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Mechanical and chemical behavior of intergranular fluids in nonhydrostatically stressed rocks at low temperature①

LIU Liang-ming(刘亮明), PENG Sheng-lin(彭省临)
(Department of Geology, Central South University, Changsha 410083, P. R. China)

[Abstract] Intergranular fluids within the nonhydrostatically stressed solids are a sort of important fluids in the crust. Research on the mechanical and chemical behavior of the intergranular fluids in nonhydrostatically stressed rocks at low temperature is a key for understanding deformation and syntectonic geochemical processes in mid to shallow crust. Theoretically, it is suggested that the fluid film sandwiched between solid grains is one of the main states of intergranular fluids in the nonhydrostatically stressed solids. Their superthin thickness makes the fluid films have the mechanical and chemical behavior very different from the common fluids. Because of hydration force, double-layer repulsive force or osmotic pressure due to double-layer, the fluid films can transmit nonhydrostatic stress. The solid minerals-intergranular fluids interaction and mass transfer by intergranular fluids is stress-related, because the stress in solid minerals can enhance the free energy of solid matter on the interfaces. The thermodynamic and kinetic equations for the simple case of stress induced processes are derived.

[Key words] nonhydrostatically stress; intergranular fluids; free energy; fluid-mineral reaction; mass transfer

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1 INTRODUCTION

In the mid to shallow crust, all deformation and syndeformatic metamorphism are closely related to the interaction between mineral and intergranular fluids and the mass transfer in intergranular fluids, which are all influenced by the nonhydrostatic stresses in the solid rocks[1~3]. The diffusion creep in intergranular fluids induced by nonhydrostatical stress is an important plastic deformation mechanism, of which the activation energy is much less than that of dislocation creep. The diffusion through intergranular fluids is much faster than that through lattice or grain boundaries[4~6] Furthermore, the different chemical species may react one another when they are diffused through the intergranular fluid nets. So the chemical and mechanical behavior of intergranular fluids in nonhydrostatically stressed rocks is very important for understanding the geological and geochemical processes in the syntectonic and low temperature settings.

2 MECHANICAL BEHAVIOR OF INTERGRAINULAR FLUIDS

Because of the weak intermolecular binding of water and their isotropy, normal fluids can not transmit shear stress. Water, even in the state of solid ice, can only stand $n \times 10^5$ Pa deviate stress, much less than the least deviate stress in the nonhydrostatically stressed solid rocks, $n \times 10^7$ Pa[7]. So the shear stress transmitting mechanism of rocks with intergranular fluids is focus of the mechanical behavior of intergranular fluids in nonhydrostatically stressed rocks. There are two different models for explaining the stress transmitting mechanism, the inert loading frame model and the fluid film model. In the inert loading frame model, it is suggested that a fluid permeated inert loading frame can transmit arbitrary intergranular traction while permitting contact between a hydrostatically stressed grain-boundary fluid and a dissolving solid. It means that the stress is transmitted by the dry intergranular contact for the interactions of the solid molecule across the contact, while fluids can only exist in the pores around the dry contact[8~10]. In the fluid film model, it is suggested that the fluids exist as fluid film sandwiched between solid surface, which is so thin that the surface forces are big enough to transmit the shear stress[7,11~14].

The inert loading frame model can explain the mechanism for transmitting stress. But as the transmitting mechanism of stress is not related to the intergranular fluids, the contact zones are diminished by dissolution of pore fluids, leading to stress elevation in the contact and resulting in crush or plastic deformation of the solid grains[11,15]. So it is not stable and can not bring stable stress inducing fluid diffusion creep. On the contrast, the fluid film model, in which the mechanical actions of fluids and solid grains are closely related each other, can bring stable fluid diffusion creep induced by stress. Furthermore, the

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pore fluids and dry intergranular contacts are also permitted in the fluid film model. So the fluid film model is more reasonable, that is, there definitely are intergranular fluid films in the nonhydrostatically stressed rocks.

The disjoining pressure is one of the most important mechanical actions of the intergranular fluids. For a flat fluid film sandwiched between solid surfaces, the disjoining pressure equals the amount by which the fluid pressure acting on the film-solid interface exceeds the hydrostatic pressure in the bulk fluids[16]. There are two different hypotheses about origin of the disjoining pressure. Heidug thought that the disjoining pressure is the hydration force resulted from the ordering of water molecules between two surfaces in close proximity, and with amount in reverse relation to the thickness of fluid film[14]. Renard et al[7] thought the disjoining pressure origins from the electrical double-layer forces on the solid-fluid interface. Because of the surface chemical reaction, surface lattice defects or the surface ions absorbed by van der Wall forces and by hydrogen bonds, solid minerals always have surface charges which attract ions with reverse charges to the intergranular contact zones to reach electrical neutral. It will result in osmotic pressure between contact fluid film and pore fluids. The osmotic pressure equals to the amount by which the normal stress acting on the solid surface exceeds pore fluid pressure. According to the Debye-Hücke osmotic layer model[8], it is written as

$$p_o = \sigma_n - p_f = -\frac{RT}{V_w}\ln\left(\frac{x_{wc}}{x_{wp}}\right) \tag{1}$$

where p_o is the osmotic pressure, σ_n is the normal stress acting on the solid surface, p_f is the pore fluid pressure, that is hydrostatic pressure, R is the gas constant, T is the absolute temperature of the system, V_w is the molar volume of water, x_{wc} is the molar fraction of water in fluid film of contact zone and x_{wp} is the molar fraction of water in pore fluids. Suppose that, the surface charge distributed on solid with density of Ψ, thickness of the fluid film of contact zone is d, the concentration of all solutes is c_{al}, it is given that,

$$x_{wc} = \frac{1}{1 + V_w\left(c_{al} + \frac{2\Psi}{Fd}\right)},$$

$$x_{wp} = \frac{1}{1 + V_w c_{al}} \tag{2}$$

where F is Faraday constant. Substitution of Eqn. (2) into Eqn. (1) gives

$$p_o = -\frac{RT}{V_w}\ln\frac{Fd(1 + V_w c_{al})}{Fd + V_w(Fdc_{al} + 2\Psi)} \tag{3}$$

If not considering the osmotic pressure, the repulsive force of electrical double layers between two sides of solid across the fluid film can decrease with increasing electrolyte concentration in the fluids, while the osmotic pressure increases with increasing electrolyte concentration in the fluids.

From above analysis, it can be concluded that the hydration forces are not related to electrolyte concentration, and the repulsive forces electrical double layers between two solid-fluid interfaces would decrease with increasing electrolyte concentration in the fluids. However, the osmotic pressure would increase with increasing electrolyte concentration in the fluids. As a fact, these two mechanisms may play some roles in transmitting stress of the fluid film sandwiched between solid surfaces. But which would be dominant depends on the thickness of fluid film and component of the fluids.

3 ROLE OF STRESS IN MINERALS-INTERGRAINULAR FLUIDS REACTIONS

In principle, the fluid-mineral interface reactions, which ultimately form aquatically soluble species and change component of solids and fluids, would go in double directions. According to the transitive state theory[18], when the reaction approaches equilibrium enough, the net rate of reaction, R_{rn}, is

$$R_{rn} = -\frac{R_{r+}\Delta G}{RT} \tag{4}$$

where R_{r+} is the rate of positive reaction, ΔG is the difference of Gibbs free energy between reactants and products. ΔG is the drive force of the reaction. When it is negative, the reaction kinetic process will be from left to right, that is, solid mineral being dissolved. So, $-\Delta G$ is usually named as chemical affinity. Nonhydrostatic stress can influence the solid mineral-intergrain fluid reaction process by changing the Gibbs free energy of solid reactant, because the Gibbs free energy of solid mineral is related closely to its stress and strain at low temperature.

The contribution of nonhydrostatic stress to free energy of solid had been noticed by Gibbs as early as 1876[19], and has been discussed by a lot of scientists since then[20~26]. But, because of the essential difference between nonhydrostatic stress and hydrostatic pressure, the scalar variable of pressure (p) in hydrostatic system can not be directly replaced by the tensor variable of stress (σ_{ij}). So all the equations established about relation between free energy of solid and nonhydrostatic stress have still been argued.

In hydrostatic equilibrium system, according to the definition of Gibbs free energy and Helmholtz free energy, we obtain

$$G = F + pV \tag{5}$$

where G is the Gibbs free energy of system, F is the Helmholtz free energy, p is the hydrostatic pressure of system, V is the volume. As to single component system, its chemical potential can be written as

$$\mu = f + pv \tag{6}$$

where μ is the chemical potential, f is its specific

Helmholtz free energy, p is the pressure, and v is the molar volume.

Suppose single component solid contacting with fluid, the chemical potential of solid surface matter of any position can be written as

$$\mu_s(x_i) = f_s(x_i) + p_f(x_i)v_s \tag{7}$$

where the subscript s denotes solid, f denotes fluid, $\mu_s(x_i)$ denotes the chemical potential of solid varied with position. In the fluid film model, the mechanical action of fluid on solid is varied with position, so it is written as $p_f(x_i)$. For the mechanical equilibrium, we can get

$$p_f(x_i) = \sigma_n(x_i) \tag{8}$$

where $\sigma_n(x_i)$ is the normal stress on solid surface, Substitution of Eqn. (8) into Eqn. (7) gives

$$\mu_s(x_i) = f_s(x_i) + \sigma_n(x_i)v_s \tag{9}$$

As a matter of fact, the contribution of nonhydrostatic stress to the free energy of solid can not only be reflected in second right item of Eqn. (9), but the Helmholtz free energy of solid, $f_s(x_i)$, would also vary with strain. From the related researches[27~29], it can be concluded that

$$f_s(x_i) = f_0 + E(\varepsilon, x_i) \tag{10}$$

where f_0 is the Helmholtz free energy of free strained solid, $E(\varepsilon, x_i)$ is the strain energy of which variation with position is induced by the variation of strain with position. Kamb[20] and Paterson[21] only consider the elastic strain energy, writing it as

$$E(\varepsilon, x_i) = \frac{1}{2}\sum_{ij}\sigma_{ij}\varepsilon_{ij}V_0$$

where V_0 is the molar volume of free strained solid. That is obviously not correct. The strain energy should include the energy stored in dislocations and interfaces of crystals by plastic deformation. In the strong shear setting with high differential stress such as ductile shear zones, the plastic strain energy is very considerable, which may be much greater than elastic strain energy[30, 31]. But the relation of plastic strain energy to stress and strain is much more complicated than that of elastic strain energy, which has still not been expressed as a correct equation. It is definite that, the bigger the differential stress, the smaller the crystals and the denser the dislocations, so the greater the plastic strain energy. Based on the above analysis, as to the nonhydrostatically stressed solid with single component, the general form of chemical potential of solid matter on the mineral-intergranular fluid interfaces can be expressed as

$$\mu_s(x_i) = f_0 + E(\varepsilon, x_i) + \sigma_n(x_i)V_s \tag{11}$$

4 MASS TRANSFER BY INTERGRAINULAR FLUIDS

During the evolution process of crust rocks, the most important role of intergranular fluids is mass transfer. The mass transfer mediated by the intergranular fluids is intrinsically important part of mechanical and chemical processes of the crust rocks, with close relation to the stress in nonhydrostatically stress setting.

For mass transfer by fluids, there are two competitive mechanisms, diffusion in fluids and mechanical motion of fluids. The diffusion in fluid is driven by the chemical potential gradient of diffused materials. The most common mechanical motion of fluids is advectively driven by pressure gradient of the fluids. The mechanism for mass transfer in the intergranular fluid films considered here is diffusion.

There are two kinetic equations to express diffusion, the Fick diffusion law,

$$J_i^D = -D\frac{\partial c_i}{\partial x} \tag{12}$$

and the Onsager diffusion law,

$$J_i^D = -L\frac{\partial \mu_i}{\partial x} \tag{13}$$

where J_i^D denotes the diffusion flux of component i, $\partial c_i/\partial x$ and $\partial \mu_i/\partial x$ denote concentration gradient and chemical gradient of component i in x direction, D and L are the Fick diffusion coefficient and Onsager diffusion coefficient. They are related as

$$L = \frac{Dc_i}{RT} \tag{14}$$

Because the minerals-fluids reactions would increase concentration of component i in fluids, while the diffusion is on the contrary the net temporal variation of the concentration of component i is controlled by the following equations.

$$\frac{\partial c_i}{\partial t} = J_i^R - \frac{\partial J_i^D}{\partial x} \tag{15}$$

$$\begin{aligned} J_i^R &= v_i^r J_r^R \\ &= v_i^r L_{rr} A_r \end{aligned} \tag{16}$$

$$\begin{aligned} J_r^R &= R_{rn} \\ &= -\frac{R_{r+}\Delta G}{RT} \end{aligned} \tag{17}$$

where v_i^r is the stoichiometric number component i produced by reaction r, J_i^R is the rate at which component i is produced by reaction r, J_r^R is rate of reaction r, and A_r is the chemical affinity of reaction r. Substitution of Eqn. (12) into Eqn. (15) gives

$$\frac{\partial c_i}{\partial t} = D\frac{\partial^2 c_i}{\partial x^2} + J_i^R \tag{18}$$

Deduced from Eqns. (13), (14), (15), (16) and (17), we can also get

$$\frac{\partial c_i}{\partial t} = \frac{1}{RT}\left[v_i^r R_{r+} A_r + D\frac{\partial c_i}{\partial x}\frac{\partial \mu_i}{\partial x} + Dc_i\frac{\partial^2 \mu_i}{\partial x^2}\right] \tag{19}$$

Suppose the solid grain is locally equilibrium with the intergranular fluid, that is, the chemical potential of any solid substance on the surface is nearly equal to that of aqueous soluble specie of same component immediately adjacent to the surface. And by deducing the diffusion from one dimension to three dimensions. Eqn. (19) will be changed to

$$\frac{\partial c}{\partial t}=\frac{1}{RT}\left[v_i^r R_{r+} A_r + D\sum_i \frac{\partial c(x_i)}{\partial x_i}\frac{\partial \mu_s(x_i)}{\partial x_i}+Dc\sum_i \frac{\partial^2 \mu_s(x_i)}{\partial x_i^2}\right] \tag{20}$$

Substitution of Eqn. (11) into Eqn. (20) gives

$$\frac{\partial c}{\partial t}=\frac{v_i^r R_{r+} A_r}{RT}+\frac{D}{RT}\sum_i \frac{\partial c(\varepsilon, x_i)}{\partial x_i}\cdot \left[\frac{\partial E(\varepsilon, x_i)}{\partial x_i}+v_s\frac{\partial \sigma_n(x_i)}{\partial x_i}\right]+\frac{Dc}{RT}\sum_i \left[\frac{\partial 2E(\varepsilon, x_i)}{\partial x_i^2}+v_s\frac{\partial 2\sigma_n(x_i)}{\partial x_i^2}\right] \tag{21}$$

This equation reflects the relation of spatial and temporal variation of solid minerals-intergranular fluids reactions and mass transfer by intergranular fluids in nonhydrostatically stressed setting.

The actual chemical reactions and diffusion processes are all irreversible dissipation; that is, a part of free energy is transformed to the energy related to entropy, which can not be used. According the local equilibrium hypothesis for the irreversible processes, we can obtain

$$T\mathrm{d}S=\mathrm{d}u+p\mathrm{d}V-\sum_i \mu_i \mathrm{d}n_i \tag{22}$$

Deduced from this premise, we can get

$$T\sigma=J_s\frac{\mathrm{d}}{\mathrm{d}x}(-T)+\sum_i J_i^D\frac{\mathrm{d}}{\mathrm{d}x}(-\mu_i)+J_r^R A_r \tag{23}$$

where σ is the local producing rate of entropy by the irreversible process, J_s is the entropy flux, and J_i^D is diffusion rate of component i. The $T\sigma$ is the dissipation function, usually signified by Θ, of which the dimension is free energy/unit time, showing the local dissipation rate of free energy in the system by the irreversible process.

Eqn. (23) shows that, the dissipation of system is actually a sum of several products of a flux and its driving force. As to a system involving n irreversible processes each of which goes on at the rate of J_i and driven by the force X_i, the dissipation function would be

$$\Theta=\sum_i^n J_i X_i \tag{24}$$

The dissipation function is the basis of dynamics of irreversible process. A system without influences from outside would evolve to dying out of all forces and fluxes, the dissipation function becomes zero. The most important influence from outside in the nonhydrostatically stressed system is continuous acting of direct forces which, together with anisotropy and heterogeneity of the system itself, produce continuous chemical potential gradient. So the irreversible processes such as diffusion can continue.

5 CONCLUSIONS

Fluid films sandwiched between solid surfaces are important forms of intergranular fluids in the nonhydrostatically stressed rocks, of which the mechanical and chemical behaviour is very different from the common fluids. By hydration forces of super-thin water films, repulsive forces of electric double-layer on solid-fluid interfaces or osmotic pressure due to the electric double-layer, which depends on thickness and component of the fluid films, the intergranular fluid films can transmit stress mainly. The mechanical and chemical processes involved in intergranular fluids are closely related to the nonhydrostatic stress. The nonhydrostatic stress can enhance solid mineral-intergranular fluid interface reaction and mass transfer in the intergranular fluids by raising the free energy of solid component on the interfaces. The thermodynamic and kinetic equations are deduced for the simplest case of stress induced solid-fluid reactions and diffusion processes in fluid films.

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