Chemical Aspects of Rock Deformation [and Discussion]

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Chemical aspects of rock deformation

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Studies of the rates of crystal growth at low supersaturations show that solution-growth processes may be dominant in the mechanism of deformation of wet rocks at very low values of differential stress. Strain rates in the order of $10^{-11}\,\mathrm{s}^{-1}$ may be attained with differential stresses of 10 MPa. Rocks undergoing progressive burial metamorphism will pass through depth–temperature regions where fluids are generated and new phases developed. During such discontinuous dehydration bursts, the rocks will be porous and permeable and of low strength. When rocks are not dehydrating, or absorbing pore fluids as during uplift, solid-state deformation mechanisms may predominate.

Introduction

The subject of this meeting is the consideration of natural strain in rocks and I was asked by Professor Ramsay to consider the role of chemical processes in the creation of such strain. In the proceedings of this meeting it has become clear that strain and its creation by deformation are approached in two distinct ways. Most workers in the rock mechanics laboratory consider the rock as a static chemical object whose equation of state can be described by variables such as confining stress, differential stress, pore fluid pressure, temperature. At the other end of the spectrum are those who see deformation processes accompanied by chemical change on the micro and macro scales. It seems, that any adequate description of rock deformation in natural systems must unite those extremes, and must consider time as a variable.

At the outset then, I divide natural strain into two types:

(*a*) strain produced during essentially isochemical processes,

(*b*) strain produced during non-isochemical processes.

As we shall see, class (*a*) are important during the deformation of high grade metamorphic rocks and during processes of uplift. Class (*b*) refer to prograde metamorphic processes where the common schists with mineral fabrics are formed.

Perhaps at the outset I would like to mention one of the dominant (but often neglected) chemical processes that must cause profound strain in cover and basement; the process of weathering. Ground and river water carry in solution about 100 parts/10^6 dissolved rock materials. Consider a region with a rainfall of 1 m per year (a), then per square centimetre of surface, 10^{-2} g/a of material is removed. For one million years this amounts to 10^4 g or about 50 m of surface. Thus a mountain range standing 3000 m in elevation, can be removed, by solution alone, in 60 Ma. The material is removed from the continental surface and transferred to the ocean basins. A profound, slow deformation, must accompany this process. The figures are conservative for much material is removed in particulate form. In the Amazon system, about 22 % of erosion is by solution; in the major tributary the Tapajos, 76 % of erosion is by solution.

METAMORPHISM

For the purposes of this discussion we may consider three important metamorphic situations; prograde or burial metamorphism, retrograde or uplift metamorphism and thirdly, igneous hydrothermal contact metamorphism. Prograde metamorphic processes, which involve initially water saturated rocks, tend to completion because of solvent catalysis of chemical reactions most of which themselves generate water. New phases tend to grow with strong preferred orientation because porosity is small. Retrograde processes tend to be incomplete and terminate when porosity is diminished and residual water is combined into hydrated minerals. Thus the partial pressure of water in any residual pore spaces is very low indeed.

What I term igneous hydrothermal metamorphism involves the convective cooling of high level igneous bodies (gabbroic rocks of the ocean ridge environment, high level granitic plutons) where the cover rocks are in extension and fractured. Permeability is large and the volumes of surface fluids which may be involved are very large indeed and are related to the size of the energy source. Metasomatic processes are extensive, but strong fabrics do not tend to develop in newly formed minerals. Spilites are typical products of such reactions. We shall not consider these situations further (see Fyfe 1975).
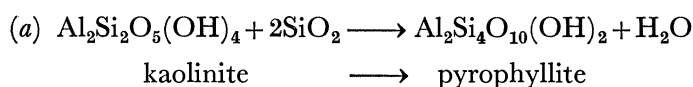
Burial metamorphism

There is abundant evidence to show that rocks once at the surface of the Earth may become buried to depths where partial melting occurs; they must reach temperatures near 1000 °C. The initial material is normally highly porous and permeable. It is also well established that at depths of 5–10 km, most porosity and pore water is eliminated and strains may reach 50 % by volume in this process.

Temperatures during this preliminary compaction step are low and the solubilities of most minerals are also low but appreciable transport can occur on account of the large fluid volume involved and there is little doubt that the compaction process involves pressure solution and redeposition of mineral substances. Some important ore bodies are formed in this temperature range (lead, zinc, uranium).
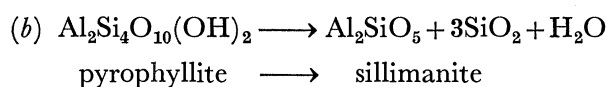
Once porosity is reduced to the percent or less level, most water in the rock is contained in hydrated minerals. Clay rich sediments may contain 7 % of chemically bound water. In general, zeolite facies rocks may contain 5–11 % bound water. If such rocks reach the amphibolite facies, water contents will be reduced to 1–2 %. The volume of water removed during progressive metamorphism is again impressive and volume strains equally impressive. From the zeolite facies onwards, as the rocks are essentially solid and water release rates slow, new phases tend to show well defined preferred orientation. If we consider the progressive burial and metamorphism of a column 1 km² in cross section and 30 km in depth, with a net water loss of near 10 %, the volume of water which must leave is of the order of 10 km³ and most of this water will be removed at temperatures between 300–600 °C. The solvent properties of such hotter water are impressive. The 10 km³ of water, if evolved near 400 °C at fluid pressures approaching load pressures, will carry towards the surface about 0.3 % silica and will form 0.01 km³ of quartz veins in the overlying rocks. The exact nature of vein chemistry may reflect the geothermal regime. Almost pure quartz veins indicate moderate fluid pressures. At higher pressures (e.g. blueschist terranes) veins are more complex and albite veins may dominate over quartz veins. Exactly how minerals deposit depends on the shape of solubility curves. Thus gold deposits in

quartz veins result from the extreme temperature sensitivity of gold solubility in halide solutions (Fyfe & Henley 1973).

When rocks in the crust dehydrate in response to increased burial (or heating), in general, water release will not be smooth but must occur in bursts. A very simple case to envisage is the progressive metamorphism of a kaolinite-quartz layer in a sediment. This simple chemical system will deydrate in two major steps:

$$(a) \quad Al_2Si_2O_5(OH)_4 + 2SiO_2 \longrightarrow Al_2Si_4O_{10}(OH)_2 + H_2O$$
$$\text{kaolinite} \qquad \longrightarrow \qquad \text{pyrophyllite}$$

Each kaolinite molecule will release about 7 % water by mass.

$$(b) \quad Al_2Si_4O_{10}(OH)_2 \longrightarrow Al_2SiO_5 + 3SiO_2 + H_2O$$
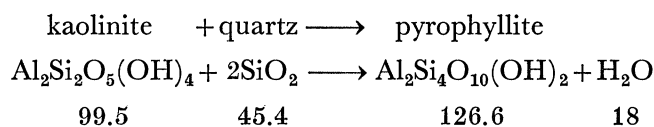$$\text{pyrophyllite} \quad \longrightarrow \quad \text{sillimanite}$$

The dehydration steps will be separated by about 100 °C or 4 km burial.

Exactly how a given layer behaves at any situation in depth-temperature space will be complex and depend on the rock chemistry, and particularly whether or not the dehydrating species involve solid solutions. The feature we wish to stress here, is that the average rock will pass through periods where it is chemically reactive and periods where it is unreactive. The mechanical properties of the rock will change drastically, in the two situations. Thus during metamorphism, the response of a rock layer to differential pressure cannot be a smooth function of the burial path.

Comparing a basaltic composition starting from the zeolite facies to the simple kaolinite sediment, the former will show at least four smeared out periods of major fluid release corresponding to the major metamorphic facies changes.
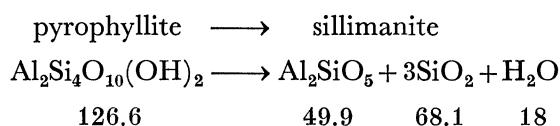
Mechanical properties during dehydration

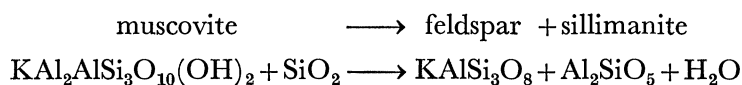Let us consider in more detail some typical reactions and the volume changes involved (in cm³ mol⁻¹),

$$\text{kaolinite} \quad + \text{quartz} \longrightarrow \quad \text{pyrophyllite}$$
$$Al_2Si_2O_5(OH)_4 + 2SiO_2 \longrightarrow Al_2Si_4O_{10}(OH)_2 + H_2O$$
$$99.5 \qquad 45.4 \qquad \qquad 126.6 \qquad 18$$
$$\Delta V_{\text{total}} \approx 0$$
$$\Delta V_{\text{solids}} \approx -18$$

$$\text{pyrophyllite} \quad \longrightarrow \quad \text{sillimanite}$$
$$Al_2Si_4O_{10}(OH)_2 \longrightarrow Al_2SiO_5 + 3SiO_2 + H_2O$$
$$126.6 \qquad \qquad 49.9 \quad 68.1 \quad 18$$
$$\Delta V_{\text{total}} \approx 10$$
$$\Delta V_{\text{solids}} \approx -8$$

$$\text{muscovite} \qquad \longrightarrow \quad \text{feldspar} + \text{sillimanite}$$
$$KAl_2AlSi_3O_{10}(OH)_2 + SiO_2 \longrightarrow KAlSi_3O_8 + Al_2SiO_5 + H_2O$$
$$\Delta V_{\text{total}} \approx 13$$
$$\Delta V_{\text{solids}} \approx -5.$$

Firstly, most such reactions lead to a volume expansion if the water is contained in the product rock. Second, the fluid void space created is not trivial and in general is several percent. Third, once the fluid escapes there is a large negative volume change. In the most common examples, the chemical processes involving the dehydrating grains must lead to volume increase and possible micro-hydraulic fracturing. The 'active' rock may become a gas fluid system ruptured at the grain boundaries of the reactive minerals. During initiation of the reaction, permeability may be low and the rate of draining small, but eventually, the porosity and permeability must be so large that draining is rapid and coupled to the rate of fluid release. During the dehydration bursts, the strength of the system must be low.

Thus the rock volume undergoing discontinuous dehydration, dependent on the chemical lithology, must show discontinuous mechanical properties. Unreactive layers will be impermeable and may float off reactive layers or they may be breached by vein swarms or shear zones (see Price 1975). It should also be emphasized, that most new phase growth occurs when the rock is in this mobile state. The situation is a long way from most of the experimental situations of the rock mechanics laboratory.

The notion that water may be trapped in large volumes at depth perhaps seems at first sight a little strange. But it seems logical that (unreactive) rocks at depth should be less permeable than rocks nearer the surface. And we know that oil and gas are trapped at quite modest depths for many millions of years, times greater than those required to supply the heat for dehydration reactions (see below).

Rate processes

The dehydration steps discussed above involve a number of rate processes the slowest of which will control the overall rate. In particular, in a fluid system, we are concerned with rates of fluid evolution and rates of solution, nucleation and growth of new phases resulting from the dehydration. In terms of natural processes, it can be generally stated that if a solvent is present, almost all metamorphic changes can be studied in the laboratory in times of days to months. These times are so short in comparison to natural times of changes of P and T, that it can be assumed that rocks remain at a close approach to the equilibrium state for any set of physical variables. This is not true of solid state processes during retrograde or uplift metamorphism when a solvent is absent or present in trivial amounts.

Most dehydration processes are highly endothermic, typical values being near 42 kJ mol^{-1}. Consider say 500 g of rock which loses 4 % water, about 1 mol. The average radioactive heat production in crustal rocks is about $4 \times 10^{-13} \text{ J g}^{-1} \text{ s}^{-1}$. Thus the 42 kJ needed for dehydration will absorb the heat production for about 10 Ma. Depending on the nature of the rock column, this heat is augmented by normal heat flow through the column. The problem has been discussed by Fyfe, Turner & Verhoogen (1958). It is clear that dehydration reactions and their rates are coupled to heat input and must be slow. This also implies that once finite permeabilities are achieved, water will 'bleed' off as fast as it is produced in reactive rocks.

Crystal growth and strain rates

It is generally recognized that differential stresses in the crust are not large, perhaps rarely exceeding a few tens of megapascals. Rocks must deform and develop their fabrics in response to such stress differences. If a mineral grain is not under hydrostatic stress, the more highly stressed part will have a larger free energy and, if a fluid is present, will have a greater solubility in the fluid. Such differences must lead to some of the compaction processes in porous rocks and

hence also to rocks undergoing dehydration and deformation at depth. In such cases, a strain rate can reflect the rate of solution of stressed grains and the rate of growth at sites of low stress.

The rate of growth of a crystal is normally some simple function of the supersaturation at the surface of the growing crystal. If differential stresses in the crust are small, then clearly stress induced supersaturation will be small.

Consider a fluid-crystal system where grains are under non-hydrostatic stress. We will assume that the most highly stressed parts of crystals are under an effective confining pressure 10 MPa greater than the less stressed crystals or parts of crystal. We will assume the rock has finite porosity and permeability (cf. a pile of spheres under a load pressure with a fluid present, the fluid pressure less than the confining pressure). With such a configuration, the free energy of a stressed grain will exceed that of the less stressed by approximately $V\Delta P$, when V is the molar volume and ΔP the difference in effective confining pressure on the grain (10 MPa). As most minerals have a molar volume in the order of 50 cm³ mol⁻¹,

$$\Delta G_{\text{differential}} = V\Delta P_{\text{differential}} \approx 400 \text{ J mol}^{-1}$$

The next question must be concerned with our knowledge of growth rates of minerals related to such small differential free energies and small supersaturations. Such data are available.

In recent years, one of the most sensitive methods of studying phase changes or mineral reactions of the type $A_{\text{solid}} \longrightarrow B_{\text{solid}}$ has been to follow the mass changes on a single crystal of A or B in the presence of crystals of the other phase and in the presence of a solvent. Microgram changes in mass can be recorded and show the direction of reaction. Near a point of equilibrium in P–T space, the ΔG causing reaction is clearly related to the P and T departure from equilibrium. If we consider equilibrium at constant hydrostatic pressure where the equilibrium is T_e and ΔS is the entropy of reaction, then the ΔG of reaction at any arbitrary T is simply:

$$\int_T^{T_e} \Delta S \, dT$$

and for small departures of T from T_e is approximately $\Delta S(T_e - T)$.

Several reactions of this type have been studied at temperatures close to equilibrium and growth rates of single crystals recorded. Such reactions include:

(a) $2\text{AlOOH} \longrightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$
(growth on corundum crystals, Fyfe & Hollander 1964).

(b) $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{SiO}_2 \longrightarrow \text{NaAlSi}_3\text{O}_8 + \text{H}_2\text{O}$
(growth on albite, Campbell & Fyfe 1965; growth on quartz, Thompson 1971).

(c) $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{SiO}_2 \longrightarrow \text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2 + \text{H}_2\text{O}$
(growth on quartz, Thompson 1970).

(d) $\text{KAl}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2 \longrightarrow \text{KAlSi}_3\text{O}_8 + \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$
(growth on corundum and adularia, Evans 1965).

In all such systems, solution rates are extremely rapid (for data on quartz see Weill & Fyfe (1964); for kyanite and andalusite see Brown & Fyfe (1971)).

For reaction (a) growth rates of micrograms per day on one single crystal are achieved 10 °C from equilibrium. As the ΔS of reaction under the appropriate condition is about 84 J mol⁻¹ K⁻¹, the ΔG of reaction is about 850 J.

The case of reaction (b) is of even greater interest. Again growth rates of micrograms per day are achieved within 10–20 °C of equilibrium at temperatures near 200 °C. This reaction has a small entropy change of about 12 J mol^{-1} K^{-1} and thus these growth rates are achieved when ΔG of reaction is 125–250 J mol^{-1}. These values are clearly appropriate to our arguments.

Let us consider a cubic centimetre of rock under a differential stress of 10 MPa. We will assume that a fluid is present in pores and that strain occurs via solution and growth. The data above indicate that we might anticipate growth rates of micrograms per day. If the cube is of material of density 2.5 g cm^{-3} then for a growth process of 2.5 μg day^{-1}, the strain rate will be about 10^{-11} s^{-1} For a 10 MPa differential stress, this is probably a very conservative estimate and we might anticipate strain rates orders of magnitude greater. Recently, Price (1975a) has discussed strain rates for various geologic situations and it is clear that the above figure is geologically realistic for a rock undergoing prograde metamorphism and deformation. It seems possible that such solution-growth processes can play an important role in deformation processes. But it should be emphasized that the processes will be most important when fluids are being generated and porosity and permeability permit a continuous transport path; the processes will be most important during the peak of a dehydration step and perhaps less active at the beginning and end when the fluid has migrated out of the rocks. During periods of little fluid evolution, the deformation mechanisms more familiar in laboratory studies may be active.

During retrograde metamorphism, and during uplift and cooling of deeply buried rocks, the common chemical reactions absorb water. Fluid pressures will be much lower than confining pressures and porosity and permeability may be very low. Thus strain will tend again to involve other deformation mechanisms and this record must be left in all rocks returning to the surface. Such events recorded in dislocation patterns might well erroneously suggest that these 'dry' mechanisms alone were responsible for all deformation observed.

Finally we may note that once crustal temperatures above 600 °C are attained, a small melt fraction will appear in most rocks. The chemical transport properties of melts will be greater than aqueous solutions and the strength of materials correspondingly reduced.

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Discussion

D. Flinn (*Department of Geology, University of Liverpool*). Professor Fyfe's remarks concerning rock deformation imply a mechanism of deformation very different to any mentioned in the previous papers. I proposed a mechanism of this type ten years ago (Flinn 1965a).

Deformation mechanisms involving dislocations and diffusion were found to operate in metals and have now been shown to operate in some rock forming minerals. They lead to grain deformation so that the rock as a whole deforms only because the grains have all changed shape. When rocks are deformed by these mechanisms the grains can be used as strain markers, but this is rarely the case and then only after low grade cataclastic or mylonitizing metamorphisms. In general the process is accompanied by recovery and even annealing recrystallization leading to a break up of the deformed grains into smaller grains by subgrain formation as a result of dislocation climb or by grain boundary migration. The resulting rather characteristic textures are quite a common result of late stage low grade metamorphism and deformation of previously higher grade rocks. In some cases the annealing recrystallization has been sufficiently complete to remove all signs of the inhomogenous strain within the grains but it does not appear to be able to increase the grain size significantly.

These effects are commonly superimposed on tectonites, that is on rocks showing evidence of a previous deformation during metamorphism. The evidence for the early deformation is of many types and includes strain markers and more frequently fabrics of the *l-s* type (Flinn 1965b). These rocks show no evidence of the operation during the earlier deformation of the mechanisms mentioned above. Grain sizes are larger than would be expected after an annealing recrystallization, original sedimentary patterns can often be recognized and where strain markers are present the individual grains are more nearly equidimensional than the deformation ellipsoid. Although the grains do not serve as total-strain markers they sometimes seem to act as incremental-strain markers.

A very good demonstration of these effects was provided by Dr Watterson's paper [not published]. His shear belts are zones of blastomylonites formed by deformation at a rate and a temperature which allow the operation of the metal-type mechanisms. Recovery and annealing has left the rocks much finer grained than the gneisses from which they are derived. Hence those gneisses themselves can never have suffered a deformation of this type. Where this not the case, grain size would provide an inverse measure of degree of deformation; for this there is no evidence.

What then is the mechanism of deformation that operated as most tectonites formed? I suggest that at appropriate strain rate and temperature and possibly water content, the grain boundaries unglue and grain boundary flow takes place. This mechanism differs from grain boundary sliding that accompanies Coble creep in that it is not rate controlled by diffusion. A sliding grain does not have to wait while an obstructing jog diffuses out of the way, instead it bulldozes it away and the damage is then repaired by diffusion.

This mechanism of deformation accompanied by grain boundary diffusion and Nabarro–Herring creep could give rise to both the grain shapes and the grain shape preferred orientations commonly observed in tectonites, but it does not seem to provide a mechanism for producing the most commonly observed preferred orientation of quartz (*c*-axes parallel to the direction of greatest shortening in the rock). However, the metallurgical type mechanisms are also in difficulty here for even if slip mechanisms were found which produced this preferred orientation,

it is common experience in metals that annealing recrystallization gives rise to a new preferred orientation more closely related to the crystallography of the original deformed grains than to the movements which deformed them.

I conclude that the experimentalists would do well to seek a superplastic mechanism of rock deformation dominated by grain boundary flow and they should recognize that the common occurrence of dislocations in quartz grains in tectonites is the result of very minor deformation at a late stage in the history of the rock and is unrelated to the formation of the tectonite fabric.

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Flinn, D. 1965 *b* On the symmetry principle and the deformation ellipsoid. *Geol. Mag.* **102**, 36–45.

A. NICOLAS

I fully agree with Dr Fyfe's statement that, in the tectonic history of metamorphic rocks derived from water rich sediments, two successive stages must be separated: the first one connected with prograde metamorphism and the second connected with retrograde metamorphism. Dr Fyfe showed that the disposal of water, mainly during phase changes, distinguishes the first stage from the second. I wish to add that this has important bearings on the flow mechanisms and the related fabrics. During prograde metamorphism, the deformation can result from compaction, pressure solution and recrystallization, sliding at grain boundaries, provided enough fluid or melt is present (the mechanism mentioned by Dr Flinn in his discussion). During retrograde metamorphism, solid state deformation results from the mechanisms advocated by Dr White in quartz rocks (which match very well those we have described in peridotites), specifically: dislocation slip and climb (plastic flow, *sensu stricto*), solid state diffusion (Coble and Nabarro–Herring flow, with superplastic flow as a particular case).