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Mineral growth in rocks: Kinetic–rheological models of replacement, vein formation, and syntectonic crystallization

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Abstract—We model three cases of coupling between mineral growth kinetics and mechanical response of the rock: (i) dispersed spherical crystals growing by replacement in a hydrostatically stressed elastic rock; (ii) growth of veins or vein networks accommodated by viscous relaxation of surrounding rock; and (iii) syntectonic crystallization in a rock undergoing bulk pure shear. Such models for the microscopic environment of mineral growth, together with additional assumptions or knowledge about rheological behavior and aggregate geometry, provide refined estimates of the behavior of a macroscopic volume element, which could be combined with geochemical reaction–transport models. Crucial in the models are the various consequences—pressure solution, creep, fracturing—of the local stress that is necessarily generated by mineral growth in rocks (other than in pores).

In the first model, the dispersed spherical crystals of mineral A are assumed to grow within a spherical volume of rock consisting of mineral B, the “mineralized zone” (MZ), itself embedded in elastic rock. The macroscopic stress in the MZ and the far-field stress in the surrounding rock are uniform and hydrostatic. Mineral growth of the A crystals is driven by supersaturation with respect to mineral A, is accommodated by replacement of B grains, and leads to an expansion of the MZ described by an infinitesimal strain. The radial growth rate of a spherical crystal of mineral A, with replacement of mineral B, is

$$da/dt = k_A R T \ln(\Omega_A) [k_B V_0^B / (k_B V_0^B + k_A V_0^A)],$$

where k_A and k_B are kinetic constants, R is the gas constant, T the temperature in kelvin, and V_0^A and V_0^B are specific volumes. Reference saturation states of mineral A, $\Omega_A > 1$, and host mineral B, $\Omega_B = 1$, are specified at the far-field hydrostatic stress, σ_0 . The microscopic environment of each crystal of A is modeled by a representative volume element (RVE) consisting of a sphere of mineral A embedded in a spherical shell of mineral B. In each RVE, stress is neither uniform nor hydrostatic. The model links the local microscopic stress with the macroscopic stress in the MZ and surrounding rock.

The second model refers to veins that make room for themselves by growing, not to veins that form by cementation of previously opened, or opening, cracks. If the growth of mineral A as propagating veins or as an interconnected vein network takes place by deformation and expansion of the MZ—with the deformation itself driven by the stress arising from the supersaturation-driven growth—the surrounding rock undergoes deformation and is treated as viscous. The rate of growth in vein width, w , is

$$dw/dt = 2k_A [RT \ln(\Omega_A) - S V_0^A] / (1 + M),$$

where $M = 16\eta k_A V_0^A c^2 / (3b^3)$, η is the medium viscosity, c is the vein radius, and each vein is treated as centered in a spherical RVE of radius b . S is an effective tensile stress required for vein propagation. For a vein network, in which veins surround equant polyhedra of rock of radius b , we set $c = b$ and drop the term in S for simplicity. Veins may also widen by replacement. The ratio of vein widening by expansion to that by replacement is

$$(dw/dt)_{\text{expansion}} / (dw/dt)_{\text{replacement}} = \{(3b/16\eta) / [(3b/16\eta) + k_A V_0^A]\} / [k_B V_0^B / (k_B V_0^B + k_A V_0^A)].$$

Both mechanisms of accommodation contribute equally when $\eta = 3b / (16k_B V_0^B)$; at higher viscosity, replacement is dominant.

The incipient growth of a cylindrical crystal with circular cross section in a medium deforming in pure shear simulates syntectonic crystallization. Both dissolution and deformation of the host accommodate growth. In the model, the crystal tends to grow faster in the direction of maximum rate of extension. In this direction, the host mineral may either dissolve to accommodate growth, or precipitate to form a pressure shadow. Accommodation by host dissolution is greatest in the direction of maximum rate of shortening. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

A crystal of pyrite in shale or a garnet in schist must have pressed outward on the surrounding host as it grew because there could not have existed a cavity—much less one with the

right shape—for the crystal to grow into. Growth of a crystal in a solid rock thus necessarily generates a local state of stress around the crystal. Growth of many dispersed crystals or crystal aggregates should modify the macroscopic stress. The host rock may respond to the local stress by pressure solution (this response produces replacement), by flow, or by fracturing. These responses may in turn feedback on the stress and the growth itself. The local and bulk stress that arise because of

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mineral growth loosely correspond to the “force of crystallization” introduced by Becker and Day (1916), the “excess pressure” measured by Ostapenko (1976), and the “induced stress” of Carmichael (1986).

Here we model quantitatively three specific cases of the kinetic–rheological interaction triggered by mineral growth in rocks. The models we present refer to widespread phenomena: replacement, vein formation, and syntectonic crystallization, respectively. The cases are chosen for simplicity and tractability. We obtain relations that link stress and deformation of host and crystal to supersaturation and to the mechanism of accommodation. These describe the microscopic state of stress and deformation about growing crystals and the relation between changes in local and macroscopic stress in a representative element of the rock. (Inward growth of a reaction rim replacing an inner spherical crystal of a polymorph has been modeled recently by Mosenfelder et al., 2000.)

In the models, mineral growth is restricted to a macroscopic volume of rock, the mineralized zone (MZ), which is mechanically constrained by the surrounding rock. The macroscopic stress in the MZ and the far-field stress in the surrounding rock is hydrostatic¹ and uniform. Growth of the mineral in the MZ is described by a simple model for its microscopic environment in the form of a representative volume element (RVE). The microscopic stress in the RVE is inhomogeneous. In the replacement model, growth is accommodated by host mineral dissolution, thus by replacement in a hydrostatically stressed elastic rock; that dissolution is caused by the stress induced by the growth. The vein model refers to veins that make room for themselves by growing (Taber, 1918)—that is, veins that both propagate and force the host rock to expand driven by supersaturation with respect to the mineral that makes up the vein. The use of a simple RVE to characterize details of the microscopic process and deformation has been found to be useful in other mechanical systems (Bhatt et al., 1975). A third model treats the “syntectonic” growth of a single crystal in a rock undergoing viscous creep. Table 1 summarizes the symbols used.

2. GEOCHEMICAL REACTION–TRANSPORT IN WATER–ROCK INTERACTION

Insofar as the models indicate that growth kinetics is generally modified by the very stress the growth generates in rocks, and by the effects of that stress, we point out the relevance of the models in this paper, or at least of the kinetic–rheological feedbacks underlying our models, for existing models of coupled geochemical reaction–transport (e.g., Steefel and Lasaga, 1994), which do not take account of such feedbacks. Incorporation of kinetic–rheological models into geochemical water–rock reaction–transport calculations would warrant close consideration of the work of Thompson (1955) and Bruton and Helgeson (1983; see their figs. 30 and 31), who considered

¹ We use the term “hydrostatic” to denote a state of stress in which the normal stress components are equal and the shear stress components vanish. If this is so in one Cartesian coordinate system, it is so in any other, and the stress tensor is therefore an isotropic tensor. Although the term etymologically refers to the state of stress in water at rest, it is commonly used to indicate stress in any medium. A nonhydrostatic stress, or anisotropic stress, denotes a stress that has a deviatoric part.

mineral equilibria when mineral grains in a solid rock are in communication with a fluid in porosity or cracks with $p_f < p_{\text{rock}}$ ² and of Dahlen (1992), who clarified the relation between macroscopic and microscopic (e.g., nonlocal and local) stresses and their relation to water–mineral equilibria. Kamb (1959) studied grain growth and dissolution in the development of preferred orientation in a nonhydrostatically stressed rock. The variable state of equilibrium on grain boundary elements between elastically anisotropic crystals results in a dynamic process tending to produce a preferred lattice orientation by local growth of crystals. Kamb’s analysis does not lead to a condition of equilibrium for a macroscopic representative volume but rather to the description of a dynamic process tending to transform it.

3. PREVIOUS WORK

We summarize published insights into the connection among crystal growth in rocks, the stress it produces, and one or another of the effects of this stress—pressure solution, deformation, and fracturing.

Maliva and Siever (1988) proposed that the force of crystallization associated with crystal growth in solid rock can pressure-dissolve host grains, and they used this concept to understand the genesis of the phenomenon of mineral replacement—petrographically characterized by preservation of volume and often of morphologic details. Their novel view of replacement is that it involves simultaneous growth of a grain of new mineral and pressure-solution of the host driven by the force of crystallization. Dewers and Ortoleva (1990) and Merino et al. (1993) modeled such replacement—and its kinetics—quantitatively. Despite the insights of Lindgren (1912, 1918, 1925), Bastin et al. (1931, p. 603), and Carmichael (1986), a clear explanation of the petrographic features of replacement (i.e., preservation of both internal morphologic details and bulk volume³) was first given by Nahon and Merino (1997, part 2), who showed how the growth-driven normal stress quickly adjusts towards the value for which the growth rate of the new mineral and the dissolution rate of the host mineral become equal. This is why replacement preserves volume, independent of whether the new and host minerals have elements in common or are isostructural, or of which mineral has the greater molar volume. The condition of constant volume found by alert petrographers for replacements in many kinds of rocks (see references in Merino and Dewers, 1998) was deduced theoretically by Carmichael (1986), and also, independently, by Dewers and Ortoleva (1990) for the infinite-viscosity limit (or “Reuss limit”) of a Navier-Stokes equation applying to simultaneous deformation, growth, and pressure-solution in a rock.

The growth-induced stress (though not with this name) was

² We take compressive normal stress negative, following engineering convention. Pressure is the negative of the mean normal stress and is thus generally positive.

³ Note that the term “replacement” is also used to denote cases (a few cited in Merino and Dewers, 1998) where a void produced by dissolution is later filled, wholly or in part, by cement. The result in those cases may texturally resemble the kind of replacement our model herein refers to (and the kind to which Maliva and Siever, 1988, referred), but the detailed mechanism and sequence of events is different. The difference between the two types of replacement parallels the difference between the two types of veins we discuss in the Conclusions.

Table 1. Table of symbols.

a	radius of spherical crystal of mineral A
a'	inner radius of spherical shell of mineral B
b	radius of rock sphere containing one vein or one growing spherical crystal
a^*, b^*	semi axes of elliptical cross-section of cylindrical crystal
C_A, C_B	arbitrary constants in solution for chemical potentials, Appendix
c	radius of penny-shaped vein
c_0^A, c_0^B	concentrations of components A and B in fluid film
dW	differential of work required to propagate vein by infinitesimal change in radius dc
$D\phi/\tau$	effective diffusivity in representative volume element, where D is diffusivity in bulk fluid, ϕ is porosity, and τ is tortuosity
D_{xx}^{T*}, D_{yy}^{T*}	rates of transformation strain in model for syntectonic crystallization
δ	vein aspect ratio
E	Young's modulus of isotropic elastic solid
$\varepsilon_{\xi\xi}^{T*}, \varepsilon_{\theta\theta}^{T*}, \varepsilon_{\alpha\alpha}^{T*}$	inelastic transformation strains in mineralized zone
ε_{rr}^{T*}	inelastic transformation strain in representative volume element
η	host rock viscosity
η^*	critical value of host viscosity at which concretion growth and vein growth modes are equally rapid
F_A, F_B	arbitrary constants in solution for chemical potentials
f	volume fraction of growing crystals
G	shear modulus of isotropic elastic solid
J_r^A, J_r^B	radial component of mass flux of components A or B in host rock
k_A, k_B	constants in kinetic law for precipitation/dissolution of minerals A and B
K_I, K_{IC}	stress intensity factor and its critical value
M	function appearing in expression for rate of vein growth
M_A, M_B	quantities characterizing diffusion in a spherical shell of host mineral, Appendix
$\mu^{A(\text{film})}, \mu^{B(\text{film})}$	chemical potentials of the components of minerals A and B in intergranular fluid
$\mu^{A(\text{eq})}, \mu^{B(\text{eq})}$	local equilibrating values of the chemical potentials of the components of minerals A and B in intergranular fluid
μ_0^A, μ_0^B	stress-independent parts of chemical potentials of components A and B
$\Delta\mu^A$	increment in reference chemical potential of component of mineral A in "reservoir"
$n_A(\theta)$	normal growth rate around the periphery of a crystal with local position described by an angle, θ
ν	Poisson's ratio
P_f, P_{rock}	pore fluid pressure, mean stress in rock expressed as pressure
r, θ, α	spherical coordinates
R	radius of spherical mineralized zone
R	gas constant
T	absolute temperature
S	stress difference required for crack propagation
σ_0	far-field hydrostatic stress
σ_n	normal stress at crystal surface
σ_R	macroscopic stress in mineralized zone
$\sigma_{rr}, \sigma_{\theta\theta}, \sigma_{\alpha\alpha}$	components of normal stress in spherical coordinates, generally in host rock
$\sigma_{rr}^{(A)}, \sigma_{\theta\theta}^{(A)}, \sigma_{\alpha\alpha}^{(A)}$	components of normal stress in spherical crystal
Σ	function in rate of growth of crystal radius
Σ_A, Σ_B	quantities in which diffusion and kinetics parameters are grouped, Appendix
u_r, u_θ, u_α	components of displacement in spherical coordinates
u'_r	radial displacement in spherical shell of RVE
u_ξ	radial displacement in mineralized zone or surrounding medium
V_0^A, V_0^B	specific volumes of minerals A and B
ξ	radial coordinate in mineralized zone or surrounding medium
w	maximum thickness of a penny-shaped vein
$Z(\theta)$	ratio of accommodation mechanisms around periphery of cylinder of growing mineral
Ω_A, Ω_B	saturation states of minerals A and B in reference state

invoked by Misch (1971) to explain the controversial phenomenon of deformation of schistosity around porphyroblasts, an origin also supported by Yardley (1974), Ferguson and Harvey (1980), and Wheeler (1987). Ferguson and Harvey (1980) comment on the arguments for and against local deformation of the host caused by porphyroblast growth. They describe an instance in which clear evidence for such deformation is present (Fig. 1a). Similarly, some sedimentary petrologists accept that a concretion may push apart sedimentary laminations, but most routinely interpret that wrap-around structure as resulting from differential compaction around a concretion, assumed preexisting. The fibrous barite body shown in cross section in Figure 1b, is disk shaped, with a sharply tapered

edge. We interpret this body started as a vein that later grew as a stubby vein or as a concretion. In either case, fiber growth (normal to the walls) was accommodated by deformation of the surrounding mudstone.

Finally, mineral growth in rocks might be accommodated by fracturing or by mineral growth in the form of veins, a mechanism that might have unexpected geophysical and geochemical consequences: where several crystals or crystal aggregates grow simultaneously within a few diameters of each other, fractures propagating from their host/crystal interfaces may interact cooperatively, forming fractures equal to or much larger than the interconcretion distance. These fractures, when occurring within fault zones, just might help trigger an earth-

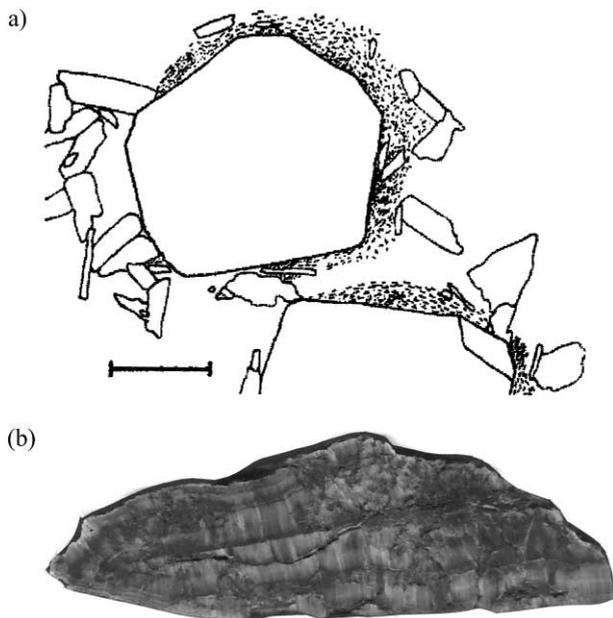


Fig. 1. (a) Garnet crystal that has pushed aside matrix during growth (reproduced from Ferguson and Harvey, 1980). Scale bar is 0.5 mm. Residual fine micas have been pushed aside, and much of the intervening quartz has either been incorporated into the growing crystal or pressure-solved and removed. (b) Left-terminating approximately radial section of a fibrous barite vein of small aspect ratio; length is 10 cm. The vein mechanically displaced its mud or mudstone host during growth (Mancos Formation, San Ysidro, New Mexico). The vein has grown outward from a medial, impurity-rich septum. In the later stage, the vein may have been growing more as a concretion.

quake. Modest examples of rupture produced by stress arising from mineral growth are the shattering of rocks in deserts by salt growth in pores and joints (Cooke and Warren, 1973, p. 68) and the bursting of cured concrete by crystallization of minerals such as calcite, gypsum, brucite, or ettringite (Dolch and Diamond, 1995). (See also the section on Vein Initiation and Growth.)

4. MINERAL GROWTH ACCOMMODATED BY REPLACEMENT

4.1. Mineralized Zone and Representative Volume Element

Consider a MZ in the form of a sphere of radius R (Fig. 2). Within it, growth of mineral A is accommodated by dissolution of mineral B: mineral A replaces mineral B. The MZ undergoes a slight swelling in this process on the order of an elastic strain. This effect does not warrant dropping the term “replacement,” but the process is not rigorously one of zero volume change.

Equant grains of mineral A are approximated as spheres of uniform radius a uniformly dispersed in the MZ, with center-to-center distance $2b$. Thus, the MZ may be thought of as a densely packed array of RVEs, each of which consists of a spherical grain of mineral A surrounded by a spherical shell of mineral B with outer radius b (Fig. 2). Models in which grain radius and center-to-center distance have continuous distributions or vary with radius within the MZ might be approached by means of averaging procedures for composite materials.

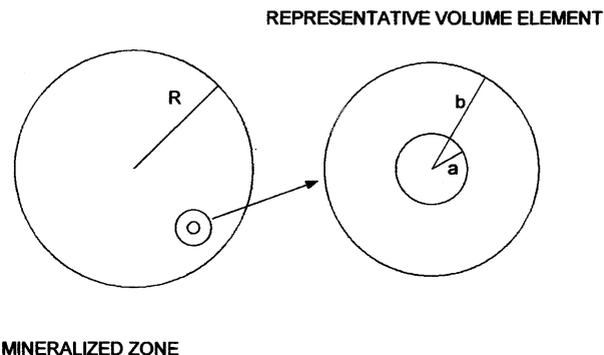


Fig. 2. Spherical zone of uniformly distributed mineral growth (MZ) embedded in an infinite confining medium and a microscopic RVE of which it is composed.

The homogeneity of the MZ in terms of its structure at the microscopic scale implies that geochemical transport is not a rate-controlling process at the macroscopic scale. Otherwise, the rate of mineral growth would tend to be nonuniform and would be greater near the periphery of the MZ. This simplification might be justified for some natural systems, but the present aim is to isolate effects arising from mechanical constraint. Diffusive transport at the RVE scale is discussed in the Appendix.

The stress far from the MZ is a homogeneous hydrostatic stress, σ_0 . Because mineral growth in the MZ is homogeneous, the macroscopic stress state within it is also a hydrostatic stress, σ_R . The stress σ_R will differ from σ_0 because mineral growth in the zone results in macroscopic dilation. Because of homogeneity, σ_R is also the radial normal stress acting on the outer surface of an RVE. The stress distribution in the RVE is inhomogeneous, but depends only on the radial coordinate, r . The macroscopic stress in the medium surrounding the MZ is inhomogeneous.

We determine the stresses based on the approximation that all mechanical components are isotropic elastic solids, with the same Young's modulus, E , and Poisson's ratio, ν . Derivation of the stress and deformation is not given. Sufficient background may be found in a reference such as Sokolnikoff (1956). The model is completed by the relations fixing the growth rate of the mineral A with concomitant dissolution of the host mineral B at their interface (Nahon and Merino, 1997).

Stress and displacement in the RVE are described in terms of the spherical coordinates r , θ , and α , where r is radius, with origin at the center of the RVE, and θ and α are orthogonal angular coordinates in the tangential directions. Here, quantities depend only on r , and the two angular coordinates are equivalent. The nonvanishing stress components are σ_{rr} and $\sigma_{\theta\theta} = \sigma_{\alpha\alpha}$. The radial displacement is u_r , with $u_\theta = u_\alpha = 0$.

The radial normal stress on the exterior of the host shell is

$$\sigma_{rr}(b) = \sigma_R. \quad (1)$$

The normal stress at the A/B interface is

$$\sigma_{rr}(a) = \sigma_n. \quad (2)$$

To describe the growth of mineral A and dissolution of mineral B, it is necessary to specify the values of the chemical potentials of their components at the interface. Ignoring transport, we specify the chemical potentials of the two components as

$$\begin{aligned}\mu^{A(\text{film})} &\cong \mu_0^A - \sigma_0 V_0^A + \Delta\mu^A \\ \mu^{B(\text{film})} &\cong \mu_0^B - \sigma_0 V_0^B.\end{aligned}\quad (3)$$

The approximation, following Kamb (1959), omits second-order terms in stress multiplied by elastic strain. Component A is supersaturated by amount $\Delta\mu^A = RT\ln(\Omega_A)$ relative to an equilibrating value at the far-field normal stress, σ_0 . Component B is just saturated at this value, or $\Omega_B = 1$. V_0^A and V_0^B are the specific volumes of the minerals in an unstressed state. On the other hand, the equilibrating chemical potentials of the two components at the A/B interface are

$$\begin{aligned}\mu^{A(\text{eq})} &\cong \mu_0^A - \sigma_n V_0^A \\ \mu^{B(\text{eq})} &\cong \mu_0^B - \sigma_n V_0^B.\end{aligned}\quad (4)$$

We suppose that the rates of precipitation or dissolution are given by

$$\begin{aligned}da/dt &= k_A[\mu^{A(\text{film})} - \mu^{A(\text{eq})}] \\ da'/dt &= k_B[\mu^{B(\text{film})} - \mu^{B(\text{eq})}].\end{aligned}\quad (5)$$

where k_A and k_B are kinetic rate constants and da'/dt is the rate of change in the radial position of the interface due to the growth of host mineral B. Because the only mechanism of accommodation in this model is replacement,

$$da/dt + da'/dt = 0 \quad (6)$$

As suggested in the Introduction, elastic accommodation to a suddenly applied supersaturation leads to a rapid transient in the value of the normal stress to a condition in which it may be ignored. From Eqns. 3 to 6,

$$da/dt = k_A[\Delta\mu^A - (\sigma_0 - \sigma_n)V_0^A] = k_B(\sigma_0 - \sigma_n)V_0^B. \quad (7)$$

The second relation in Eqn. 7 fixes the normal stress at the A/B contact as a function of the supersaturation

$$\sigma_0 - \sigma_n = k_A\Delta\mu^A/(k_A V_0^A + k_B V_0^B). \quad (8)$$

Because $\sigma_n < \sigma_0$, or more compressive, this quantity is positive. If the supersaturation is constant during the deposition of mineral A in the MZ, the interfacial normal stress must be constant as well.

The difference $\sigma_0 - \sigma_n$ will be greatest if the kinetic constant of the host mineral is small relative to that of the precipitating mineral, or $k_A/k_B \gg 1$, because the specific volumes for most minerals are, relatively speaking, not greatly different. The maximum stress difference is therefore

$$(\sigma_0 - \sigma_n)_{\text{max}} = \Delta\mu^A/V_0^A. \quad (9)$$

On the other hand, if $k_A/k_B \ll 1$, the stress difference 8 will be small; the growth rate will be nearly equal to that in a fluid.

If the stress difference (Eqn. 8) is large, other mechanisms of accommodation may become operative or dominant. These include cracking or flow of the host. Not only the stress difference (Eqn. 8) but the normal stress, σ_R , determines the condition for the inception of these mechanisms. It is rather the difference $\sigma_R - \sigma_n$ that is pertinent. The microscopic stress in the mineral A is the uniform hydrostatic stress

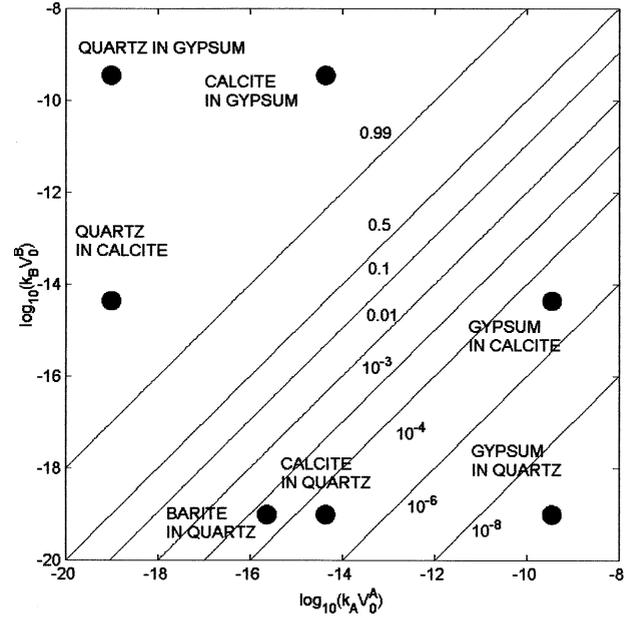


Fig. 3. Contour plot of $(da/dt)_{\text{solid}}/(da/dt)_{\text{unconstrained}}$ in replacement of mineral B by mineral A for the range of products of the values of k and V_0 given in Table 2. Where this is small, the bulk of the free energy associated with the supersaturation of mineral A goes into the dissolution of the host mineral B; where it is nearly unity, the growth of mineral A is practically unconstrained.

$$\sigma_{rr}^{(A)} = \sigma_{\theta\theta}^{(A)} = \sigma_{\alpha\alpha}^{(A)} = \sigma_n. \quad (10a)$$

The stress in the surrounding shell of mineral B is

$$\begin{aligned}\sigma_{rr}^{(B)} - \sigma_0 &= (1-f)^{-1} \{ [(\sigma_0 - \sigma_R) - (\sigma_0 - \sigma_n)](a/r)^3 \\ &\quad + f(\sigma_0 - \sigma_n) - (\sigma_0 - \sigma_R) \} \\ \sigma_{\theta\theta}^{(B)} - \sigma_0 &= (1-f)^{-1} \{ -1/2 [(\sigma_0 - \sigma_R) - (\sigma_0 - \sigma_n)](a/r)^3 \\ &\quad + f(\sigma_0 - \sigma_n) - (\sigma_0 - \sigma_R) \}.\end{aligned}\quad (10b)$$

where $f = (a/b)^3$ is the volume fraction of mineral A.

Figure 3 is a contour plot in $k_A V_0^A$, $k_B V_0^B$ space of the ratio of the radial rate of growth of mineral A, da/dt , when embedded in a mineral B to the unconstrained rate. The former is, from Eqns. 7 and 8:

$$da/dt = k_A RT \ln(\Omega_A) [k_B V_0^B / (k_A V_0^A + k_B V_0^B)] \quad (11)$$

The variables $k_A V_0^A$ and $k_B V_0^B$ are dominated by the variation in the kinetic constants rather than the specific volumes (Table 2). When they are equal, the constraint reduces the growth rate to one half the unconstrained value. If the $k_B V_0^B$ is an order of magnitude greater than $k_A V_0^A$, the mechanical constraint of the solid is negligible. For example, if the host mineral is gypsum, with a large kinetic constant, and the new mineral is either calcite or quartz, with much smaller kinetic constants, the constraint is negligible. If, on the other hand, gypsum were to grow in either quartz (sandstone) or calcite (limestone), the constraint would be strong, the growth rate of gypsum would be reduced by many orders of magnitude from its unconstrained value, and the excess normal stress at

Table 2. Molar volumes and experimental low-temperature growth rate constants for minerals.

Mineral	V_0 (cm^3/mol)	ρ (g/cm^3)	Molecular weight	k (s/cm) ^a at $\approx 100^\circ\text{C}$	c_0 (mol/cm ³) ^b at $\approx 100^\circ\text{C}$
Gypsum	74.2	2.32	172	4.76×10^{-12c}	5×10^{-6}
Anhydrite	45.7	2.99	136	2.55×10^{-14c}	
Celestite	46.3	3.96	183	1.30×10^{-16d}	9×10^{-7}
Calcite	36.8	2.72	100	1.19×10^{-16e}	6×10^{-8}
Barite	51.9	4.5	233	4.50×10^{-18d}	1×10^{-8}
Quartz	22.7	2.65	60	4.34×10^{-21f}	1×10^{-7}
Gibbsite	32.5	2.40	78	1.69×10^{-21g}	
Analcite	97.0	2.27	270	8.63×10^{-22h}	
K feldspar	108.3	2.57	278	3.87×10^{-22i}	3×10^{-10}
Kaolinite	97.4	2.65	258	1.1×10^{-22j}	

^a Rate constant consistent with the rate law used in the text, da/dt (cm/s) = k (s/cm) $\Delta\mu$ ((cm/s)²). The values of k are calculated with $k = k^*/\rho_m R/T$, where k^* (=the reported value) is in mol/cm²s; ρ_m is in mol/cm³ (molar density = $1/V_{\text{molar}}$); T is temperature in kelvin; R' is R in (ergs/mole \times deg)/molar weight (g/mole) = R' (ergs/(g of min) \times deg).

^b Sample concentrations used in the Appendix.

^c Liu and Nancollas (1971).

^d Dove and Szank (1995).

^e Shiraki and Brantley (1995).

^f Rimstidt and Barnes (1980).

^g Nagy and Lasaga (1992).

^h Murphy et al. (1996).

ⁱ Murphy and Helgeson (1989).

^j Nagy et al. (1991). Oelkers et al. (1994).

the contact, $\sigma_0 - \sigma_{rr}(a)$, would take its maximum value, $\Delta\mu^A/V_0^A$.

The stress difference $\sigma_0 - \sigma_n$, Eqn. 8, is contoured in $k_A V_0^A$, $k_B V_0^B$ space for a saturation state $\Omega_A = 2$ and a temperature $T = 373$ K in Figure 4. For convenience, V_0^A is taken as $50 \text{ cm}^3/\text{mole}$. For the combination quartz (chert) growing in calcite (limestone), the mechanical constraint is negligible, and alternative mechanisms of replacement, such as host flow or fracture, would not be expected. The growth of euhedral quartz crystals in limestone or of chert replacing limestone is commonly observed. If quartz veins form in limestone, the role of nonhydrostatic macroscopic stress in fracturing the rock is likely, and the veins might be expected not to show a fibrous habit.⁴

On the other hand, mechanisms other than replacement are likely for the growth of calcite in quartz (sandstone, shale).

4.2. Macroscopic Quantities in the MZ and Embedding Medium

Because of the approximation of uniformity in size and spacing of crystals of mineral A, the normal stress acting on the external surface of the RVE, σ_R , is also the macroscopic radial normal stress acting on the surface of the MZ. Its value is determined as follows. Consider additional stress, strain, and

⁴ We take the point of view, first proposed by Taber (1918), that at least some fibrous veins are formed by supersaturation-driven vein widening and propagation rather than by deposition into open space created a priori by fracture under far-field stress and internal fluid pressure. "Open space" includes the small increments postulated to occur for crack-seal veins.

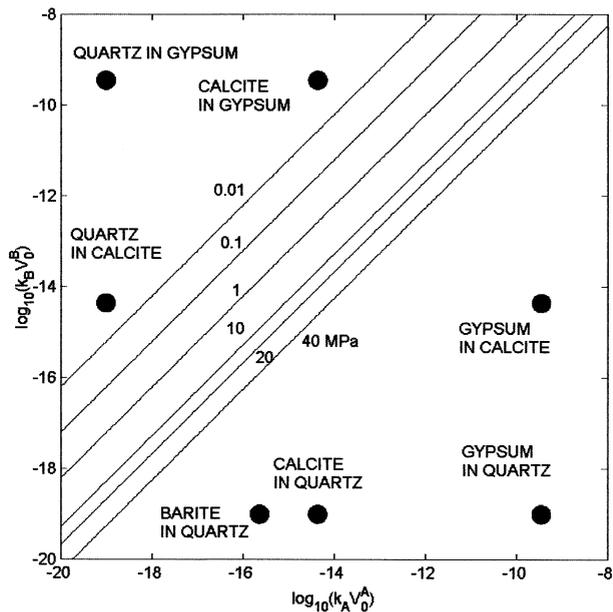


Fig. 4. Contours of interfacial normal stress generated by growth driven by a supersaturation of only $\Omega_A = 2$, at $T = 100^\circ\text{C}$, by use of $V_0^A = 50 \text{ cm}^3/\text{mole}$, for several mineral pairs. Note the asymmetry inherent in Eqn. 8: quartz replacing calcite generates a negligible stress, whereas calcite replacing quartz generates ~ 100 MPa. Contours of 30 and >40 MPa are not labeled.

displacement relative to a reference state corresponding to the far-field hydrostatic state, σ_0 , rather than to a state of zero stress. Although σ_R and σ_n are total stresses, their differences with σ_0 are the quantities of interest.

In the medium surrounding the MZ,

$$\sigma'_{\xi\xi} = \sigma_{\xi\xi} - \sigma_0 = (\sigma_R - \sigma_0) (R/\xi)^3, \quad (12)$$

where ξ is the radial distance from the center of the MZ. The same symbols used for the angular coordinates in the RVE, θ and α , are used in the MZ and embedding medium. The macroscopic stress in the MZ is the hydrostatic stress σ_R . Thus, the equivalent additional displacement associated with mineral growth in the MZ is

$$u'_\xi = [(1 + \nu)/2E] (\sigma_0 - \sigma_R) R (R/\xi)^2 \quad \xi \geq R \quad (13a)$$

$$u'_\xi = -[(1 - 2\nu)/E] (\sigma_0 - \sigma_R) \xi \quad \xi \leq R. \quad (13b)$$

Notice that these do not match at the boundary of the MZ, $\xi = R$. The reason for this is that the growth of mineral A results in a bulk inelastic swelling of the MZ. At the microscopic scale, the same dilation can be seen in the expansion of the RVE, measured at its exterior boundary, $r = b$. At the macroscopic scale, it results in an increase in compressive stress within the MZ. Indeed, the additional displacement within the zone, Eqn. 12b, represents a homogeneous bulk contraction, which is due to the restraint by the embedding medium.

Continuity of radial displacement at the MZ/embedding medium boundary is satisfied in a relation that incorporates an inelastic transformation strain (Eshelby, 1957). Here, the isotropic expansion is

$$\varepsilon_{\xi\xi}^{T*} = \varepsilon_{\theta\theta}^{T*} = \varepsilon_{\alpha\alpha}^{T*}. \quad (14)$$

The expansion of an RVE, equivalent to that of the MZ, is obtained by computing the displacement from the reference state at the exterior of the shell, $r = b$,

$$u_r'(b) = (1/E)(1-f)^{-1}\{(3/2)f(1-\nu)(\sigma_0 - \sigma_n) - [(1-2\nu) + (f/2)(1+\nu)](\sigma_0 - \sigma_R)\}b \quad (15)$$

where $f = (a/b)^3$ is the volume fraction of mineral A in the RVE, or MZ. The displacement at the exterior of the MZ, at $\xi = R$, is obtained by replacing b with R , and r by ξ , in Eqn. 15. Since the macroscopic strains in the MZ are homogeneous and isotropic, the additional displacement may be converted to a macroscopic strain by dividing by the radius. In particular, the total strain is

$$u_r'(b)/b = u_\xi'(R)/R \quad (16a)$$

Thus, the matching of the total macroscopic displacement in the MZ and that in the embedding medium requires

$$\begin{aligned} u_\xi'(R)/R &= -[(1-2\nu)/E](\sigma_0 - \sigma_R) + \varepsilon_{rr}^{T*} \\ &= [(1+\nu)/2E](\sigma_0 - \sigma_R) \end{aligned} \quad (16b)$$

From Eqns. 13, 15, and 16,

$$\sigma_0 - \sigma_R = f(\sigma_0 - \sigma_n) \quad (17a)$$

$$\varepsilon_{\xi\xi}^{T*} = [3(1-\nu)/2E](\sigma_0 - \sigma_R) = [3(1-\nu)/2E]f(\sigma_0 - \sigma_n). \quad (17b)$$

The excess normal stress acting on the MZ increases linearly with the volume fraction of new mineral growth, but the total stress cannot exceed the value σ_n . The inelastic swelling of the MZ is also proportional to f . If the MZ were cut out of the rock in which it is embedded, and the stresses relaxed down to the background value, σ_0 , its volume dilation would be $3\varepsilon_{\xi\xi}^{T*}$. Although such an imaginary operation would indeed relax the macroscopic stress in the MZ from σ_R to σ_0 , an additional state of self-stress would remain due to the inhomogeneous microscopic growth-related stress state in the RVE. The self-stress is locked in and remains even though the traction on the body is removed.

For the simplifying approximations of this model, the macroscopic stress in the MZ is the uniform hydrostatic stress σ_R . The increment associated with mineral growth is $\sigma_R - \sigma_0$. On the other hand, the microscopic stress increment at which growth of mineral A and dissolution of mineral B take place is $\sigma_n - \sigma_0$, and the stress within the RVE is generally inhomogeneous. The exception is as f approaches unity and σ_R approaches σ_n . The state of the MZ is alternatively described by the isotropic transformation strain, with radial component $\varepsilon_{\xi\xi}^{T*}$.

The build-up of the macroscopic stress difference, $\sigma_R - \sigma_0$, has no effect on the rate of mineral growth because this is buffered by the value of the supersaturation, $\Delta\mu^A$. However, it would affect other mechanisms within the RVE, such as viscous flow of the host shell or cracking, because it leads to a reduction in nonhydrostatic stress or in the increment of tangential tension, $\sigma_{\theta\theta} - \sigma_0$. Expansion of the MZ stresses the embedding medium. It thus makes this more liable to brittle

failure or to creep. From the viewpoint of the increased compressive macroscopic stress in it, the MZ is stabilized against failure or creep, but the microscopic stress in the RVE may be such as to give rise to either of these processes locally.

5. VEIN INITIATION AND GROWTH DRIVEN BY SUPERSATURATION

Mineral growth in a solid may be accommodated by fracturing, with mineral growth in the form of veins. This mechanism may have unexpected geophysical and geochemical consequences: when two or more crystals or crystal aggregates grow simultaneously within a few diameters of each other, fractures propagating from their host/crystal interfaces may interact, forming fractures equal to or much larger than the interconcretion distance—fractures that, within fault zones, might help to trigger an earthquake. Examples of rupture produced by stress arising from mineral growth are cited in the Introduction.

Fracturing due to crack propagation driven by stresses around dispersed growing grains, or mineral growth starting in small preexisting fractures, will focus mineral precipitation in the form of veins. Following Taber (1916, 1918), we suppose that some veins wedge themselves into the host rock, with the vein opening caused by the local state of stress generated by the supersaturation-driven growth. Taber inferred this type of vein from field observations indicating that the space for mineral deposition did not preexist.

Because vein growth results in an expansion of the MZ well beyond the level resulting when the mechanism of accommodation is replacement, we treat the surrounding rock as a stiff viscous fluid. Here, viscous creep may be viewed as a simply treated proxy for any other mechanism allowing expansion of the MZ. We suppose that the veins develop in the MZ with arbitrary orientation, consistent with a hydrostatic macroscopic stress within it. We also suppose that the veins are separated far enough from each other so as not to interact mechanically. These approximations are likely to be poor in any natural situation, but the intent here is to achieve a tractable analysis. Let each vein be embedded in a spherical region of radius b , as in the previous model. We exclude any dependence of vein growth on the radius b . This would mean, in reality, that the vein, treated as a penny-shaped, cracklike body, would have a radius, c , with $c \ll b$. Hence, the vein volume, $(2/3)\pi c^2 w$, where $w \ll c$ is the maximum aperture, would be very much smaller than the volume of the RVE, $(4/3)\pi b^3$. The volume fraction would be

$$f = (c^2 w)/(2b^3) \ll 1 \quad (18)$$

Relations governing the growth and propagation of a flat, penny-shaped vein may be taken, with two modifications, from Walder and Hallet's (1985) treatment of the growth of an ice lens in a rock or soil driven by a difference in the chemical potential of pore water. The aperture to radius ratio is

$$w/c = (4/\pi)[(1-\nu)/G](\sigma_R - \sigma_n) \quad (19)$$

where G is the elastic shear modulus and ν is Poisson's ratio. The so-called mode I stress intensity factor, which describes the stress concentration at the tip of a sharp opening crack, is given by

$$K_I = (4c/\pi)^{1/2}(\sigma_R - \sigma_n) \quad (20)$$

In contrast to the stress-corrosion mechanism used in Walder and Hallet (1985), the condition for crack propagation is taken as

$$K_I = K_{IC} \quad (21)$$

where K_{IC} is the critical stress intensity factor. Because crack opening is due to the elevated normal stress maintained by vein growth, the opening rate is governed by the kinetic relation

$$dw/dt = 2k_A[\Delta\mu^A - (\sigma_0 - \sigma_n)V_0^A] \quad (22)$$

where the factor of two is present because the vein grows at both external surfaces. Because the supersaturation is specified relative to the reference far-field stress, σ_0 , the macroscopic homogeneous normal stress in the MZ, σ_R , does not appear in this relation.

The growth of an isolated crack in a medium subjected to the far field stress, σ_0 , would be completely described by the four relations 19 to 22. An additional relationship for the accommodation of expansion of the MZ by viscous creep of the surrounding rock, obtained from the solution for the expansion of a spherical cavity in a viscous fluid, is

$$d(c^2w)/dt = (9b^3/8\eta)(\sigma_0 - \sigma_R) \quad (23)$$

where η is the viscosity of the surrounding rock.

Application of Eqns. 19 to 22 raises certain questions. For plausible values of the shear modulus and critical stress intensity factor, the aperture-to-radius ratio

$$w/c = (4/\pi c)^{1/2}[(1 - \nu)K_{IC}/G] \quad (24)$$

is very much smaller than that observed, by a factor of at least 10^{-2} . Second, observations of natural vein arrays commonly give an aspect ratio that is independent of the absolute size of the vein. These seeming disagreements with observation can be overcome by introducing the following simpler relations. Let the aspect ratio be independent of radius

$$w/c = \delta \quad (25)$$

and suppose that crack growth requires a constant stress difference

$$\sigma_R - \sigma_n = S \quad (26)$$

Some support for these relations comes from the following argument. In treatment of cracks in wholly brittle materials, such as glass, for which the relations 19 to 21 apply, the work done over the periphery of the crack is proportional to the perimeter, $2\pi c$. The work per unit perimeter is constant because the scale of the damage zone is controlled by atomic dimensions and the crack is truly sharp. On the other hand, the zone in which subsidiary cracking occurs at the tips of mode I fractures and veins in rock has a dimension much larger than the grain size. The fracture propagates not as a sharp crack but by selective coalescence of discrete fractures at its tip. Further, the size of the process zone in which such cracking and coalescence takes place scales with the size of the fracture as a whole. If this is so, the work done to advance the fracture or vein is proportional to the periphery times the area of the

damage zone, or to the cube of the crack radius. The work done by a constant stress over the area of the crack through an increment in aperture proportional to the crack radius is also proportional to the cube of the crack radius.

The same argument can be made for the previous model of cracking. The normal traction on the vein surface when the condition for propagation is met is $\sigma_R - \sigma_n \sim 1/\sqrt{c}$. Thus, the work done in an increment of opening over the surfaces of the vein is $dW \sim c^2(\sigma_R - \sigma_n)dw$. But, by Eqn. 28, $dw \sim dc/\sqrt{c}$. Then combining, $dW \sim cdc$. As in the previous case, this has the same proportionality as the energy consumed in the process zone during the increment of crack growth.

The rate of vein formation is then determined by the four relations, Eqns. 22, 23, 25, and 26. Writing $\sigma_0 - \sigma_R = (\sigma_0 - \sigma_n) - (\sigma_R - \sigma_n)$, and noting that the second term must equal the stress required for vein propagation,

$$\sigma_0 - \sigma_n = (1 + M)^{-1}\{S + M[RT\ln(\Omega)/V_0^A]\}, \quad (27a)$$

where

$$M = (16/3)\eta k_A V_0^A (c^2/b^3). \quad (27b)$$

Substituting Eqn. 27a into the kinetic relation, Eqn. 22, the rate of vein growth is

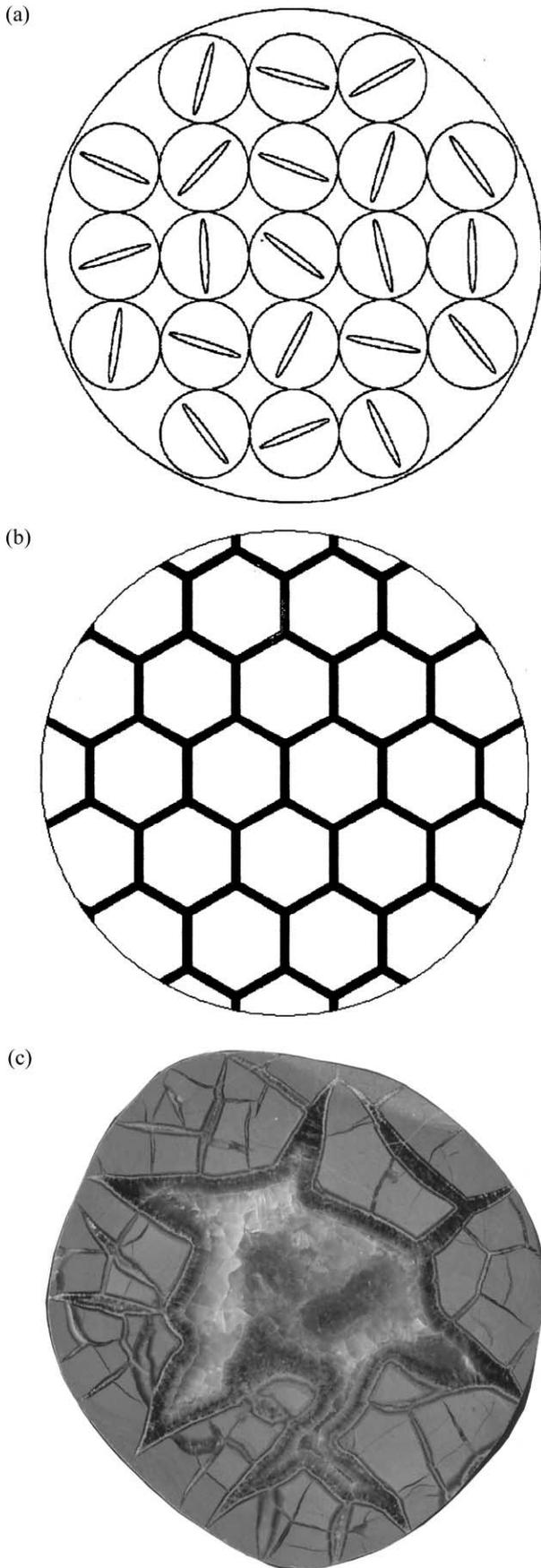
$$dw/dt = (1 + M)^{-1}2k_A[RT\ln(\Omega) - SV_0^A]. \quad (28)$$

That is, the supersaturation must be at least sufficient to establish the normal stress required for vein propagation at fixed aspect ratio at a vanishingly small rate of opening, the value obtained by setting $dw/dt = 0$. For greater supersaturation, a finite rate of vein growth occurs. From the form of M , Eqn. 27b, c may be taken to vanish when vein growth begins, and, thus, initially, $M = 0$. For $S = 5$ MPa, $T = 373$ K, $V_0^A = (60/2.65)$ cm³/mole, for quartz, the marginal condition for growth

$$[\ln(\Omega_A)]_{\text{marginal}} = SV_0^A/RT \quad (29)$$

yields $[\ln(\Omega_A)]_{\text{marginal}} = 0.037$, or $[\Omega_A]_{\text{marginal}} = 1.037$, a very low supersaturation. For quartz at 100°C, $k_A = 4.34 \times 10^{-21}$ s/cm, and the unconstrained growth rate for $\ln(\Omega) = 0.037$ is only 0.005 cm/ka.

The factor M might be estimated with a variety of applications in mind, since no absolute scale is imposed on the radii of the MZ or the RVE. For example, septarian concretions (Fig. 5c) ranging in size from 10 cm to several meters contain internal arrays of calcite veins. The concretions may have formed in soft sediment at a modest to moderate depth below the sediment–water interface. Application of the present model to the growth of the internal veins in these concretions does not have a firm observational basis. The veins are often blocky rather than fibred, and they appear rather to have crystallized into opening cracks. On the other hand, how such crack opening arises is not clear, so a mechanism of supersaturation-driven crack growth might still be entertained. In the concretions, most of the veins have interacted and coalesced to give a regular pattern not unlike the analog, in a sphere, of mud cracks. At any rate, we might suppose an early array of veins in a meter-scale concretion having radii of 5 to 10 cm and separated by distances of a few times this value, so $c \approx 5$ cm and



$b \approx 10$ cm. For these values, mechanical interaction would be appreciable, as evidenced by the regular vein structure developed. The “viscosity” of the sediment might be left open for speculation. By use of $k_A = 1.19 \times 10^{-16}$ s/cm for calcite and by use of $\delta = 0.1$ to reflect the relatively small aspect ratios of veins in this setting,

$$M \approx 3 \times 10^{-18} \eta (\text{Pa-s})$$

If the term M is to be significant in magnitude, the effective viscosity of the sediment would have to be $\eta \approx 10^{18}$ Pa-s. This would lead to a reduction in growth rate to about a quarter of that in the mechanically unconstrained value. In application to an array of quartz veins growing in a MZ within moderately high temperature crystalline rock, we might take $\eta \approx 10^{21}$ Pa-s, $\delta = 0.02$, $c \approx 0.5$ m, and $b \approx 1$ m. This gives $M \approx 1$, a modest value that would reduce the growth in vein thickness to a third of its unconstrained rate. These examples, if typical, indicate that much of the “locally available” supersaturation goes into mechanical work rather than growth kinetics.

5.1. Choice between Replacement and Vein Growth as Accommodation Mechanisms

Mineral growth in solid rock may occur by replacement, in which case the accommodation by host deformation is negligible, or by vein growth, in which case a mechanism to accommodate the volume increase is necessary. Here, we adopted viscous deformation of the surrounding rock. A question arising is under what circumstances will one or the other mechanism dominate? Because the increase in normal stress at a vein surface will tend to cause dissolution of the host, both processes may be quantitatively significant under special conditions. An estimate for the transition condition is obtained by equating the rate of radial growth of a sphere of mineral A and the rate of growth on one side of a vein. By use of Eqns. 11a and 28, the ratio is

$$\frac{1/2(dw/dt)_{\text{vein}}}{(da/dt)_{\text{crystal}}} = \frac{\{(3b/16\eta)/[(3b/16\eta) + k_A V_0^A]\}}{(k_B V_0^B)/(k_B V_0^B + k_A V_0^A)} \tag{30}$$

← Fig. 5. (a) Schematic diagram of the central section of a MZ made up of RVEs of radius b , each of which contains a randomly oriented penny-shaped vein of radius c and thickness w . The volume fraction of veins is here $f \approx 0.06$. The size of the veins, selected for visual appearance, is too large for an assumption of no interaction. Moreover, because the veins are randomly oriented within spheres, this two-dimensional representation does not convey a quantitatively accurate picture. The stress outside the MZ is σ_0 . Stress inside the MZ is σ_R . Stress inside each RVE is σ_r . (b) Schematic diagram of the central section through an MZ containing a network of connected veins. Because the veins bound polyhedral volumes of rock in the proper three-dimensional representation, the central section will not look like this picture, but it does express the concept qualitatively. (c) Section through a septarian concretion 12 cm in diameter, showing a network of late calcite veins. The siderite concretion is embedded in a mudstone (not shown) and corresponds to the MZ of the model herein. The veins form a network, the form of which cannot be adequately represented by a single section. Most veins terminate within the concretion and have fibrous texture with a seam in the center of each vein. The MZ underwent expansion driven by the growth of the veins.

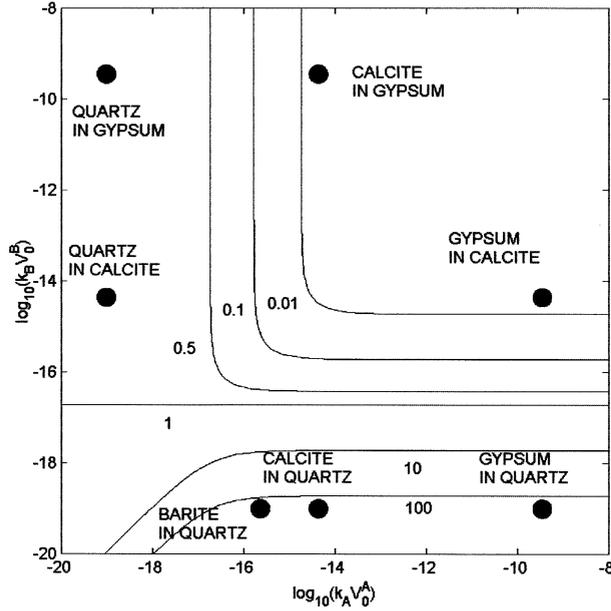


Fig. 6. Contours of $\frac{1}{2}(dw/dt)_{\text{vein}}/(da/dt)_{\text{crystal}}$ in $k_A V_0^A, k_B V_0^B$ space for a matrix rock viscosity of $\eta = 10^{17}$ Pa-s and $b = 1$ m. The points are for the mineral pairs also shown in Figure 3, with A and B indicating the growing mineral A in host mineral B.

Values of this ratio greater than unity would imply tendency to grow as veins. Values less than unity would imply tendency to grow as equant concretions replacing their surroundings. To obtain a simpler result, we adapted Eqn. 28 for a vein network by setting $c = b$, as a condition for vein intersection, and dropped the term in S because the intersecting veins have broken through the coherent rock. The ratio of rates is unity when

$$3b/16\eta = k_B V_0^B \quad (31)$$

Interestingly, this result is independent of the kinetic constant of the growing mineral, k_A , although the criterion for a ratio other than unity does depend upon it. For a given RVE scale, b , and for a given host mineral, the viscosity of the embedding medium at which Eqn. 31 is satisfied is

$$\eta^* = 3b/(16k_B V_0^B) \quad (32)$$

For values of the actual viscosity smaller than η^* , the vein mechanism will give the larger growth rate (and would then be predicted to take over). For values of the actual viscosity larger than η^* , replacement would give the larger growth rate, and is thus predicted to dominate. Note that the viscosity is that of the surrounding rock, not the host mineral. For $b = 1$ m, the value for gypsum is $\eta^* = 5.3 \times 10^9$ Pa-s, for calcite, $\eta^* = 4.3 \times 10^{14}$ Pa-s, and for quartz, $\eta^* = 1.9 \times 10^{19}$ Pa-s.

Figure 6 shows contours of $\frac{1}{2}(dw/dt)_{\text{vein}}/(da/dt)_{\text{replacement}}$ in $k_A V_0^A, k_B V_0^B$ space, by use of $\eta^* = 10^{17}$ Pa-s and $b = 1$ m. Points for the new mineral/host mineral pairs are also given. If the surrounding medium of the MZ has this relatively small viscosity, the mineral pairs barite in quartz (sandstone, shale, or mudstone), calcite in quartz, and gypsum in quartz ought to form veins because the ratio in Eqn. 30 favors vein growth by

a factor of more than 100. Both calcite growing in gypsum and gypsum growing in calcite would grow as an equant crystal or concretion, by replacement. For the pairs quartz in gypsum and quartz in calcite (limestone or marble), the mechanism ratio lies between 0.5 and 1, implying a predicted tendency to grow as single crystals or concretions.

Chert commonly does form nodules or layers in limestone, by replacement (Maliva and Siever, 1988). Considering replacement alone, these pairs, as well as calcite in gypsum, were shown (Fig. 3) to grow by replacement with little mechanical constraint, because $k_B \gg k_A$. Whether the quantitative results are reliable, what is significant in any case is that the theory above predicts the shape of the new mineral aggregate—vein-like or concretionary—in terms of pertinent physical parameters. The values of these may be obtained from experiments, or estimated from the interpretation.

5.2. Growth of an Interconnected Vein Network by MZ Expansion and Replacement

The kind of vein distribution in Figure 5a is restrictive because the volume fraction of A to B in each RVE, which is $f = c^2 w/2b^3$, has the small limiting value $f = \frac{1}{2} \delta$, when $c = b$. Typical values for natural arrays of veins might be in the range $\delta = w/c \approx 0.01$ to 0.05. The use of a sphere to contain a single vein is simply to fix the rate of dilation that must be accommodated by viscous flow of the embedding medium. The possibility that veins intersect to create a three-dimensional network bounding “polyhedra” of MZ rock (Figs. 5b,c) allows for a large dilation. The septarian nodule shown in cross section in Figure 5c illustrates such a natural vein network—and one that probably did cause the MZ to expand.

We now treat the simultaneous operation of both mechanisms for a vein network. The normal stress on the vein interfaces will now be σ_R . The stress, S , is set to zero, as above. Approximating a polyhedron of rock bounded by veins as a sphere, the rate of dilation of the MZ due to vein growth is

$$3\varepsilon_{\xi\xi}^{T*} = \frac{1}{2}(dw/dt)_{\text{expansion}} \left[\frac{4\pi b^2}{4/3\pi b^3} \right] = (1/6b)(dw/dt)_{\text{expansion}} \quad (33)$$

Half the rate of growth of vein width is used because each vein is shared by two polyhedra. The dilation rate for the MZ by viscous flow of the embedding medium is

$$3\varepsilon_{\xi\xi}^{T*} = (9/16\eta)(\sigma_0 - \sigma_R). \quad (34)$$

Equating,

$$(dw/dt)_{\text{expansion}} = (27b/8\eta)(\sigma_0 - \sigma_R). \quad (35)$$

Because the stress difference $\sigma_R - \sigma_0$ will lead to local undersaturation of the host mineral, widening of the vein can also take place by mineral growth accommodated by host dissolution. (Host dissolution may also occur in the isolated vein model of the previous section, but it was ignored there.) Since supersaturation drives both mechanisms,

$$\begin{aligned} (dw/dt)_{\text{total}} &= 2k_A[RT\ln(\Omega_A) - (\sigma_0 - \sigma_R)V_0^A] \\ &= 2k_B(\sigma_0 - \sigma_R)V_0^B + (27b/8\eta)(\sigma_0 - \sigma_R). \end{aligned} \quad (36)$$

Then

$$\sigma_0 - \sigma_R = k_A RT \ln(\Omega_A) [k_A V_0^A + k_B V_0^B + (27b/16\eta)]^{-1}. \quad (37)$$

The total rate of widening is then

$$\begin{aligned} (dw/dt)_{\text{total}} &= 2k_A RT \ln(\Omega_A) [k_B V_0^B + (27b/16\eta)] \\ &\cdot [k_A V_0^A + k_B V_0^B + (27b/16\eta)]^{-1}. \end{aligned} \quad (38)$$

The first term in brackets gives the relative contributions from host dissolution and expansion against the resistance of the embedding rock. The ratio of widening due to each is then

$$(dw/dt)_{\text{expansion}} / (dw/dt)_{\text{replacement}} = 27b / (16\eta k_B V_0^B) \quad (39)$$

The viscosity of the embedding medium at which Eqn. 39 is satisfied for a given polyhedron (or sphere) of radius, b , and for a given host mineral, is

$$\eta^* = 27b / (16k_B V_0^B) \quad (40)$$

For smaller values of η^* , the vein mechanism will dominate; for larger values, replacement will dominate. For $b = 1$ m, the value for gypsum is $\eta^* = 8.2 \times 10^{12}$ Pa-s, for calcite, $\eta^* = 3.9 \times 10^{17}$ Pa-s, and for quartz, $\eta^* = 1.0 \times 10^{22}$ Pa-s. Values for other b are readily obtained. The viscosity is *that of the embedding rock* or sediment rather than that of the host mineral. In the growth of calcite veins in the septarian nodule (Fig. 5c), driven by supersaturation, we may assign the host an “effective viscosity.” Since the groundmass of the concretion is silt cemented by fine-grained carbonate, replacement would be important only if this viscosity were greater than the above values for quartz or calcite. In replacement, the fine-grained carbonate might be dissolved and residual silt concentrated at the vein surface. Because vein spacing is only a few centimeters, the value of b would be reduced by a factor of 100 from that above, and the limiting medium viscosity would be $\eta^* = 3.9 \times 10^{15}$ Pa-s. This value might be substantially higher than the effective viscosity of mud at a modest degree of compaction, and vein expansion would be accommodated by expansion of the concretion into the host. For a fully lithified mudstone, the effective viscosity might be substantially larger than this value, and vein widening would be accommodated by replacement.

6. CRYSTAL GROWTH UNDER NONHYDROSTATIC STRESS IN A HOST UNDERGOING VISCOUS FLOW IN PURE SHEAR

Much growth and dissolution of mineral grains in sedimentary and metamorphic rocks takes place in a rock subjected to macroscopic nonhydrostatic stress. We consider here the growth of an isolated crystal of mineral A in a rock that is undergoing deformation or *syntectonic crystallization*. To simplify, let the crystal be in the form of a cylinder with an axis normal to the plane of a two-dimensional plane flow. Suppose also that its cross section is circular, and consider only the

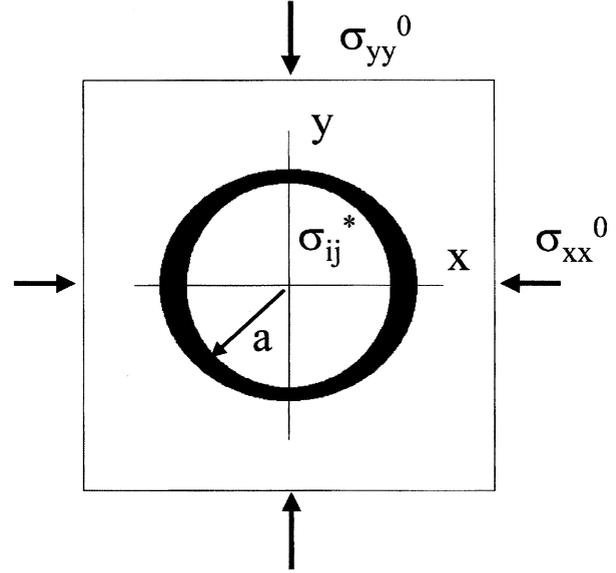


Fig. 7. Growth to predicted elliptical form of an initially circular cylindrical crystal embedded in a host subjected to a nonhydrostatic far-field stress.

incipient growth and tendency to assume an elliptical form (Fig. 7).

Crystal growth is accommodated by replacement, with both dissolution of host mineral and local viscous flow in addition to that associated with the far-field deformation. The crystal, or crystal aggregate, itself is taken to be rigid. The additional viscous flow in the host that accommodates growth is equivalent to that which would accompany a homogeneous rate of deformation of the crystal, and it is represented by a “stress-free transformation strain” (Eshelby, 1957). The far-field deformation is taken to be pure shear.

The radius of the cross section is a , and the position on its surface is denoted by the angle θ measured from the x -axis, parallel to the direction of far-field extension. The local normal rate of growth of the grain, $n_A(\theta)$ and its accommodation by host dissolution and flow, are given by the relations

$$n_A = k_A[\Delta\mu^A - (\sigma_0 - \sigma_n)V_0^A] = k_B(\sigma_0 - \sigma_n)V_0^B + v_n(\theta), \quad (41)$$

where $v_n(\theta)$ is the normal velocity of the host at the interface. The state of stress in the crystal is found to be homogeneous. The two components are σ_{xx}^* in the direction of maximum extension and σ_{yy}^* in the direction of maximum shortening. Because the deformation is pure shear, the shear stress component, σ_{xy}^* , is zero. The stress values were obtained from a solution given in Lehknskii (1963) for an elliptical cylindrical cavity and Eshelby’s (1957) method for treating an inclusion; this long derivation is omitted. The normal stress, σ_n is given by

$$\sigma_n = 1/2(\sigma_{xx}^* + \sigma_{yy}^*) + 1/2(\sigma_{xx}^* - \sigma_{yy}^*)\cos 2\theta, \quad (42)$$

where

$$\begin{aligned} \frac{1}{2}(\sigma_{xx}^* + \sigma_{yy}^*) &= \frac{1}{2}(\sigma_{xx}^o + \sigma_{yy}^o) - 2\eta[\frac{1}{2}(D_{xx}^{T*} + D_{yy}^{T*})], \\ \frac{1}{2}(\sigma_{xx}^* - \sigma_{yy}^*) &= 2[\frac{1}{2}(\sigma_{xx}^o - \sigma_{yy}^o)] - 2\eta[\frac{1}{2}(D_{xx}^{T*} - D_{yy}^{T*})], \end{aligned} \quad (43)$$

and D_{xx}^{T*} and D_{yy}^{T*} are the rates of stress-free transformation strain. Here, σ_{xx}^o and σ_{yy}^o are the components of the far-field homogeneous stress, and we set the reference mean stress $\sigma_0 = \frac{1}{2}(\sigma_{xx}^o + \sigma_{yy}^o)$. The normal displacement of the host at the crystal surface is

$$v_n(\theta) = \frac{1}{2}(D_{xx}^{T*} + D_{yy}^{T*}) + \frac{1}{2}(D_{xx}^{T*} - D_{yy}^{T*})\cos 2\theta. \quad (44)$$

Substitution of Eqns. 42 and 44 into Eqn. 41 and use of Eqn. 43 leads to explicit expressions for the stress components σ_{xx}^* and σ_{yy}^* and the components of rate of transformation strain D_{xx}^{T*} and D_{yy}^{T*} . For example

$$\begin{aligned} \frac{1}{2}(\sigma_{xx}^* + \sigma_{yy}^*) &= \frac{1}{2}(\sigma_{xx}^o + \sigma_{yy}^o) - k_A \Delta\mu^A [(a/2\eta) \\ &+ k_A V_0^A + k_B V_0^B]^{-1} \\ \frac{1}{2}(\sigma_{xx}^* - \sigma_{yy}^*) &= 2[\frac{1}{2}(\sigma_{xx}^o - \sigma_{yy}^o)](a/2\eta) [(a/2\eta) \\ &+ k_A V_0^A + k_B V_0^B]^{-1}. \end{aligned} \quad (45)$$

For a circular crystal, the mean stress in the crystal will be equal to that in the host in the absence of supersaturation, $\Delta\mu^A = 0$, but will otherwise be more compressive. The deviatoric stress component, given by the second expression in Eqn. 45, is independent of supersaturation, but this is true only for a circular crystal. The expression also shows that the factor of two stress concentration in the rigid crystal is diminished if dissolution and precipitation of the crystal and host phases occur.

It would be possible to include rate control due to diffusive transport along the crystal/host interface. This subprocess is generally evoked in models for the development of a pressure shadow around a stiff inclusion (Bayly, 1992; Finley, 1996; Fletcher, 2000) by dissolution and reprecipitation of the host phase alone. This model still describes pressure shadow growth, but the rate control is through kinetics or viscous flow. Dissolution or precipitation of either mineral may occur. A pressure shadow of the host mineral would form if it had the larger kinetic constant.

Rates of growth in the direction of maximum extension, x , and of maximum shortening, y , are obtained by specializing Eqn. 41 for angles $\theta = 0$ and $\pi/2$

$$\begin{aligned} n_A(0) &= k_A \{ \Delta\mu^A [(a/2\eta) + k_B V_0^B] \\ &+ 2[\frac{1}{2}(\sigma_{xx}^o - \sigma_{yy}^o)] V_0^A (a/2\eta) \} [(a/2\eta) \\ &+ k_A V_0^A + k_B V_0^B]^{-1} \\ n_A(\pi/2) &= k_A \{ \Delta\mu^A [(a/2\eta) + k_B V_0^B] \\ &- 2[\frac{1}{2}(\sigma_{xx}^o - \sigma_{yy}^o)] V_0^A (a/2\eta) \} [(a/2\eta) \\ &+ k_A V_0^A + k_B V_0^B]^{-1}. \end{aligned} \quad (46)$$

Only the sign of the second term in the numerator differs. As

anticipated, the crystal will grow to become elongate *in the direction of extension*. This result is in contrast with the shape of a body growing as a vein: a vein is elongate *in the direction normal to the direction of extension*. The tendency toward elongation is determined by the ratio of the two terms in the numerator. Expressed in terms of the rate of change in ellipticity, where b is taken as the length of the minor axis of an elliptical section, with current value $b = a$, and a is retained as the length of the major axis

$$\begin{aligned} [d(a/b)/dt]_{b=a} &= (1/a)[n_A(0) - n_A(\pi/2)] \\ &= 4k_A [\frac{1}{2}(\sigma_{xx}^o - \sigma_{yy}^o)] V_0^A (1/2\eta) [(a/2\eta) + k_A V_0^A + k_B V_0^B]^{-1}. \end{aligned} \quad (47)$$

For the circular inclusion, this does not depend on the supersaturation. Whether the tendency to elongate increases with ellipticity cannot be decided from this result.

The relative amounts of accommodation by flow and replacement vary around the crystal. The ratio of that by flow to that by replacement is given by

$$Z(\theta) = v_n(\theta)/k_B(\sigma_0 - \sigma_m^*)V_0^B. \quad (48)$$

In much mineral growth, the host provides a substantial fraction of the material making up the new crystal; this case is not treated here.

7. DISCUSSION

7.1. Replacement and Force of Crystallization

Our initial motivation to model the coupling of mechanical constraint and kinetics came from the question of the actual stress distribution around mineral bodies growing by constant-volume replacement. Such replacement, reported for many mineral pairs in most rock types (see references in Merino and Dewers, 1998), requires that growth and dissolution occur at the same volumetric rate, for which they would have to be coupled. Maliva and Siever (1988) were, to our knowledge, the first to propose that the coupling factor in replacement was the “force of crystallization.” Merino et al. (1993) and Nahon and Merino (1997, part 2) achieved a proper reformulation of the coupling condition in terms of an adjustment in normal stress across the interface between the replacing and replaced minerals for given initial states of saturation. That formulation, carried out in the present article also for other cases, eliminates the need for a concept of “force of crystallization” defined a priori. Indeed, the induced stress is not a matter of definition, but a function of both the affinity for crystal growth impressed on the system via some supersaturation and the mechanical and rheological properties and response (to the growth) of the host rock. The requirement for an adjustment of the normal stress makes it clear that supersaturation-driven mineral growth *in a solid*, or in any other mechanically stiff medium, leads to an induced state of stress in addition to that due to external loads. Such a state of self-stress will remain if the external loads are removed. An aim of this study was then to determine the nature of this stress distribution in several specific cases.

It is clear that mechanisms other than dissolution might act to accommodate mineral growth, as considered by Dewers and Ortoleva (1990). Like them, we consider, at the microscopic

scale, accommodation by viscous creep of the host. In addition, we have studied above a case of syntectonic crystallization, where the rock in which mineral growth is occurring undergoes bulk deformation. Turning to the brittle response of the host rock, we have studied the formation of veins by the mechanism first proposed by Taber (1916, 1918), in which it is the supersaturation of the intergranular aqueous solution with respect to a mineral that, via its growth, initiates and propagates a vein. We suppose, as did Taber, that at least some fibrous veins (with crystal fibers normal to the walls) have formed predominantly by supersaturation-driven widening and propagation of the vein, rather than by incremental passive cementation of episodic cracking events that open up new space for growth. A full quantitative development for such a process could not be carried out in Taber's day because fracture mechanics had been barely initiated. The modern development of this topic, summarized in Lawn (1993), allowed a model for the formation of ice lenses in rock and soil to be set out by Walder and Hallett (1985), and we have used this to investigate vein formation by mineral growth—again, in this picture it is the increased normal stress at the vein faces, induced by supersaturation-driven mineral growth, that drives vein widening and propagation.

7.2. Vein Textures and Vein Origins

How could the Taber (1918)-type veins, or “active” veins, be distinguished by observation from those that form in two steps, first opening, then “passive” cementation in the open space? One might expect that the crystalline texture of active-vein cement would display a definite geometric relation to the vein walls, such as fibers normal to the walls (as in the septarian concretion of Fig. 5c) because it is the fibers that, by growing, open up the vein, whereas in passive veins, there would be no, or less, reason for there to exist a geometric relation between the crystalline cement texture and the vein walls. However, it is still possible that crystals growing on an open surface become fibrous too, so that more sophisticated petrographic differences should be looked for to distinguish between the two types of veins.

For fibered veins that contain repeated, parallel planes of inclusions Ramsay (1980) proposed the crack-seal mechanism, according to which the planes of inclusions are derived from the wall rock. Tensile failure is inferred to occur at the fiber/wall rock interface, tearing off a sheet of inclusions and opening additional space for mineral growth, which then reseals the contact. Because in such veins growth takes place at both interfaces, cracking must alternate between the two. Wiltshko and Morse (2001), however, have cast doubt on this crack-seal mechanism and have proposed that these veins are instead of the kind Taber (1916, 1918) proposed—that is, caused by the growth itself. It would be desirable to deepen petrographic, experimental, and field studies of veins and vein fills in light of these evolving ideas of vein genesis.

7.3. Shape

Shape of the growing crystal or mineral aggregate is an important factor—both cause and effect—in the kinetic-rheological interaction attending crystal growth in rocks. Even in models that do not involve mechanical constraint, shape may

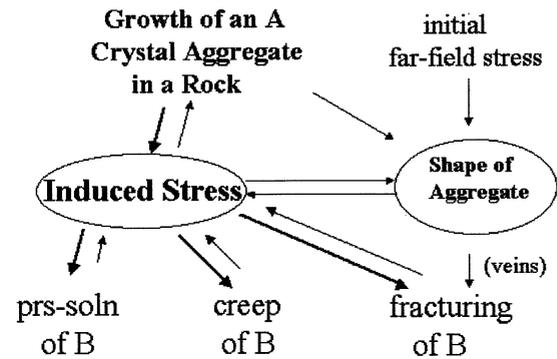


Fig. 8. Summary of possible consequences of the stress induced by crystal growth in a solid medium. A is the growing crystal or crystal aggregate; B is the matrix or host. Growth is driven by supersaturation of the pore fluid with respect to A. Transport of intergranular aqueous species (not shown) is necessary for both the growth of A and the pressure solution of B. The macroscopic far-field stress enters in determining the initial shape of the A aggregate—if the response of the host to the induced stress is creep. There exist feedbacks (double arrows) among growth kinetics, induced stress, response of the B host (pressure solution, creep, or fracturing), and aggregate shape (spherical, lenticular, rodlike, vein). In vein-shaped growth, the growth itself initiates and propagates the fracturing; in contrast, lenticular growth proceeds by replacement, creep, or both, but without fracturing.

enter into considerations of surface-to-volume effects, of surface energy, or of efficiency of diffusional transport to the growth surface. Nabarro (1940) showed how the shape of a growing crystal modifies the elastic energy added to the host solid and how it might thus affect the growth of crystals in a solid medium. We have modeled above the tendency for growth as veins vs. growth in equant bodies and also the tendency for unequant growth in a rock undergoing syntectonic crystallization. In all cases, the effect on stress distribution, elastic strain energy, and brittle failure create strong feedbacks between shape and further growth.

7.4. Transport

Of course, the supersaturation-driven crystal growth that takes place in the three models of this article necessitates transport of intergranular species. And so does the dissolution of host minerals where growth is accommodated by dissolution, as in replacement. Nonetheless, we have placed consideration of transport in the Appendix to focus in the main body of the paper on mineral reactions in a solid rock and on the kinetic consequences of mechanical constraint.

8. CONCLUSIONS

1) In the flow chart of Figure 8 we summarize possible feedbacks between growth of crystals or crystal aggregates in rocks, the local stress induced by the growth, and the possible effects of this stress—namely, pressure solution, deformation, and fracturing.

2) Growth of a spherical crystal of A in a rock generates a local stress that dies off with $(a/r)^3$, where a is the radius of the crystal and r radial distance (Eqn. 10b). Where the A growth, driven by a given supersaturation, is volumetrically accommodated by the stress-driven dissolution of host mineral, B, as

happens in replacement, the radial growth rate of A is given by Eqn. 11. (This equation also gives the pressure-solution rate of B.) The key controls on this rate are the supersaturation and the ratio of rate constants for A and B. The growth rate and the induced normal stress at the A/B interface are both greatest for $k_A/k_B \gg 1$ and lowest for $k_A/k_B \ll 1$. In other words, for $k_A/k_B \ll 1$, growth of A replacing B happens under no or negligible mechanical constraint, whereas for $k_A/k_B \gg 1$, A replaces B under a high mechanical constraint. Mineral rate constants range over at least 10 orders of magnitude (Table 2).

3) Where several spherical A crystals grow, each replacing B in its RVE within a confined MZ (Fig. 2), there is a necessary increase in the macroscopic mean stress in the MZ. This stress will be partly or wholly relieved by elastic or inelastic strain in the surrounding rock. The process is accordingly not precisely isovolumetric. The increase in mean strain stabilizes the MZ against brittle failure, but may result in brittle failure in the embedding medium, which will lead to growth in the region in which the new mineral precipitates. It might also destabilize the surrounding medium with respect to faulting.

4) Our second model applies to veins that “wedge” themselves into the host rock, with the vein opening caused by the local induced stress generated by the supersaturation-driven growth. This vein origin was first proposed by Taber (1918). Growth of a new mineral in the form of a vein-shaped crystal aggregate is accommodated at the vein walls in principle by both replacement and deformation of the host rock, and at the vein tip by fracture propagation. Replacement and deformation would contribute equally to the accommodation when the viscosity of the host is that given by Eqn. 32, $\eta^* = 3b/(16k_B V_0^B)$. Note that this equal-contribution-to-accommodation viscosity value, η^* , is proportional to b , the radius of the RVE and of the penny-shaped vein inside it. For actual viscosity values $> \eta^*$, accommodation by replacement of B host at the vein walls is predicted to dominate. Small veins are thus more likely to widen by replacing their wall host than large veins are, all else being equal. Conversely, large veins are more likely to widen by displacing their wall host rock than small veins are.

5) For the growth of an interconnected set of veins, such as in a septarian concretion (Fig. 5c), replacement and deformation contribute equally to the accommodation of vein growth for a rock viscosity given by Eqn. 40, $\eta^* = 27b/(16k_B V_0^B)$, an order of magnitude greater than for a single vein, Eqn. 32.

6) In the third model in this article, we predict quantitatively that incipient growth of an initially equant crystal, or crystal aggregate, of a strong mineral in a rock undergoing creep, or syntectonic crystallization, will be more rapid in the direction of host extension (Fig. 7). The host material may dissolve in all directions to accommodate growth of the new crystal, or it may also precipitate in the direction of extension, forming a pressure shadow. Note that this kind of growth would be oriented parallel to the direction of maximum host extension. By contrast, an “active” vein would have its walls normal to the direction of maximum host extension.

7) Study of the microscopic environment of mineral growth (or dissolution) by means of simple models of RVEs, or by means of other models, and incorporation of the results into models for geochemical water-rock transport and reaction would lead to markedly different results, especially in cases where circumstances would favor strong mechanical constraint

on growth (for instance, in cases where $k_A/k_B \gg 1$). The models will also serve to determine the circumstances in which this is the case.

Acknowledgments—R.C.F. recalls first hearing of Hal Helgeson through anecdotes, most of which seemed to imply the breaking of one or more of the laws of thermodynamics. Because of his poor eyesight, R.C.F. also especially appreciated the large data points used by Dr. Helgeson and his colleagues in their papers. He attended a conference at Airlie House, Virginia, where it was suggested that Helgeson had contributed as much to geochemistry as J. Willard Gibbs, a suggestion with which he is in total agreement. At the same conference, he witnessed a stirring swimming competition between Helgeson and Dr. Hugh P. Taylor, Jr. The author does not recall who won, but both this and the previous incident were conducted in an atmosphere in which the partial pressure of scotch was anomalously high. This author feels that the activity of Helgeson, a_H , was as influential as the intrinsic interest of the subject in keeping him engaged in his geochemical sideline. Both authors wish Hal a happy 70th birthday, and they thank Dugald Carmichael of Queen’s University, Andrew Fowler of the University of Ottawa, J.-P. Gratiot of the University of Grenoble, and associate editor Eric Oelkers of the University of Toulouse for incisive reviews and detailed and helpful comments.

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APPENDIX

Local Diffusional Transport

To limit the complexity of the models, diffusional transport of chemical components is not treated in the models. An aspect of diffusional transport may be treated in the replacement model, and it seems instructive to do so. To insure no variation in rates of mineral growth or dissolution within the MZ, we must suppose that transport of mineral components to or from its exterior is sufficiently rapid to exclude the need for appreciable macroscopic gradients in their chemical potentials. That is, it is necessary to suppose that the chemical potentials are uniform at the exterior surfaces of the RVEs.

However, we may still suppose that the chemical potentials of the two mineral components at the growth/dissolution surface of the RVE are determined by diffusion to and from the external surface, $r = b$. Such a situation might arise if the MZ were cut by a regular array of fractures along which diffusion, or convective transport, were rapid at the scale of the MZ. Rate-control by diffusion would only involve slow diffusion across an RVE. It might then be more realistic to suppose that the mineral A grew as an exterior rim about a shrinking core of mineral B. Such a modification could easily be implemented, but it will not be done here. Transport of the components from the surface of the RVE to the A/B interface may then be used to show how both diffusional transport and kinetics might enter a model.

Treat diffusive transport by a quasisteady approximation. Let D be the diffusivity in the bulk fluid, and let diffusivity in the rock be approximated by $D\phi/\tau$, where ϕ is an effective porosity and τ is tortuosity. Suppose that both components have the same diffusivity. The mean concentrations of components A and B are denoted c_0^A and c_0^B . Then, the radial mass flux of component A is given by the relation

$$J_r^{(A)} = -(D\phi/\tau)(c_0^A/RT)d\mu^A/dr, \quad (A1)$$

with a similar expression for $J_r^{(B)}$. The external values of the chemical potentials of components A and B are

$$\begin{aligned} \mu^{(A)}(b) &= \mu_0^{(A)} - \sigma_0 V_0^A + \Delta\mu^A \\ \mu^{(B)}(b) &= \mu_0^{(B)} - \sigma_0 V_0^B. \end{aligned} \quad (A2)$$

Because no reaction takes place within the spherical rim, the divergence of the fluxes must vanish, or, because J_r is a function of r alone,

$$dJ_r/dr + 2J_r/r = 0 \quad (A3)$$

From Eqns. A1 and A3, we find

$$\begin{aligned} \mu^{(A)} &= C_A/r + F_A \\ \mu^{(B)} &= C_B/r + F_B, \end{aligned} \quad (A4)$$

where C_A , C_B , F_A and F_B are constants to be found from Eqn. A2 and further conditions on reaction rates and associated fluxes at the interior surface, $r = a$. Therefore,

$$\begin{aligned} da/dt &= k_A \{ \mu^A(a) - [\mu_0^A - \sigma_r(a) V_0^A] \} = -V_0^A J_r^A \\ &= -k_B \{ \mu^B(a) - [\mu_0^B - \sigma_r(a) V_0^B] \} = V_0^B J_r^B, \end{aligned} \quad (A5)$$

where accommodation to growth is limited to replacement. With Eqn.

A4, Eqns. A2 and A5 suffice to determine the constants plus the radial stress $\sigma_{rr}(a)$.

By suitable arrangement and clustering of parameters, we may obtain a form for the growth rate that clearly indicates the nature of the rate control from diffusion and kinetics. The final form is

$$da/dt = \Sigma_A \Sigma_B V_0^B \Delta\mu^A / (\Sigma_A V_0^A + \Sigma_B V_0^B), \quad (\text{A6a})$$

where

$$\begin{aligned} \Sigma_A &= k_A M_A / (M_A + k_A) \\ \Sigma_B &= k_B M_B / (M_B + k_B) \end{aligned} \quad (\text{A6b})$$

and

$$\begin{aligned} M_A &= [(D_A \phi / \tau)(c_0^A / RT)] V_0^A \{b / [(a(b-a))]\} \\ M_B &= [(D_B \phi / \tau)(c_0^B / RT)] V_0^B \{b / [(a(b-a))]\}. \end{aligned} \quad (\text{A6c})$$

Quantities Σ_A , k_A , and M_A and the corresponding quantities for component B all have dimensions of time/length. M_A and M_B characterize the diffusive transport of components A and B, whereas k_A and k_B characterize the growth or dissolution kinetics. The forms (A6b) select

for the subprocess that is rate-controlling for each mineral: the diffusional transport of its component or its interfacial kinetics. Σ_A assumes, or is approximated by, the value of the smaller quantity, excluding the special case when both M_A and k_A are comparable in magnitude. The rate-controlling subprocess could be different for the two minerals, although this might be an uncommon situation. As the shell thickness, $b - a$, decreases, a point will be reached when diffusive transport is no longer rate controlling.

In the form (A6a), a comparable selection is made for the rate-controlling process. In the present case, in which both kinetics and transport are considered, both must be "fast" for the host phase to achieve a situation with minimal mechanical constraint. The growth rate of mineral A may then be limited either by its kinetics or by diffusive transport to its surface. Evidently, if transport is excluded as a rate-controlling process, the result obtained may be unrealistic. A crude way of bypassing this problem is to think of $\Delta\mu^A$ as the supersaturation that may be maintained at the growth surface itself.

The radial normal stress at the crystal surface is

$$\sigma_0 - \sigma_{rr}(a) = \Sigma_A \Delta\mu^A / (\Sigma_A V_0^A + \Sigma_B V_0^B). \quad (\text{A7})$$

This is maximal when $\Sigma_A \gg \Sigma_B$.