Experimental study of polycrystal growth from an advecting supersaturated fluid in a model fracture

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ABSTRACT

We present real-time observations of polycrystal growth experiments in transmitted light in an accurately controlled flow system with the analogue material alum $\text{(KAl(SO}_4\text{)}_2\cdot12\text{H}_2\text{O)}$. The aim of the experiments is to obtain a better insight into the evolution of vein microstructures. A first series of experiments shows the evolution of a polycrystal at supersaturations between 0.095 and 0.263. The average growth rate of the crystals is influenced by growth competition and the depletion of the solute along fracture length. Growth competition is controlled by crystallographic orientation, crystal size and crystal location. In addition, the growth rate of an individual crystal facet also shows variations depending on the facet index, facet size and flow velocity. These variations can influence the morphology of the grain boundaries and the microstructures. The aim of the second series of experiments is to investigate the growth evolution of rough/dissolved facets in detail. The growth distance required for the development of facets is around 15 $\mu\text{m}$. In all the experiments, we observe that the measured growth rates have a much larger range than predicted by alum single-crystal growth kinetics. This is due to the combined effect of the facet index and the crystal size. Furthermore, at high supersaturations, the facet growth rate measurements do not fit the same growth rate equation as for the experiments at lower supersaturations (<0.176). This can be explained by a change in the growth mechanism at high supersaturations with more influence of volume diffusion, relative to advection of the bulk solution on the growth rate. This effect can also cause a more homogeneous sealing pattern over fracture length. At high supersaturations, the larger crystals in these experiments incorporate regularly spaced fluid inclusion bands and we propose that these can be used as an indicator for high palaeo-supersaturation. The final microstructures of the experiments show no asymmetry with respect to the flow direction.

Key words: advection, crystal growth, supersaturation, veins

INTRODUCTION

Dissolved material is transported through rocks by diffusive or advective mass transfer. Diffusive transport of material takes place in a stationary fluid, driven by a gradient in chemical potential (Durney & Ramsay 1973; Fisher & Brantley 1992). It is a slow process, acting on small-length scales (cm-scale) and resulting in a rock-buffered chemistry (Fisher & Brantley 1992; Elburg et al. 2002). In contrast, advective transport is driven by a hydraulic gradient, can transport material over large distances, and may induce a geochemical disequilibrium between the fluid and the host rock (McManus & Hanor 1993; Sarkar et al. 1995; Verhaert et al. 2004).

Fluid flow through permeable rocks is described by Darcy’s law. In fractures, the flow can be described by the cubic law (Wood & Hewett 1982; Jamtveit & Yardley 1997; Bjørlykke 1999; Taylor et al. 1999):

$$Q = \frac{-a^2 \rho g}{12 \mu} \left( \frac{dh}{dT} \right)^w,$$

where $Q$ is the volumetric flow rate, $a$ the aperture, $\rho$ the density of the fluid, $g$ the acceleration due to gravity, $\mu$ the
dynamic viscosity, \( \frac{dh}{dL} \) the hydraulic gradient and \( w \) the width.

Fracture networks result in focused fluid flow with fluid velocities in fractured geological media up to \( 10^{-2} \text{ m s}^{-1} \) (Dijk & Berkowitz 1998; Cox 1999; Oliver 2001). Fluid flow in the upper crust is often episodic and influenced by fault movements (seismic pumping model and fault-valve mechanism), resulting in transiently even higher fluid velocities, immediately after seismogenic slip events (Sibson et al. 1975; Sibson 1990; Jamtveit & Yardley 1997).

Precipitation of material takes place when the fluids become supersaturated. The resulting veins preserve valuable information on the origin of the fluids, the deformation history and palaeo-overpressures of fluids in the rocks (Ramsay & Huber 1983; Capuano 1993; Nollet et al. 2005a). When a fluid is flowing through a fracture, there is an interplay between advection, diffusion and reaction kinetics (Dijk & Berkowitz 1998). The relative importance of these processes is expressed by the dimensionless Péclet number, defined as \( Pe = \frac{v h}{D_m} \), where \( v \) is the flow velocity, \( h \) the fracture aperture and \( D_m \) the molecular diffusion coefficient, and the Damköhler number, defined as \( Da = \frac{k r}{D_m} \), where \( k \) is the first-order kinetic reaction rate coefficient. The Péclet number describes the relative importance of advection and diffusion, whereas the Damköhler number describes the relative importance of diffusion and reaction kinetics (Lasaga 1998, p. 267). The rate of precipitation of minerals can be expressed in terms of supersaturation and the flow velocity (Garside & Mullin 1968; Garside et al. 1975; Rimstidt & Barnes 1980). The supersaturation ratio \( S \) is defined by the ratio between the solution concentration \( c \) and the equilibrium concentration \( c^* \) or \( S = c/c^* \). The relative supersaturation is defined as \( \sigma = S - 1 \).

Calcite precipitation by advective flow was experimentally simulated at room temperature by Lee et al. (1996). They calculated that an extremely large amount of fluid is required to precipitate calcite veins in nature (Lee & Morse 1999). Dissolution and precipitation experiments with HCl and \( \text{H}_2\text{SO}_4 \) solutions flowing in fractured carbonate rocks result in calcite dissolution and gypsum precipitation (Singsurindy & Berkowitz 2005). In these experiments, the overall hydraulic conductivity was measured and it shows oscillatory behaviour, which is explained by the fluctuating dominance of precipitation or dissolution (Singsurindy & Berkowitz 2003, 2005).

Hilgers & Urai (2002a) described crystal growth experiments in a transparent see-through cell. They used alum as an analogue material which allows a microstructural analysis of the growing crystals, in contrast to the experiments by Lee et al. (1996). A growth rate decrease along the fracture length is observed when the flow velocity is sufficiently small. This is caused by a depletion of the solution’s concentration in the flow direction. A numerical model based on alum growth kinetics confirmed these results and was applied to quartz. This model predicted that the characteristic length at which the effects of depletion of the solution’s concentration are manifested is around 1 km and will not be visible in an outcrop (Hilgers et al. 2004). It is not clear how a typical microstructure resulting from advective flow transport at low flow velocities is recognized and how it differs from a microstructure resulting from diffusional transport, although geochemical arguments, such as stable isotope chemistry can provide clear evidence (Suckewer & Land 1983; Verhaert et al. 2004).

Crystal growth in crack-seal veins was numerically simulated based on a kinematic model (Urai et al. 1991; Bons 2001; Hilgers et al. 2001; Nollet et al. 2005b). An open question with respect to these simulations and the understanding of the crack-seal mechanism is how crystal facets develop on a dissolved or a fractured crystal surface. Until now, it is unclear how much space is required for crystals to develop crystal facets (Urai et al. 1991; Nollet et al. 2005b). This aspect is interesting with respect to the evolution of crystals after a crack increment in the crack-seal model.

In this paper, we present new see-through experiments with alum in an improved experimental set-up. We investigate the temporal evolution of the microstructures and the crystal growth rate on a polycrystal scale and on a single-crystal scale and we analyse the effect of different boundary conditions, such as flow velocity, supersaturation, flow direction and facet index on the crystal growth rate.

**METHODS AND EXPERIMENTAL SET-UP**

**Flow and pressure system**

The experimental set-up is a modified version of the one described in Hilgers & Urai (2002a) and Hilgers et al. (2004). It is a single-path flow unit where a saturated fluid flows from a reservoir into a transparent reaction cell in which the temperature is a few degrees lower than in the reservoir and the fluid thus becomes supersaturated (Fig. 1A,B). Fluid flow into the reaction cell is driven by a High Performance Liquid Chromatography (HPLC) pump at a flow rate of \( 0.01 \pm 0.000019 \text{ ml min}^{-1} \). This flow rate results in flow velocities in the cell of approximately \( 0.1 \text{ mm s}^{-1} \), corresponding to flow velocities in natural fractures. Before running an experiment, we prepared an equilibrium solution in the reservoir at a temperature of \( 39 \pm 0.05^\circ\text{C} \), by continuously stirring the solution and alum crystals over 2–3 days.

A nonmiscible, clean paraffin oil is pumped by the HPLC pump into the upper part of the reservoir and this displacement by the oil drives flow of the saturated solution out of the reservoir into the reaction cell, without diluting the saturated solution (Fig. 1A). In the fluid reser-
voir, a small air bubble is present which is used as pressure indicator. The outflow volume of the fluid at the end of the reaction cell is measured continuously by a burette during an experiment. Pressure pulses in the pump have no significant influence on the flow through the cell.

The reaction cell consists of an upper and a lower glass plate and two metal plates in between acting as spacers between the two glass plates (Fig. 1C,D). The metal plates have a thickness of 0.5 mm and one of them has a 10-mm-long groove where the seed crystals are located (Fig. 1D). With an average aperture of 1.5 mm and taking $k = 0.008 \text{ s}^{-1}$ and $D_m = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, the Péclet and Damköhler numbers are approximately 680 and 36 respectively. This indicates that the dominant transport and crystal growth mechanisms are advection and reaction kinetics respectively.

Pressure is controlled by two pressure valves. The first valve is located between the pump and the fluid reservoir and the second valve is located at the end of the system and causes a back-pressure (Fig. 2). This system results in a maximum pressure difference of 0.2 MPa between the two valves. The first pressure valve ($P_1$ in Fig. 2) prevents damage to the cell once the fracture is sealed. Shortly before sealing of the fracture, the pressure rises at the inlet of the reaction cell and the air bubble in the fluid reservoir is compressed, until the pressure limit of 0.4 MPa in $P_1$ is reached (Fig. 2). Based on the cubic law, the aperture of the fracture is then around $1 \mu m$, which is no longer observable in the experiment. The back-pressure in $P_2$ minimizes air bubbles in the system.

**Temperature**

Temperature is controlled by a master–slave Eurotherm controller system combined with four Pt100 temperature sensors located at: (i) the reservoir, (ii) the reaction cell,
(iii) the connecting tube between the reservoir and the reaction cell and (iv) the connecting tube between the reaction cell and the outflow reservoir (Fig. 1A). In the tubes, the temperature is set up to 5°C higher than in the reservoir to avoid nucleation. The temperature was measured with a high-precision thermometer (PREMA 3040 box), which has both a Pt100 temperature sensor and a K-type thermocouple. The Pt100 temperature sensor was calibrated by the manufacturer to a precision of 0.03°C and is used as reference thermometer. The ultra-thin K-type thermocouple (0.25 mm diameter and 0.05°C precision) is calibrated against the reference thermometer in an isothermal block and is used to measure the temperature inside the reaction cell and the fluid reservoir in dummy flow experiments (Fig. 3A). In these calibrations, the temperature in the reaction cell was measured at three different positions (in, mid and end in Fig. 1D) at flow rate of 0.01 ml min⁻¹ to characterize the temperature profile across the reaction cell. Figure 3B shows the measured temperature profile at four different set-points and verifies that the higher temperature in the inlet tubing has no influence on the temperature at the inlet section of the fracture at a flow rate of 0.01 ml min⁻¹. In the middle of the reaction cell, the temperature can be 0.2°C lower than at the outer parts, with only a minor influence (0.006) on supersaturation. The temperature difference at the three different positions is due to the heating system of the cell, which allows more heating at the outer parts of the cell and cooling of the glass by air in the middle part. A validation of the calibration was carried out by an experiment with settings corresponding to zero supersaturation, confirming that no growth or dissolution takes place.
Material characterization

In the experiments presented here, alum [KAl\((SO_4)_2\cdot12H_2O\), Roth \(\geq 97.5\%\) quality] is used as the mineral analogue. This highly soluble material was chosen because of its well-known growth kinetics and high growth rates at temperatures between 30 and 40\(^\circ\)C. At room temperature, the crystal structure of potash alum is cubic with eight \{111\} facets, but crystals commonly show an octahedral habit with the \{111\}, \{100\} and \{110\} facets as main habit facets (Bhat et al. 1992) (Fig. 4). When a dissolved crystal starts to grow, minor \{221\}, \{112\} and \{012\} facets grow in the initial growth stages (Klapper et al. 2002) (Fig. 4A). Because of their higher growth rate, these are rapidly outgrown. The occurrence of the octahedral crystal habit for the alum used in the experiments was confirmed in single-crystal growth experiments.

Seed crystals of alum for the reaction cell are prepared by melting alum powder, after adding approximately 1\% volume of water, and pouring this melt in between the two metal spacers. This is followed by pressing the melt quickly into the fracture shape to a thin plate with a thickness of 0.5 mm. Before we run an experiment, we flow slightly undersaturated solution through the cell for 15 min to remove alum nuclei in the set-up and slightly dissolve the seed crystals. In all experiments presented here, the same seed crystals were used by dissolving the grown crystals each time after an experiment.

To calculate the supersaturation in the experiments, the solubility data for alum in \(H_2O\) are required. The solubility of the alum was measured by adding a controlled mass to \(H_2O\) at a constant temperature until no more alum could dissolve over a period of 1 day, indicating that saturation of the solution has taken place. The solution was permanently stirred to achieve equilibrium. The results are compared with solubilities given in Synowietz & Schäfer (1984), Mullin (2001) and Barrett & Glennon (2002) and correspond very well to these (Fig. 5). However, the solubility of hydrated alum with 12 molecules of \(H_2O\) (which we used in the experiments) was only measured directly by Barrett & Glennon (2002) whereas the other authors measured the dehy-

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**Fig. 4.** Single crystal of alum. (A) Development of cubic alum crystal with \{111\} facets, starting from a crystal with high index facets. Relative growth rates of the crystal facets are \{111\}: 1.0, \{110\}: 4.8, \{001\}: 5.3, \{221\}: 9.5 and \{112\} 11.0 (after Klapper et al. 2002). The faster growing facets are outgrown by the slower growing facets. (B) Single alum crystal in 3D, with the commonly observed \{100\}, \{110\} and \{111\} facets.

**Fig. 5.** Solubility of alum in mol/100 g \(H_2O\) as a function of temperature according to different authors and measured in this study. The data from Synowietz & Schäfer (1984) and Mullin (2001) are based on measurements of dehydrated alum whereas the data from Barrett & Glennon (2002) and in this study are based on hydrated alum with 12 molecules of \(H_2O\). The melting point (90\(^\circ\)C) of alum is indicated.
drated type of alum. Therefore, solubilities are calculated based on an equation derived from the data from Barrett & Glennon (2002).

According to Garside & Mullin (1968), the overall growth rate of alum depends on the supersaturation and the flow velocity; both these parameters are controlled precisely in this set-up.

**Image analysis**

During an experiment, the transparent reaction cell is placed under the microscope, which is connected to a high resolution digital camera. Images of 748 × 576 pixels were grabbed every 2 min over a period of around 20 h. Image analysis of the experiments is done by tracing the grown distance orthogonal to the crystal facet and tracing the grown area in a specific time interval. The latter measurements are followed by dividing the measured area by the crystal surface length. The grown area for the whole experiment was also divided into three parts (in, mid and end section) to compare the average growth rate evolution along the fracture length.

**MICROSTRUCTURAL EVOLUTION OF POLYCRYSTALS**

A series of polycrystal growth experiments at different flow velocities and supersaturations is carried out (Fig. 6). In all experiments, the flow rate is constant and is set at 0.01 ml min⁻¹. The initial flow velocity, determined based on the initial fracture morphology, varies between 0.12 and 0.27 mm s⁻¹ in the individual experiments. The supersaturation in the different experiments varies between 0.095 and 0.263 (±0.006), depending on the temperature difference between the fluid reservoir and the reaction cell (2.5 and 6.3 ± 0.12°C).

All experiments start with a rough, irregular surface composed of dissolved alum seed crystals. Faceted crystals are well established after about 15 min of growth (Fig. 6A). In the initial stages of the experiments, numerous seed crystals grow, whereas at the final stages, fewer crystals grow (Fig. 6A). Most of this growth competition occurs at the initial stage of the experiment, when the crystals are small (e.g. experiment 4 in Fig. 6). Growth competition is the result of different factors. First of all, the crystallographic orientation plays an important role. This can be seen in A...
in Fig. 6A, where crystals initially have the same size. The only difference between the different crystals is the crystallographic orientation, which is indicated by the orientation of the developed facets. After 2 h, the central crystal is outgrown and the growth competition in this example is influenced mainly by the crystallographic orientation (Fig. 7).

Secondly, crystals, which are located on ridges on the fracture surface, have a better chance to survive, whereas crystals located in the depressions or at the back with respect to the flow direction hardly grow, independent of their orientation (B in Fig. 6A).

The crystals themselves also undergo a microstructural evolution over time. This is visible in Fig. 6B, where the evolution of the crystals can be analysed in the traced images. In the first stages, the crystals have developed numerous facets, including high-index facets. After 60 min of growth, it can be seen that some facets are outgrown in the larger crystals (e.g. the central crystal in the mid section in experiments 2 and 3) whereas others are preserved. We also observe that the direction of a facet can evolve, indicating that minor high-index facets are not completely outgrown yet. This is visible in the largest crystal of the in section in experiment 2, which has at first a stable orientation after 150 min. The surviving facets are the slower growing low-index facets ([100], [110], [111]) and their length can show variations during their further evolution.

**FACET GROWTH RATE MEASUREMENTS**

The growth rate of individual facets in the polycrystal growth experiments is analysed by measuring the grown distance, orthogonal to the facet, in a specific time interval. Because identical crystals grow in the different experiments, this method allows a comparison of the growth rate of identical facets under different supersaturation conditions (Figs 8 and 9). We observed that the growth rate of identical facets increases with increasing supersaturation, as expected according to the growth kinetics of alum (Garside & Mullin 1968).

**Variations and trends over time**

The growing crystals have not only developed cubic [111] facets, but also octahedral [100] and [110] facets, which
will subsequently be referred to as non-(111) facets (Fig. 8, see also Ristic et al. 1996). In all experiments, the growth rate of (111) facets is more constant over time than the non-(111) facets, which show large amplitude variations in growth rate (up to $5 \times 10^5$ mm s$^{-1}$) (Fig. 9). This is especially clear for facets 5 and 6 in experiments 2 and 3 (Figs 8B, C and 9B, C). In both experiments, facet 5 is a non-(111) facet which initially grows slowly. After 175 min in experiment 2 and after 225 min in experiment 3, the growth rate increases suddenly and the facet tends to disappear. In contrast, facet 6 (111 facet) grows in both experiments steadily over time.

In experiments 2, 3 and 4, flow is blocked when facet 6 grows until it meets the opposing metal plate. This facet is oriented parallel to the metal plate and the aperture of the fracture decreases significantly over time at this position, resulting in an increase in flow velocity, up to 2 mm s$^{-1}$ shortly before sealing. According to alum growth kinetics, growth rate increases with increasing flow velocity (Garside & Mullin 1968). Therefore, we would expect an effect on the growth rate of this facet, especially at the latest growth stages, but this is not observed (Fig. 9B–D).

**Dispersion growth rate of different facets: orientation effects?**

The results of the facet measurements show that in all experiments, except in experiment 1, the growth rates of the different (111) facets display a relatively large scatter in a range of $5 \times 10^5$ mm s$^{-1}$ (Fig. 9B–D). One aspect which can result in variations of growth rate between the different measured facets is the facet orientation with respect to the flow direction. According to Prieto et al. (1996), facets which are oriented perpendicular to the flow direction can grow faster than facets oriented parallel with the flow direction. Facets, which are located in the shade position with respect to the flow direction, have the lowest growth rates. These aspects were observed in KDP (KH$_2$PO$_4$) crystals under laminar flow conditions, where growth rates of well-oriented facets can be twice as high as growth rates of unfavourable oriented facets (Prieto et al. 1996).

In experiment 1, facets 9 and 10 both belong to the same crystal, have approximately the same size and are both (111) facets. The only difference between these two facets is their orientation with respect to the flow direction. In contrast to
the results of Prieto et al. (1996), the growth rates of facets 9 and 10 show no significant dependence on orientation.

If we compare facets 5 and 7, both non-{111} facets, we see that before 200 min, facet 7 grows faster than facet 5, in contrast to what is expected according to their orientation in relation to the flow direction (Fig. 9B). After 200 min, the growth rate of facet 5 is significantly higher than that for facet 7. A similar trend is observed for facets 5 and 7 in experiment 3 (Fig. 9C).

Based on these observations, we conclude that we do not observe a significant influence of the facet orientation with respect to the flow direction on the growth rate in our experiments. It is more likely that the variation in growth rates between the different facets is caused by the length of the facets (larger facets grow faster), the facet index and the irregular seed crystal morphology. It is possible that there are effects of the flow direction but these are probably overwhelmed by the other effects.

OVERALL GROWTH RATE MEASUREMENTS

Variations and trends over time

We observe in all experiments that the average growth rate is not constant but shows variations over time, keeping in mind the errors in measurements of growth rate ($\pm 2.9 \div 6.8 \times 10^{-6} \text{ mm s}^{-1}$) (Fig. 10). This could be due to an influence of growth competition on the growth rate. This is visible in experiment 4, where growth competition between equal-sized crystals is visible near the end of the experiment. Shortly before a crystal is outgrown, the average growth rate of the measured area shows a decrease (Fig. 11). The outgrown crystal itself is no longer able to integrate new material at that time, because it is almost completely enclosed by the two neighbouring crystals. After the enclosed crystal is outgrown, the growth rate of the neighbouring crystals increases again.

In experiments 2, 3 and 4, we observe that the growth rate at the in sector decreases over time (Fig. 10B–D). The initial aperture was large in this sector and, therefore, there is no significant influence of increasing flow velocity with time in this sector. On the other hand, outgrowth of crystals and disappearance of fast-growing, high-index facets, on the scale of individual crystals, can result in a decrease of the growth rate over time and these are, therefore, negative effects on the growth rate evolution.

In experiments 2 and 3, the average growth rate at the mid section increases slightly over time (Fig. 10B,C). This can be explained by the decreasing aperture and increasing flow velocity over time. The fact that this effect is only visible in the mid sector is due to the fracture morphology with initially the smallest aperture (1.2 mm) in this sector. In the mid sector, the negative effects (e.g. outgrowth of fast-growing facets) on the growth rate are also expected to occur but cannot be recognized because the increase because of the increasing flow velocity is larger. In experiment 4, where the initial aperture of the mid section was even smaller, we also expect an increase in growth rate over time but observe a slight decrease (Fig. 10D).

In all experiments, the growth rate shows no decreasing or increasing trend at the end sector. The above-described positive and negative effects on the growth rate also occur in this sector, but presumably the combination of these results in a constant growth rate over time.
Trends between the different areas

After comparing the growth rate evolution over time, we will now analyse the growth rate evolution along fracture length. In experiments 2 and 3, the growth rate at the *in* section and *mid* section is initially clearly larger than at the *end* section and thus, the growth rate decreases along the fracture length (Fig. 10B,C). During the further evolution of the experiment, this trend is less apparent, because of influences of other effects, which cause decreases and increases in growth rate over time.

In experiment 1, at very low supersaturations, the differences in growth rate between the *in*, *mid* and *end* sections are initially also visible but are significantly smaller (Fig. 10A). This was already shown in Hilgers & Urai (2002a) and can be explained by the exponential relation between supersaturation and growth rate, which results in less growth rate decrease along fracture length for low supersaturation.

In experiment 4, at very high supersaturations, there is initially no trend of decrease in growth rate over fracture length. In the final stage of the experiments (after

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**Fig. 11.** Details of growth competition and effects on the growth rate in three examples in the end section of experiment 4. (A) Image of the final situation of the experiment. (B) Growth rate evolution shown by traced grain boundaries in time intervals of 10 min. (C) Growth rate versus time for the end section of the experiment. Shortly before a crystal is outgrown, the average growth rate decreases. After the crystal is outgrown, the average growth rate of the surviving crystals increases again.

**Fig. 12.** Fluid inclusions in the experimentally grown alum crystals in (A) experiment 3 (supersaturation = 0.176) and (B) experiment 4 (supersaturations = 0.263). The inclusions are regularly spaced and contain one fluid phase. In experiment 3, inclusions show a band spacing of 50–150 μm, whereas in experiment 4, the band spacing is around 20 μm.
175 min), the growth rate is even higher at the end section than at the in and mid section (Fig. 10D). The initial seed crystal morphology with a significantly smaller aperture and higher flow velocity at the mid section, compared to the in and end section can explain the observed trend in the first growth stages. However, this cannot explain the trend at the final stage of the experiment. In the traced images of the experiment, we also observe that the growth rate is more constant over fracture length at the final stages of the experiment (Fig. 6B).

**FLUID INCLUSION GENERATION IN CRYSTALS**

Fluid inclusions are formed in experiments 3 and 4, at high supersaturations (0.176 and 0.263 respectively) (Fig. 12). They are only visible in the largest crystals and are present in both the [111] and non-[111] sectors, at different orientations with respect to the flow direction. The inclusions contain one fluid phase, have a rounded shape and are arranged in regular bands. The band spacing is around 50–150 μm in experiment 3 and 20 μm in experiment 4 (Fig. 12). Based on the measured facet growth rate, this corresponds to a time interval of around 10 min in experiment 3 \(v_{growth} = 7.16 \times 10^{-5} \text{ mm s}^{-1}\) and 3.5 min in experiment 4 \(v_{growth} = 9.5 \times 10^{-5} \text{ mm s}^{-1}\). The difference in band spacing in the same crystal facet in the two experiments, carried out at different supersaturation, suggest that it is related to the supersaturation and that spacing decreases with increasing supersaturation.

**FACET DEVELOPMENT OF SINGLE CRYSTALS WITH A ROUGH SURFACE**

Flow experiments were run at two different supersaturations and at a constant flow rate of 0.01 ml min\(^{-1}\), focusing on the evolution of a single dissolved crystal with a diameter of 500 μm (Fig. 13).

In the first experiment, with a supersaturation of 0.095, the first facet develops at the front with respect to the flow direction after 5 min of growth (Fig. 13A). After 6 min, facets develop at the back of the crystals and after 7 min, the crystal has clearly evolved from a rounded, dissolved crystal to a faceted crystal. The grown band has at that time a thickness of 18 μm. This indicates that the growth rate in this time interval was around \(4.44 \times 10^{-5} \pm 0.5 \times 10^{-5} \text{ mm s}^{-1}\). Compared with the facet growth rate and area growth rate measurements at the same supersaturation, this growth rate is very high, suggesting that growth on an irrational crystal surface occurs extremely rapidly in the first stages.

In the second experiment, the supersaturation was set at 0.263 and the same crystal as in the first experiment was observed (Fig. 13B). Facets again develop at first at the front and later at the back with respect to the flow direction. The difference with the first experiment is that the evolution to a completely faceted crystal happens faster (5 min) and the crystal needs only to grow 12 μm to evolve from a dissolved crystal surface to a faceted crystal. The growth rate in this time interval is \(7.69 \times 10^{-5} \pm 0.5 \times 10^{-5} \text{ mm s}^{-1}\), which corresponds to the highest range of the facet growth rate measurements and is higher than the area growth rate measurements.

**DISCUSSION**

**Comparison of growth rate data with literature**

We can compare the growth rates of individual facets and the measured average growth rate with the growth rate predicted by the alum growth kinetics (Mullin 2001; Hiltgers & Urai 2002a) (Fig. 14). The alum growth kinetics is
Variations in growth rate over time are observed in both the facet growth rate measurements and the area growth rate measurements. With respect to naturally occurring vein minerals, growth rate variations in individual facets are described in experimentally grown calcite and dolomite (ten Have & Heijnen 1985; Nordeng & Sibley 1996). The results of ten Have & Heijnen (1985) suggest that cathodoluminescence patterns in calcite are caused by changes in the crystal growth rate, independent of variations in the pore fluid chemistry. Penniston-Dorland (2001) observed similar patterns in natural hydrothermal quartz. In halite grown under stable evaporitic conditions, the varying spacings observed for growth striations also suggest variations in growth rate (Warren 1999; Schleder & Urai 2005).

Growth rate oscillations with an amplitude of $8 \times 10^{-9}$ mm s$^{-1}$ have been described in alum crystals over a period of 50 min (Gits-Leon et al. 1978; Zumstein & Rousseau 1987; Bhat et al. 1992; Ristic et al. 1996; Trevis 1997). The growth sectors of the $\{111\}$, $\{100\}$ and $\{110\}$ facets were analysed by X-ray topography in Bhat et al. (1992) and Ristic et al. (1996), and they concluded that the growth rates of $\{100\}$ and $\{110\}$ facets vary considerably over time with respect to the growth rate of the $\{111\}$ facets. Bhat et al. (1992) and Ristic et al. (1996) explain these variations by a dislocation flux from the non-$\{111\}$ sectors towards the finally surviving $\{111\}$ sectors.

Based on the arguments outlined above, we suggest that natural crystal growth in open fractures can vary over time, even under constant flow rate and supersaturation conditions.

We can now model a microstructure with crystals growing at a constant growth rate and compare it with a microstructure with crystals growing at a variable growth rate (Fig. 15). At constant growth rate, the grain boundaries and the crystal facet boundaries are straight lines. The grain boundary changes its direction only when a crystal is consumed (Fig. 15A). In contrast, when the growth rate of one facet is increased in one time increment, the grain boundary and the crystal facet boundary is no longer a straight line but changes its direction. The final grain boundary then becomes serrated instead of a straight line in the case of a constant growth rate (Fig. 15B–D). Different microstructures can be modelled, depending on variations in the growth rate for different facets. With respect to naturally growing polycrystals, we can conclude that irregular or serrated grain boundaries (e.g. Cox 1987) can be the result from small variations in growth rate in at least one neighbouring crystal facet, although they can also be the result of grain boundary migration during deformation.

On a larger scale, we observed in most experiments that the average growth rate decreases along the fracture length (in the flow direction) in the initial growth stages. During further evolution of the experiment, this trend is also influenced by the growth competition, the increasing flow velocity and the outgrowth of high-index facets. Hilgers &...
explained by the decreasing aperture over time, causing a higher flow velocity and a higher Péclet number.

**Facet development of crystals and implications for the crack-seal model**

Fibrous veins with host rock solid inclusions are commonly thought to have formed by incremental crack-seal events (Ramsay 1980). Numerical simulations of this process show that completely fibrous crystals are only formed when the crystal growth rate is higher than the opening rate of the fracture and if the fracture surface is sufficiently rough (Urai et al. 1991; Hilgers et al. 2001; Nollet et al. 2005b). Transitional structures between fibrous and elongate-blocky microstructures are formed when the crystal growth rate is lower than the opening rate of the fracture (Nollet et al. 2005b). Until now, the critical growth distance at which facets develop is unknown (Urai et al. 1991; Nollet et al. 2005b). In the experiments presented here, we have demonstrated that the transition between dissolved and faceted alum crystals occurs very rapidly. At supersaturation of 0.263, crystals can develop facets and nonparallel grain boundaries when crack increments are larger than 12 μm. This distance is comparable with the critical distance required to simulate a natural fibrous vein (Hilgers et al. 2001). In the initial stages of crystal growth on a rough surface, we observed that the growth rate is much higher than predicted by the growth kinetics. It is very likely that this also occurs when the crystals are fractured, as in the crack-seal mechanism. The crystal growth kinetics which is valid for large, faceted crystals is, therefore, not always valid for the initial stages of growth, after fracturing or dissolution.

**Palaeo-supersaturation indicator**

In this work, we present for the first time alum polycrystal growth experiments at high supersaturations (>0.176). The experiments are characterized by epitaxial overgrowth of seed crystals but the crystals have incorporated primary fluid inclusions, in contrast to the clear inclusion-free crystals grown at lower supersaturations. Prieto et al. (1996) described the occurrence of fluid inclusions in single KDP crystals at the back of the crystal with respect to the flow direction, because of ‘eddy’ currents. The inclusions that are observed in the experiments presented here are observed in all crystal sectors, irrespective of the relation between their orientation and the flow direction. Therefore, it is not very likely that the generation of the inclusions is related to the hydrodynamic environment. It would be interesting to be able to compare the supersaturation range used in the experiments with values of supersaturation in nature. However, there is some discussion in the literature about the degree of supersaturation in natural

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fluid systems. Walther & Wood (1986) suggest that the required supersaturation for nucleation is relatively small, whereas the variety of growth habits in nature suggests the existence of a wide range of supersaturations (Sunagawa 1984; Putnis et al. 1995). The spacing of primary fluid inclusion bands in natural vein crystals can be around 50 µm (Roedder 1984), similar as in the alum crystals. Because the fluid inclusions are observed only in experiments at high supersaturations (>0.176), we suggest that this type of regularly spaced primary inclusions in natural crystals could be used as an indicator for high supersaturations.

Palaeo-flow direction

We can now discuss whether the microstructures in experiments presented here contain indicators for the flow direction and advective material transport. In single-crystal growth literature, it is described that there is an influence of the flow direction on the growth rate of facets located at the downstream side of crystals (Janssen-van Rosmalen & Bennema 1977; Prieto et al. 1996). In natural systems, it was suggested that crystals grown by advective flow show a shape-preferred orientation (Newhouse 1941; Babel 2002). In the polycrystal growth experiments presented here, we could not observe any preferred crystal orientation or facet development related to the flow direction.

A second aspect which could indicate the flow direction is the effect of depletion of the fluid over fracture length, as shown by Hilgers & Urai (2002a). However, in experiments presented here, this effect is only visible in the initial stages of the experiments with moderate supersaturation. During further evolution of the crystals, we observed that effects on the crystal scale (outgrowth of crystals and crystal facets) and the increasing flow velocity, which are not included in the numerical model used in Hilgers & Urai (2002a), significantly influenced the growth rate trends. On the other hand, the rough fracture morphology did not result in more sealing at the inlet of the fracture. Therefore, there is no clear evidence for the effect of depletion of the fluid based on the microstructures only.

A third aspect that could indicate the palaeoflow direction is the location of fluid inclusions (Prieto et al. 1996). As already outlined above, we only observed fluid inclusions at high supersaturations (>0.176) and these are not related to a specific direction.

These aspects indicate that the final microstructures of the experiments do not contain indicators for the palaeoflow direction. The crystal size with respect to the aperture size of the simulated fracture is in good agreement with natural veins, suggesting that the crystal-scale effects, as seen in the experiments, will also occur in natural veins. A rough fracture morphology is also observed in natural veins, but is commonly less rough than the one used in the experiments (Hilgers & Urai 2002b). The aspects discussed above suggest that the microstructure will not contain significant evidence for the palaeo-flow direction in natural fracture sealing systems, when the flow velocity was low.

CONCLUSIONS

Our experiments with the mineral analogue material alum result in a better understanding of natural fracture sealing because the parameters that we can control in our experiments are the flow velocity and the supersaturation. These are key parameters that control natural fracture sealing.

Polycrystal growth experiments result in elongate-blocky microstructures with epitaxial growth on existing seed crystals at supersaturations in a range between 0.095 and 0.263 and flow rates of 0.01 ml min⁻¹ along the fracture. On an individual crystal scale, a variation of growth rate in different facets is due to the size of the individual facets, their orientation with respect to the flow direction and differences in the flow velocity. Individual facets also show variations in growth rate over time.

Variations in the average growth rate over time are explained by growth competition, which is influenced by crystallographic orientation, crystal size and the fracture roughness.

All of these factors are likely to influence the growth of natural elongate-blocky veins. During the growth of natural veins, at constant flow rate and supersaturation conditions, growth rates are likely to be variable.

A detailed observation of single-crystal growth indicates that the critical distance to grow facets is very small (12–18 µm). This indicates that fibrous alum veins would only form under crack-seal conditions when opening increments are smaller than 12 µm. The initial growth stages on a rough surface are characterized by very high growth rates.

The growth rates measured in our experiments are lower and show a slightly different trend with respect to the supersaturation, when compared with the alum growth kinetics described in the literature. At high supersaturations (≥0.176), the growth rate changes its slope, indicating that there is a change in crystal growth kinetics. This change in crystal growth kinetics, with volume diffusion becoming more dominant, could induce homogeneous sealing along fracture length.

At high supersaturations (≥0.176), fluid inclusions form parallel to the crystal facets and with regular spacing of 20 µm, similar to natural primary fluid inclusions. Therefore, we propose that it is possible that natural crystals in elongate-blocky veins also grow under high supersaturations and that the fluid inclusions are an indicator of these conditions.

The final microstructures of the experiments are not influenced by the flow direction. Therefore, we suggest that the microstructure cannot be used as a tool to derive
flow direction in natural veins when the flow velocity was small.

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