

# Volume changes in solids induced by chemical alteration

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## Résumé :

*Le couplage entre altération chimique et mécanique est un problème fondamental en sciences des matériaux. Le remplacement d'un constituant chimique dans un solide induit souvent des changements de volume localement. Des expériences sur des matériaux modèle montrent deux cas limites en fonction que les contraintes sont transmises à travers l'interface de réaction, ou non. Dans le premier cas, la réaction présente une dynamique complexe avec l'accumulation de contraintes, la nucléation et propagation de fractures dans le matériau et l'ouverture de surface non-altérée. Cette nouvelle surface est exposée au fluide réactif et une rétroaction positive est mise en place sur le processus. Dans l'autre cas, le changement de volume réarrange le matériau solide sans présenter de contrainte ou de nucléation de fracture. Des exemples géologiques importants sont présentés.*

## Abstract :

*The coupling between chemical alteration and mechanical effects is a fundamental issue in material science. The replacement of one chemical component by another in a solid material often induces local volume changes. Experiments on chemical alteration in model materials reveal two limiting cases, one where stress is transmitted through the reactive interface and one where it is not. In the former case, the reaction reveals an intricate dynamics of elastic stress build-up, subsequent fracturing and opening of new surface area. This new surface area is exposed to reactive fluids and in that way a positive feedback on the overall process rate is established. In the latter case, the volume change rearranges the solid material locally without a stress build up and material fracturing. Important examples from geology are discussed.*

**Mots clefs :** volume change, elastic stress, chemical alteration, fracturing

## 1 Introduction

Chemical alteration such as weathering or metamorphic reactions are examples where one solid material is transformed into another in the presence of a reactive liquid. Such processes have important consequences for the rheology of the Earth's lithosphere and the transformation of rocks into soil at the Earth's surface. In a lot of cases, these reactions induce volume changes accompanied by a build-up of internal stress, and a possible fracturing of the solid.

This coupling between volume change and fracturing is known in different systems. Thermal stress [1] is an example, where in the absence of external stress a crack is nucleated and propagate[2]. In composite systems where materials with different thermal expansion coefficient are connected, material heating can produce high stress gradients at the interface of the solids and potentially cause catastrophic failure. Examples include coating of a protective oxide layer of an alloy [3] or resistance to temperature of concrete [4]. Drying processes are also known to exhibit different fracturing patterns ranging from polygonal [5] to hierarchical [6] structures. In the case of chemical alteration, recent works [7, 9, 8] suggest that fracturing of the material could feed back on the reaction processes by increasing transport and exposure of fresh material to reactive chemicals. For reactions producing a local volume increase, this feedback may be dramatic. Field observations supported by numerical simulations, suggest that the volume change leads to spalling, but also to a strong fracturing, dividing the material into several pieces [10, 11]. In general, the reaction rate is strongly enhanced by this process compared to the diffusion-limited reactions.

Other systems do not form fractures even when exposed to large volume changes. Pseudo-morphic reactions [12] are chemical alterations preserving the shape, external volume and crystallographic orientations of the initial solid. Volume change is then traduced by a change in the solid porosity, but in general no fractures are nucleated in this case.

We present here two different experiments in order to understand the mechanisms of stress transmission at reactive interfaces undergoing local volume changes. Dissolution of Poly(methyl methacrylate), PMMA, is an example where chemical alterations at the surface induces stresses which are easily transmitted into the bulk of the material. The mechanical feedback on the reaction is investigated experimentally. Alteration of salts

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is used as a model of pseudo-morphic reaction. Observation of the reaction front gives insight into the local mechanism and why there is an absence of stress build-up.

## 2 Experimental setups

### 2.1 PMMA dissolution

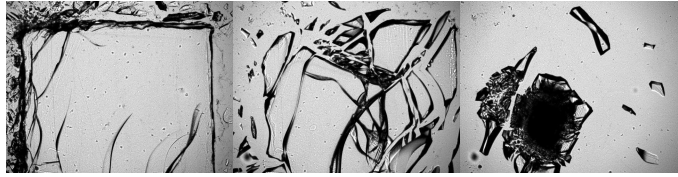


FIGURE 1 – Different stages in the PMMA dissolution.  $t=0$ , 100 and 350 min.

Dissolution of polymers is reviewed in Miller-Chou *et al.* [13] and was first reported by Ueberreiter *et al.* [14]. Polymer dissolution occurs when a polymer is put into contact with a solvent. The polymer glass made of entangled polymer chains lost its cohesion, chains disentangle and are finally isolated in the solvent. Usually, observation of the process reveals two simultaneous reactions : a first reaction front transforms the glassy polymer into a gel made of entangled polymer chains penetrated by solvent molecules, and a second reaction front disentangles the chains leading to the complete dissolution. No fracture is formed during the normal dissolution. Other modes of dissolution have been observed [15]. Dissolution of PMMA performed under the glass transition temperature leads to the disappearance of the gelly intermediate layer and catastrophic-like fracturing has been reported [18, 19, 17]. Osmotic pressure or deformation of the polymers in contact with the solvent are possible sources of stress build-up at the interface of the reaction [16].

A "2D" setup is built to allow for direct visualization of the system evolution. Samples of typical size  $3 \times 3 \times 0.3$  mm<sup>3</sup> are obtained by polishing an initial 2 mm thick PMMA piece. The polymer is then put 4 hours in an oven at 120°C to remove residual stresses. The sample is placed inside a Hele-Shaw cell of 0.3 mm spacing. Different types of coating are used to prevent or allow reaction in the third dimension. At time  $t = 0$  acetone is introduced inside the cell.

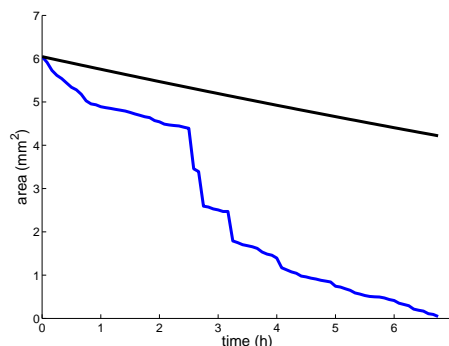


FIGURE 2 – Reaction evolution. Area of unreacted PMMA versus time for one experiment and the normal-dissolution model.

An image analysis of the pictures reveals different behaviors : spalling on the edges, hierarchical fracturing splitting the sample into different size of blocks ranging from the sample to smaller scales. In all cases, fracturing is followed by the dissolution of the fragments, which controls the time evolution of the reaction. Comparison is made with a normal-dissolution law and shows a process ten times quicker (Fig. 2). Explosive-like event and geometrical effects due to reaction in the third dimension are also reported.

### 2.2 Pseudo-morphic reactions

Pseudo-morphic reaction is modeled by the crystalline system KCl-KBr-H<sub>2</sub>O. It is a relevant for a lot of geological situations since the reaction leads to a solid solution [12]. In that experiment, KBr crystals are immersed in a K<sup>+</sup>Cl<sup>-</sup> saturated solution. The reaction is pseudo-morphic (Fig. 5) and induces volume decrease (a few 10%) leading to porosity.

A setup is built to allow for direct visualization of the interface between non-altered and altered crystals (Fig. 4). An o-ring closed by two glass plates entraps a K<sup>+</sup>Cl<sup>-</sup> saturated solution ( $V=0.54$  mL). The saturated solution is obtained by dissolving KCl crystals in deionized water. KBr crystals (typical dimensions  $3 \times 3 \times 2$  mm<sup>3</sup>) are

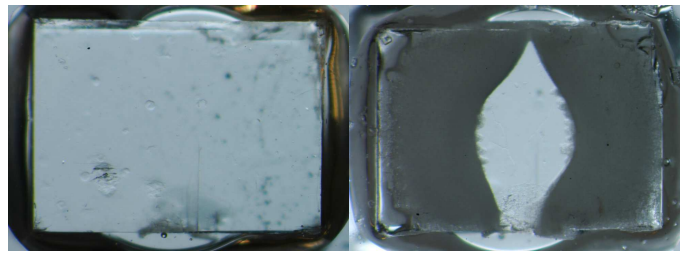


FIGURE 3 – Chemical alteration of a KBr crystal (left) leading to a KBr-KCl solid solution (right). The reaction leads to the creation of porosity. Pores diffuse the light, which explains the opacity of the new-formed crystal.

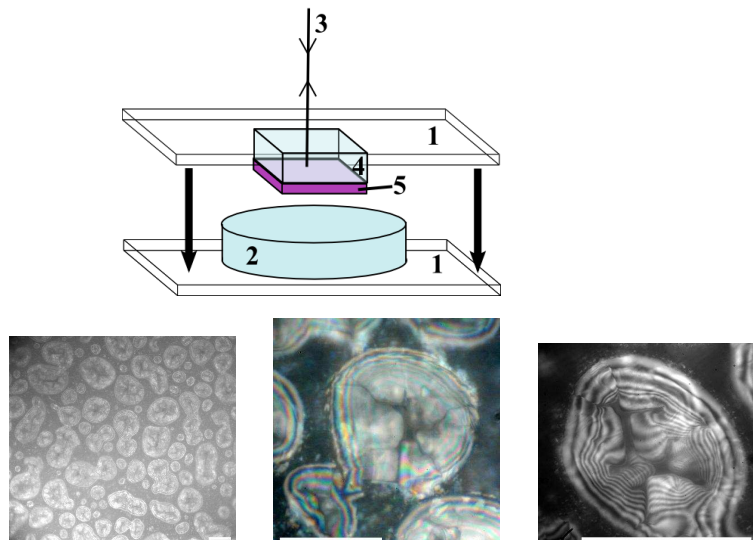


FIGURE 4 – Replacement front. Top : Setup. 1. glass plates, 2.  $K^+Cl^-$  saturated solution bath, 3. light beam, 4. parent crystal, 5. new crystal. Bottom : Different views : Large view, zoom with white light, zoom with green (547 nm) filter. bar = 100  $\mu m$ .

freshly cleaved from initially transparent crystals. The crystal is glued with an optical transparent adhesive to one of the glass plates. This has two advantages : it prevents reaction from this side of the crystal and allows the propagation of light down to the interface through the glass plate, the adhesive and the transparent crystal. This side of the crystal is then imaged with an optical microscope working in reflection light mode once the KBr crystal is placed in the saturated  $K^+Cl^-$  solution bath. The time scale for a complete replacement of the sample is 1 hour.

The images show that the reaction interface exhibits a strong roughening, which takes the shape of cylindrical structures composed of altered material advancing into the non-altered one. The top of the cylinders is seen as a circular shape in Fig. 4. Size and shape of the structures do not evolve significantly during the whole process, although a few big structures divide into smaller ones. Samples of the cylinder top areas give a distribution between 0.1 and 2  $\cdot 10^4 \mu m^2$ . Roughening (distance between foot and top of the cylinders) is approximately a few 10  $\mu m$ . Zoom on one structure reveals concentric Newton rings under white light and concentric rings by using a green filter (Fig. 4). These interference fringes suggest the presence of an open space, filled by the liquid, between the non-altered and altered crystals. This spacing is a few  $\mu m$  large. The middle of the structure is open, like a channel which allows a liquid transport from the bulk solution to the interface.

### 3 Discussion

The reactive interface behaves differently in the two experiments. In PMMA dissolution, the pattern suggests the presence of a small layer which increases in volume [10, 11] at the interface between the unreacted polymer and the solution. This layer is pulling on the unreacted polymer and consequently leads to strong fracturing and spalling. The catastrophic scenario reported in the literature is explained as a consequence of the strong enhancement of the permeability.

In the other case, direct observation of the pseudo-morphic reaction shows that the process occurs in a small space between the non-altered and altered crystals. This reactive cell advances inside the non-altered crystal. It dissolves the initial crystal on one side and re-precipitates the stable components on the other side. The volume-deficit reaction leads to a smaller area of precipitated material, which keeps the channel open and allows the

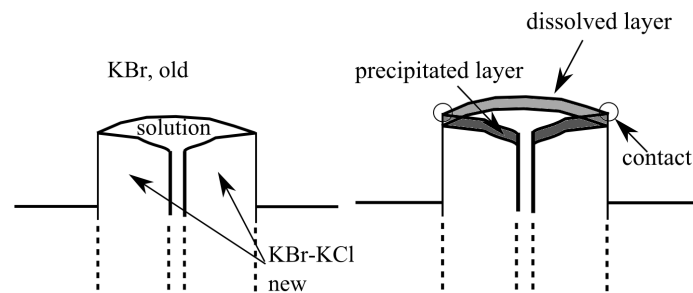


FIGURE 5 – Reactive cell. Left : geometry and composition. Right : sketch of the reaction evolution. The light gray layer is dissolved and the dark gray layer is precipitated. The only contact between the two crystals are shown.

reaction to proceed. The small space (a few  $\mu\text{m}$ ) between the two crystals is enough to prevent a direct contact between them (excepted on the edges) and is probably the reason of the no stress transmission. Geological relevance of the two cases is the subject of current research.

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