiment (Figs 3 and 4). Observations were made of the free crystal face next to the hole at the point where the compressive stress (vertical) was expected to be maximum. Between the crystal face and the glass (of the see-through vessel) a layer of 50–100  $\mu\text{m}$  solution was present.



**Fig. 3.** Schematic diagram, approximately to scale, showing experimental set-up of *in situ* experiment 'Iskal-1' of Morel (2000). The K-alum single crystal platelet (c. 1  $\times$  6  $\times$  8 mm), with a central hole of c. 2 mm in diameter, was mounted in a slot-like see-through vessel consisting of two 5  $\times$  5 mm wide and 1.6 mm thick glass plates, separated by a U-shaped 1.1 mm thick Ertalon spacer. Glass and spacers were glued together using Loctite UV-activated glue. The set-up is seen from the side. The sample was loaded using a dead weight, corresponding to a bulk stress of c. 2.8 MPa. Saturated K-alum solution was added from above with a syringe.



**Fig. 4.** Images obtained from experiment Iskal-1. (a) Schematic drawing of geometry. (b) At the beginning of the experiment. Note scratches at the K-alum surface. (c) After 25 hours, regularly spaced fine dissolution grooves have developed at left side of the hole. (d) After 50 hours, grooves have propagated further towards the left, away from the central hole. (e) After 75 hours, further propagation of grooves. Note that a fracture (F) has developed. Note also bending of grooves (above) towards the fracture. (f) Situation at the end after 100 hours. Renewed fracturing. Note that the fracture has migrated somewhat to the right. Note also increased bending of the grooves.

Six experiments were carried out in all (Iskal-1 to -6). In this paper only results from experiment Iskal-1 will be reported. This is the only experiment in which we did not vary the concentration of the solution and/or vary the stress during the experiment; see Morel (2000) for a description of all experiments. In experiment Iskal-1, the sample was cut parallel to the  $\{100\}$  face. It was

loaded with the maximum compressive stress direction parallel to  $\langle 110 \rangle$ . The calculated maximum stress left and right of the hole was *c.* 10 MPa. Initially the added solution was undersaturated by 0.3°. The temperature during the experiment was  $21.2 \pm 0.2$  °C.

Potassium (K-) alum was used in these experiments as a rock analogue material, as in

experiments by den Brok & Morel (2001), primarily because it is an elastic/brittle material at room temperature and atmospheric pressure. K-alum single crystals can be loaded up to 20 MPa without measurably deforming. At higher stresses crystals break cataclastically. In this way any possible effects due to crystal plastic deformation could be excluded. Furthermore, K-alum has a high solubility, and dissolution and growth takes place relatively fast (at rates comparable to NaCl) so that geologically relevant processes can be studied at room P-T conditions in experiments that do not require an excessively long period of time.

### Observations

We started making observations immediately after the solution was added. Several stages of the experiment are depicted in Figure 4 and some of the essential observations are depicted in Figure 5. Within an hour, some very fine grooves had already developed at the edge of the hole drilled in the crystal. These grooves seemed to have nucleated at tiny concave irregularities at the edge of the hole. As soon as they were discernible, the grooves were oriented with their long axis ( $g$ ) approximately perpendicular to the maximum compressive stress ( $\sigma$ ). The grooves propagated outwards jerkily (not steadily) at an average velocity of the order of  $10 \mu\text{m/hr}$ , with peak velocities up to  $\sim 100 \mu\text{m/hr}$ . They propagated parallel to  $\langle 110 \rangle$ . Some grooves did not nucleate at the edge of the hole, but further to the left *on* the crystal face. In some cases, these grooves appeared to have nucleated at previously existing scratches in the surface. These grooves also had their long axis  $g$  oriented approximately perpendicular to  $\sigma$  and parallel to  $\langle 110 \rangle$ .

Grooves increased in length by propagating sideways (parallel to  $g$  and sub-perpendicular to  $\sigma$ ). They did not nucleate at one moment, but grew during the entire experiment. At the end of the experiment (after 100 hr) the longest grooves had reached a length of almost 1 mm. During the entire experiment, groove width ( $15\text{--}25 \mu\text{m}$ ) and depth remained approximately constant. Long grooves were not wider than short grooves. Grooves did not increase in width when they were propagating. Grooves also moved (translated) over the surface at velocities up to  $10 \mu\text{m/hr}$ , in directions at various angles to  $g$ . Some grooves moved upwards, others moved downwards. Some grooves moved in a jerky, unsteady fashion, others moved more continuously. Some grooves moved, in the meanwhile increasing in

length. Others moved while decreasing in length. The groove pattern was therefore not static, but dynamic. Grooves increased in length, then stopped increasing in length and sometimes decreased in length. Others moved upwards, then stopped and moved downwards again. Grooves linked up or split in two grooves. Some grooves started off straight, then the entire groove, or only part of it, rotated and attained an oblique orientation. Other grooves started in oblique orientation, then (partly) straightened out. Most of the grooves were slightly undulating during the experiment.

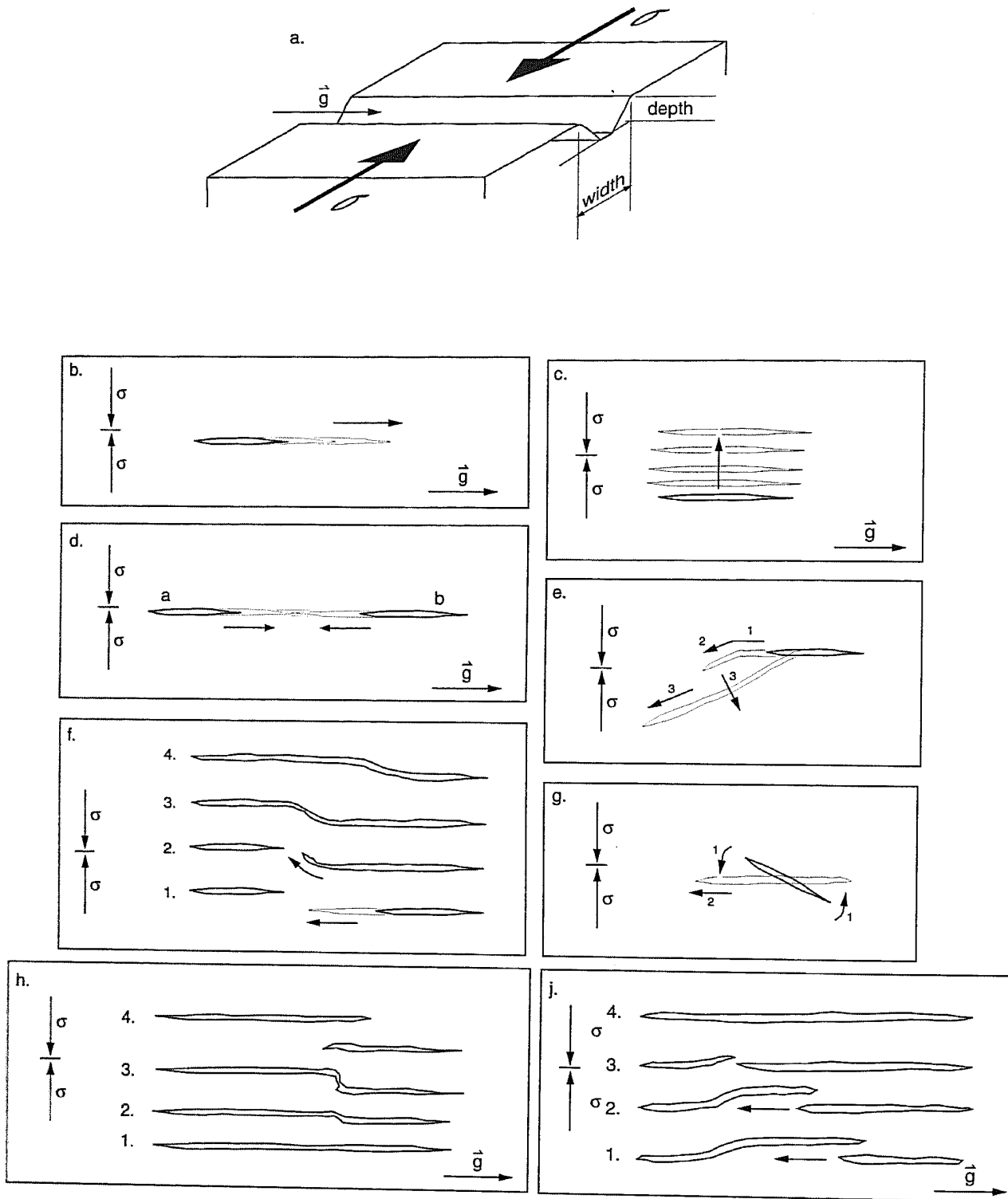
After 71.25 hours a fracture developed in the sample (see F in Fig. 4e). This fracture developed instantaneously. It must have led to a sudden increase in compressive stress at the right side of the fracture (in Fig. 4e). Within an hour after the fracture had developed, the number of grooves per unit area had almost doubled there, the width and depth of the grooves remaining unaffected (cf. Fig. 4d with Fig. 4f). Also immediately after the fracture developed the grooves near the fracture tip rotated with their long axis towards the fracture tip, suggesting of a reorientation of the maximum compressive stress after the fracture developed. The fracture partly healed in the following hours. The crack tip turned into an array of elongated fluid inclusions. The lower part remained open, but translated slowly to the right, possibly driven by the difference in elastic strain energy between the crystal lattice to the left and the right of the fracture. It moved towards the right, i.e. in the direction of the highest strain, similar to the behaviour observed by den Brok *et al.* (1999) of grain boundaries in elastically strained sodium chlorate aggregates.

Finally a second fracture nucleated from the first one, and soon thereafter the entire sample broke.

In experiments Iskal-2-6 (Morel 2000) it was observed that the grooves disappeared when either the stress was taken off (see also den Brok & Morel 2001) or when the solution was oversaturated.

### Discussion and conclusion

The observations made essentially confirm those of den Brok & Morel (2001). Grooves developed on the elastically strained surface in orientations approximately perpendicular to the maximum compressive stress ( $\sigma$ ) and parallel to  $\langle 110 \rangle$ . The grooves are also comparable in size. At the end, the surface structure was similar to that reported by den Brok & Morel (2001), who



**Fig. 5.** (a) Schematic drawing of geometry (width, depth) of a single groove developed in a crystal face. Grooves developed mostly with their long-axis ( $g$ ) sub-perpendicular to the maximum compressive stress ( $\sigma$ ). (b) Propagation (growth) of groove parallel to  $g$ . This took place typically at velocities up to  $100 \mu\text{m/hr}$ . (c) Translation of groove in a direction perpendicular to  $g$ . This took place typically at velocities up to  $10 \mu\text{m/hr}$ . (d) Propagation of two grooves a and b linking up to form one single groove. (e) Propagation of groove, first parallel to  $g$  (1), then at an angle to the initial  $g$  (2). Finally the groove starts translating (3) while propagating further in oblique orientation (3). (f) Linking of two grooves that are slightly off-set. (g) Rotation (1) of initially oblique groove and further translation. (h) Splitting of groove. Only left part of the groove starts translating upwards while right part remains fixed. First the groove starts to bend (2 and 3) then it breaks apart into two grooves (4).



were only able to study the surface structure before and after the experiment. The ability to study to the grooves *in situ* and observe how the grooves developed and evolved in time provided essential and new information. The stress-induced roughness consisting of dissolution grooves appeared not to be a static, but a dynamic, structure. The instabilities observed were not static instabilities, fixed in space, but could move as the local stress field changed. The instabilities readily changed position and orientation. To our knowledge we are the first to have seen and documented such a dynamic system of stress-induced surface instabilities.

This process of stress-induced grooves or channels moving along a boundary is much like the type of process envisaged by e.g. Lehner (1990) and Spiers & Schutjens (1990) in their 'dynamically stable' island-channel grain boundary model. The difference is that in our case the instabilities are purely stress induced (i.e. due to elastic strain), whereas Lehner (1990) and Spiers & Schutjens (1990) proposed that differences in crystal plastic strain (crystal defects) would be responsible for generation and mobility of the channels. This is not unlikely in the case of NaCl, which they were discussing.

Leroy & Heidug (1994), Ghoussoub (2000) and Ghoussoub & Leroy (2001) proposed that Grinfeld instabilities (rather than gradients in crystal plastic strain) would play a role in the development of grain boundary roughness. Our observations support their idea. It is important to note, however, that in the models of Ghoussoub (2000) and Ghoussoub & Leroy (2001) the instabilities are not assumed to have an equilibrium shape, such as in our experiments and such as predicted by Grinfeld (1986) and Srolovitz (1989). In Ghoussoub's and Leroy's models, the grooves are not assumed to be in equilibrium. They develop as Grinfeld instabilities, but then deepen and turn into cracklike features, wetting the grain boundaries (cf. Yang & Srolovitz 1993). In our experiments equilibrium existed between, on the one hand, stress forcing the surface to roughen, and, on the other hand, surface forces forcing the surface to straighten (cf. Eq. 1). Stress (elastic strain) led to the development of equilibrium instabilities. Gradients in stress and changes in the magnitude and orientation of the stress field led to motion and reorientation of the instabilities. Thus, according to our findings, fluid channels in the island-channel grain boundaries would be stress-induced (equilibrium) Grinfeld-type instabilities that propagate and translate as the local stress is changing, e.g. due to mass removal by PS. This structure is not expected to smooth

out as long as the stress is sufficiently high. Only if the stress is taken off it is to be expected that the roughness will disappear and fluid be trapped in individual inclusions. Den Brok & Morel (2001) observed that the grooves disappeared soon after the stress was taken off.

If stress is increased above a certain threshold value, the grooves deepen and turn into fractures. This was predicted e.g. by Yang & Srolovitz (1993) and observed on stressed K-alum surfaces by Morel (2000). Thus, an island-crack grain boundary would develop (Gratz 1991; den Brok 1998).

It remains to be demonstrated (e.g. in experiments) that the instabilities do form in *tight* grain boundaries under normal stress. Our observations were made on *free* surfaces (50–100  $\mu\text{m}$  water layer between the glass and the crystal) and caused by surface parallel stress. A preliminary *in situ* experimental study carried out by Zahid (2001) showed, however, that a mobile Grinfeld-type instability developed at a tight grain boundary under normal stress at the grain to grain contacts between two sodium chlorate ( $\text{NaClO}_3$ ) crystals. (Like K-alum,  $\text{NaClO}_3$  is an elastic/brittle salt with a relatively high solubility and fast interface kinetics.) It seems likely, that in addition to surface normal stress, surface parallel stress gradients are built up during PS, and that these may lead to the development of Grinfeld-type instabilities. If the boundary parallel stress changes in magnitude and orientation – a very likely case when PS at the boundary takes place – the instabilities should move, as in our experiments.

It also remains to be demonstrated that the instabilities do form in polycrystalline aggregates and in 'real' rocks under stress. Zahid (2001) observed that Grinfeld-type instabilities developed and moved at free grain boundaries in elastically strained polycrystalline sodium chlorate aggregates. Further experiments are planned to be carried out on quartz, NaCl and calcite.

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