Metasomatism as a Self-controlled Process

By

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Abstract: Wall-rock alteration by a reaction mineral (Korzhinskii, 1970) has been reinvestigated considering the effect of a varying porosity on the process itself. This is because a limit value of porosity at the replacement front has made it possible to analyze the alteration. In diffusion metasomatism, the porosity decreases toward a fissure due to the "salting out" effect. Strongly dependent upon the porosity, the effective diffusion coefficient decreases toward the fissure. Consequently, a steady state of "constant" concentrations of both replacing and replaced components ($\partial c_i / \partial x = 0$) is almost achieved near the replacement front. The "salting-out" also occurs even in combined diffusion and reverse-infiltration metasomatism. This process may occur in nature. In both cases, the alteration by a reaction mineral causes a porosity decrease in the replaced zone, which in turn hinders the process. In other words, this type of metasomatism is a "self-controlled" process.

The formation process of vein-type wollastonite skarn around fissures in limestone, a typical wall-rock alteration, as observed at the Fujigatani mine, SW Japan, has been numerically analyzed based on the thermodynamic assumptions. These consist mainly of constant volume and local equilibrium assumptions, essential in analyzing metasomatic processes. As a result, I have concluded that the porosity is reduced to almost zero near the fissure even when the porosity at a replacement front is extremely large. Hence, the composition of a pore solution of wollastonite zone becomes almost the same as that of the replacement front. This means that the front cannot progress. It should be emphasized that the porosity change acts as an obstacle to the development of the skarn. Therefore, to analyze naturally-occurring metasomatism, we must reexamine the assumptions used since Korzhinskii (1970).

The effect of changing porosity on the metasomatism in a solid solution mineral has also been evaluated. I have proved that only a small difference in the intrinsic diffusion coefficients of both replacing and replaced components brings about a large variation of porosity, resulting in quite different concentration profiles compared to those calculated under the constant porosity assumption.

CONTENTS

SYMBOLS

c_i —concentration of component i in a pore solution, (moles per unit volume)

c_i' —characteristic concentration of i

C_i —dimensionless concentration of i in a pore solution

D_i —effective diffusion coefficient of i in porous media, (length²/time, for example, cm²/sec)

$\bar{D}_i$ —intrinsic diffusion coefficient of i in a solution

J_i —flux of i across unit surface in unit time

K —equilibrium constant

n_m —molar density of mineral m

P —pressure

R —gas constant

s_i —concentration of i in solid phase, (moles per unit volume)

S_i —dimensionless concentration of i in solid phase

t —time

T —temperature, (°K)

v —infiltration water velocity, (length/time, for example, cm/sec)

$\bar{v}$ —volume flux, (βv)

V_m —volume of mineral m per total volume

x —space coordinate measured normal to the section

β —porosity

β_f —porosity at replacement front

$\bar{\beta}$ —initial porosity

δ_D —constrictivity for diffusion

$\Delta_t x$ —increment of variable x per unit time

ρ_i —total content of i in minerals and pore solution (moles per unit volume)

τ —tortuosity

φ_i —infiltration-effect coefficient for i

I. Introduction

Deriving transport equations for infiltration and diffusion metasomatism, Korzhinskii (1970) attempted to analyze basic features of the metasomatic columns. Hofmann (1972) examined compositional changes in solid solution minerals having various isotherms in infiltration metasomatic columns. Those of combined diffusion and infiltration metasomatism were numerically analyzed by Fletcher and Hofmann (1973). In these studies, the porosity and effective diffusion coefficient were assumed to be constant through the metasomatic processes. These assumptions have been used by many authors dealing with metasomatic processes (for example, Franz and Mao, 1976, 1979; Fisher and Lasaga, 1983; Fujimoto, 1987).

However, since the most important feature of metasomatism lies in a complete replacement of minerals, it is noted that constant porosity can rarely been retained. Moreover, porosity may change due to the "salting-out" effect, a term proposed by Franz and Mao (1976), in a zone replaced by a reaction mineral. Therefore, the assumption of constant porosity is not reasonable. On the other hand, the effective diffusion coefficient may strongly depend on the porosity (for example, Lerman, 1975; Skagius and Neretnieks, 1986; Nakashima et al., 1989). Accordingly, porosity change through the process, one of the fundamental features of metasomatism, does play an important role in metasomatism.

In contrast to analytical studies on metasomatism, those on diagenetic processes include the effect of porosity variation on material transport (for example, Berner, 1975; Lerman, 1975). In the process, the variation may be defined by initial and/or external condition(s),

but does not result from material transport. On the contrary, as stated before, metasomatic replacement alters the porosity, which in turn controls the metasomatism (Norton, 1988). Therefore, metasomatism is essentially a process of "self-organization" (Ortoleva et al., 1987a, b).

From this point of view, the author has made efforts to analyze metasomatic replacement by reaction and solid solution minerals around a fissure ("wall-rock alteration", Korzhinskii, 1970) to clarify the porosity change through the process and its effect on metasomatism itself.

The following assumptions are used to analyze the metasomatic process:

a) total volume is constant,

b) external conditions such as f_{CO_2}, temperature and pressure or pressure gradient are also unchanged,

c) total porosity is the same as effective porosity, that is, all pores are connected with each other,

d) dissolution and precipitation of minerals occur instantaneously. In other words, local equilibrium (Korzhinskii, 1970) is achieved throughout the column.

Note that the assumption of constant pressure is not adequate when the volume is kept constant. However, as was mentioned by Korzhinskii (1970), an increase in pressure on minerals in the replaced zone would be caused by an extreme decrease in porosity. In other words, the constant pressure can be assumed until the porosity decreases extremely.

Effects of concentrations of components on diffusion coefficients are neglected in all analyses. Other assumptions will be mentioned where needed.

Acknowledgements

II. Transport equation

As a fundamental equation for analyses of combined diffusion and infiltration metasomatic columns, the so-called convection-diffusion type transport equation is useful:

$$\frac{\partial \rho_i}{\partial t} = \frac{\partial}{\partial x}\left(D_i \frac{\partial c_i}{\partial x}\right) - \frac{\partial(\beta v c_i)}{\partial x} \qquad (II.1)$$

where

$$\rho_i = (1-\beta)s_i + \beta c_i . \qquad (II.2)$$

It is worth noting that the above equation is equivalent to the combined equations for diffusion and infiltration metasomatism obtained by Korzhinskii (1970) when the effective diffusion coefficient and porosity are kept constant through the column.

According to Korzhinskii, the transport equation for diffusion metasomatism derived from the Fick's law is

$$\frac{\partial \rho_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} , . \qquad (II.3)$$

while the equation for infiltration metasomatism becomes

$$\frac{\partial \rho_i}{\partial \bar{v}} = - \phi_i \frac{\partial c_i}{\partial x} , \qquad (II.4)$$

where

$$d\bar{v} = \beta v \, dt , \qquad (II.5)$$

and

$$\phi_i = v_i/v .$$ (II.6)

If it can be assumed that the retardation of solute i with respect to solvent is negligible (i.e., $\phi_i = 1$), by substituting (II.5) and (II.6) into (II.4), and combining it with (II.3), we obtain,

$$\frac{\partial \rho_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - \beta v \frac{\partial c_i}{\partial x} .$$ (II.7)

Therefore, the two equations, (II.1) and (II.7), are equal if the diffusion coefficient and porosity are constant.

Next, the dependence of v and D_i on β should be clarified. Since the volume flux of the pore solution is constant through the columns by the assumption a), the following equation should be satisfied:

$$v = \bar{v}/\beta .$$ (II.8)

According to Skagius and Neretnieks (1986), the effective diffusion coefficient can be described as

$$D_i = \frac{\beta \delta_D}{\tau^2} \bar{D}_i ,$$ (II.9)

the term $\beta \delta_D / \tau^2$ depends only on the properties of the porous materials. Nakashima et al. (1989) and Kita et al. (1989) suggest that $logD_i$ is linearly correlated to $log\beta$. Therefore,

$$D_i = \beta^n \bar{D}_i ,$$ (II.10)

where n can be roughly estimated to have a value between 1 and 1.5 (from Fig. 12 in Skagius and Neretnieks, 1986 and Fig. 6 in Kita et al., 1989).

By substituting (II.8) and (II.10) into (II.1), the final equation for analysis of porous metasomatic columns can be obtained as follows:

$$\frac{\partial \rho_i}{\partial t} = \bar{D}_i \frac{\partial}{\partial x}\left(\beta^n \frac{\partial c_i}{\partial x}\right) - \bar{v} \frac{\partial c_i}{\partial x} .$$ (II.11)

III. Metasomatic replacement by a reaction mineral

A. Concentration diagram and analytical conditions

A detailed concentration diagram is needed for quantitative analysis of metasomatic replacement. In this section, a "vein-type" wollastonite skarn of a few centimeters-wide formed around a fissure in limestone, occurring in the Fujigatani tungsten mine (Hoshino et al., 1982), SW Japan, is taken as an example to be analyzed (see App. C).

Fluid inclusion experiments on various skarns and quartz veins have shown the temperature of skarn formation in the mine to be about 400°C (Shibue,1988, Hamasaki et al., unpub. data). The formation pressure has been estimated from the sphalerite geobarometer to be about 1kb (Shimizu and Shimazaki, 1981). Log f_{CO_2} should be less than 1.16 for wollastonite to be stable under the conditions.

Figs. 1a and b show stability fields of calcite, quartz and wollastonite calculated from thermodynamic data in Bowers et al., (1984) under the conditions, T=400°C and $P_{fluid} = P_{total} = 1kb$. Assumptions used are listed in Table 1. The state of solvations of Ca^{++} and $SiO_{2(aq)}$ (hereafter expressed as Ca and Si, respectively) is not specified (Walther and Helgeson, 1980).

Table 1. Analyzed condition.

|		Reference
Temperature (°C)	400	Shibue (1988)
Pressure (kb)	1	Shimizu & Shimazaki (1981)
pore solution		Barnes & Kullerud (1961)
pH (neutral)	5.3	
density	0.7	
molar fraction of CO_2	1x10⁻³*	
concentration (10⁻³ mole/l)		Bowers et al. (1984)
C_{Ca}	1.84	
C_{Cl}	0.86	
C_{Si}	9.66	
C_{Cl}	20.66	
activity coefficient		
CO_2	6.7	Flowers & Helgeson (1983)
Ca^{++}	1*	
$SiO_{2(aq)}$	1*	
H_2O	1*	
molar density (10 mole/l)		Robie et al. (1978)
calcite	2.71	
wollastonite	2.50	
quartz	4.41	
porosity of limestone	2x10⁻³	see App. C

*: assumed tentatively
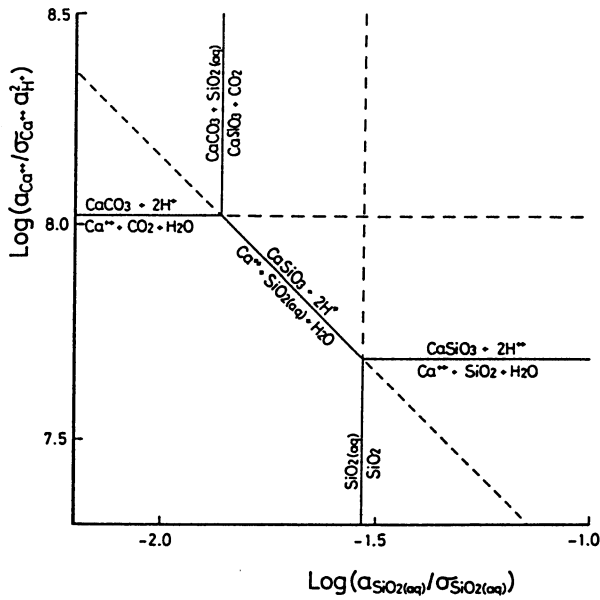
Fig. 1a Equilibrium activity diagram for the system $H_2O-SiO_2-CO_2$ at the condition listed in Table 1. For a definition of the term σ_i, see Walther and Helgeson (1980).
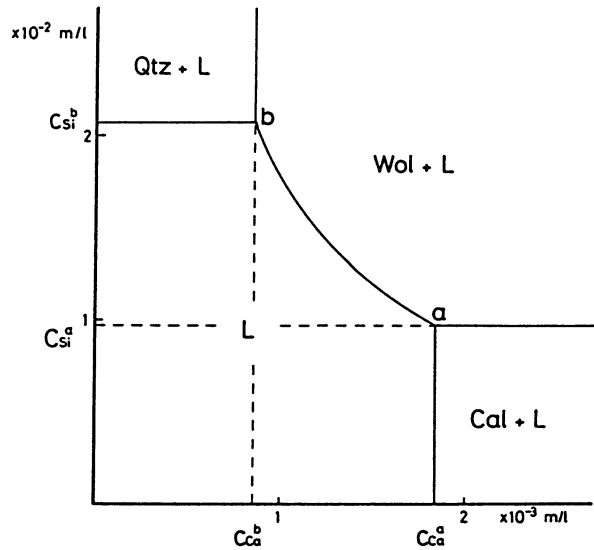

Fig. 1b Concentration diagram showing saturation curves of calcite (Cal), quartz (Qtz) and wollastonite (Wol). The points a and b correspond to the intial and boundary concentrations, respectively.

When the pressure on minerals $(P_{mineral})$ exceeds that on the pore solution (P_{fluid}), the solution may become supersaturated according to the following equation (Korzhinskii, 1970);

$$P_{mineral} - P_{fluid} = RTn_m \ln \frac{c^{ss}}{c^s}, \qquad (III.1)$$

where c^s and c^{ss} denote saturated and supersaturated concentration, respectively. Although $P_{mineral}$ may exceed P_{fluid} in geological processes, the value of the excess pressure on minerals has not been evaluated in the Fujigatani mine. Therefore, both pressures are assumed equal in the following analyses.

For simplicity, it is also assumed that the fissure solution is saturated with quartz and wollastonite (the point b in Fig. 1b) and that the composition is maintained constant by renewal. In addition, the composition of the pore solution in unaltered limestone is assumed to be slightly undersaturated with wollastonite (the point a in Fig. 1b).

Thus, the initial and boundary conditions are as follows:

$$C_{Ca} = C_{Ca}{}^a, \quad C_{Si} \simeq C_{Si}{}^a \qquad \text{at } x > 0, \ t=0$$

$$C_{Ca} = C_{Ca}{}^b, \quad C_{Si} = C_{Si}{}^b \qquad \text{at } x=0.$$

B. Diffusion replacement

1. *Porosity at the replacement front*— A limit value of the porosity at the replacement front (β_f) can be obtained directly from the finite-difference form of (III.11) as follows (see App. A):

$$\beta_f = 1 - (1-\bar{\beta}) \frac{a_a D_{Ca} + a_b D_{Si}}{a_c D_{Ca} + a_d D_{Si}}, \qquad (III.2)$$

where

$$a_a = -C_{Ca}{}^a C_{Si}{}^a,$$
$$a_b = C_{Si}{}^a (n_{Cal} - C_{Ca}{}^a),$$
$$a_c = C_{Ca}{}^a (n_{Wol} - C_{Si}{}^a),$$

and

$$a_d = C_{Si}{}^a (n_{Wol} - C_{Ca}{}^a).$$

As is clear in the above equation, the front porosity (β_f) depends on initial values, being independent of time and distance. Fig. 2 shows the relationship between the porosity and the ratio of intrinsic diffusion coefficients $(D_{Si} /$
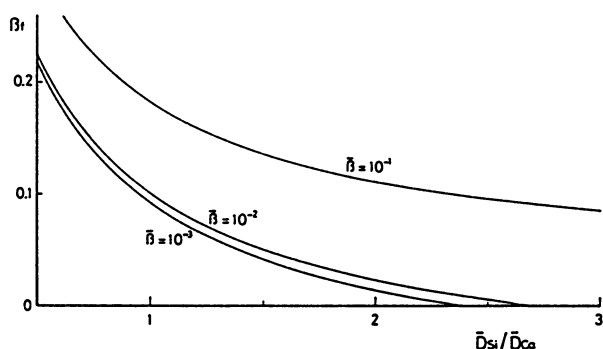
Fig. 2   Porosity at the replacement front (β_f) as a function of ratio $\bar{D}_{si}/\bar{D}_{ca}$ and initial porosity ($\bar{\beta}$).
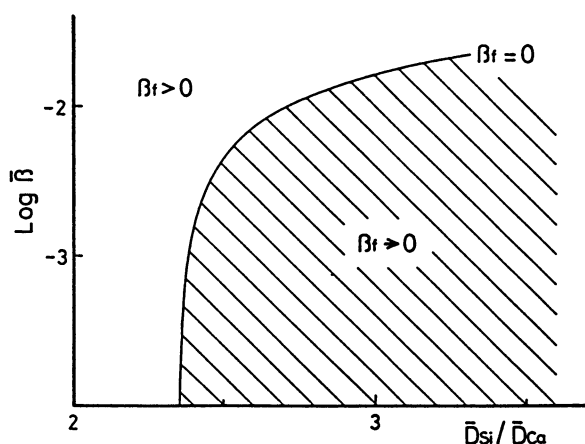

Fig. 3   Relationship between $\bar{D}_{si}/\bar{D}_{ca}$ and $\bar{\beta}$ at $\beta_f = 0$. All cavities will be filled with wollastonite before complete dissolution of calcite in the shaded field.

$\bar{D}_{ca}$) for the case of an initial porosity of 10^{-3} ~10^{-1}. Thus, the effect of the initial porosity on the front porosity is very small in geologically interesting processes ($\bar{\beta}=10^{-3}$~10^{-2}, see App. C).

A relationship between $\bar{\beta}$ and $\bar{D}_{si}/\bar{D}_{ca}$ for the case of the front porosity becoming zero is shown in Fig. 3. The assumptions b) and d) should hold on the left side of the line in the figure. However, on the right side, pore spaces in the front may be filled completely with wollastonite before perfect dissolution of calcite, with the resultant porosity becoming zero. In this case, since the effective diffusion coefficients at the front should be zero by (II.10), no material transport can occur at the front. Accordingly, the diffusion metasomatism on the right side may

be completed after dissemination of the reaction mineral in cavities in the original rock around the fissure.

2. Porosity change in replaced zone — Because of the constant compositions of solutions at both ends of the replaced zone, a "steady state" may almost be achieved through the zone. That is:

$$\frac{\partial C_{ca}}{\partial t} \simeq 0 , \qquad\qquad\qquad\text{(III.3a)}$$

and

$$\frac{\partial C_{si}}{\partial t} \simeq 0 . \qquad\qquad\qquad\text{(III.3b)}$$

Note that a *true* steady state,

$$\beta^n \frac{\partial C_{ca}}{\partial x} = \text{constant} \qquad\qquad\text{(III.4a)}$$

and

$$\beta^n \frac{\partial C_{si}}{\partial x} = \text{constant} , \qquad\qquad\text{(III.4b)}$$

cannot be achieved whenever the composition of pore solution varies through the zone. The reason is as follows: according to the assumption d), the following equation should hold through the zone:

$$C_{ca} C_{si} = K . \qquad\qquad\qquad\text{(III.5)}$$

Consequently, (III.4b) can be rewritten as:

$$\beta^n \frac{\partial C_{si}}{\partial C_{ca}} \frac{\partial C_{ca}}{\partial x} = \text{constant} . \qquad\text{(III.4b')}$$

Therefore, from (III.4a),

$$\frac{\partial C_{si}}{\partial C_{ca}} = \text{constant} . \qquad\qquad\text{(III.4b'')}$$

This means that the concentration gradients of both components should be zero in the state.

Let us consider the net mass flow of both components across surfaces at $x=\zeta$ and $x=\zeta+d\zeta$ into lamina of thickness $d\zeta$ per unit time in the wollastonite zone. According to Fick's first law, the net addition of both components to the

lamina per unit area per unit time is:

$$(J_{Ca})_{x=\tau} - (J_{Ca})_{x=\tau+d\tau} = -\bar{D}_{Ca}(\beta^n \partial c_{Ca}/\partial x)_{x=\tau}$$
$$+\bar{D}_{Ca}(\beta^n \partial c_{Ca}/\partial x)_{x=\tau+\Delta\tau}, (III.6a)$$

and

$$(J_{Si})_{x=\tau} - (J_{Si})_{x=\tau+d\tau} = -\bar{D}_{Si}(\beta^n \partial c_{Si}/\partial x)_{x=\tau}$$
$$+\bar{D}_{Si}(\beta^n \partial c_{Si}/\partial x)_{x=\tau+\Delta\tau}. (III.6b)$$

Substituting (III.5) into (III.6b) yields

$$(J_{Si})_{x=\tau} - (J_{Si})_{x=\tau+d\tau} = \bar{D}_{Si}\{(c_{Si}/c_{Ca})\beta^n \partial c_{Si}/\partial x\}_{x=\tau}$$
$$-\bar{D}_{Si}\{(c_{Si}/c_{Ca})\beta^n \partial c_{Si}/\partial x\}_{x=\tau+d\tau}. (III.6b')$$

When the "steady state" (III.3a and b) is achieved

$$(J_{Ca})_{x=\tau} - (J_{Ca})_{x=\tau+d\tau} = (n_{wol} - \bar{c}_{Ca})V \qquad (III.7a)$$

and

$$(J_{Si})_{x=\tau} - (J_{Si})_{x=\tau+d\tau} = (n_{wol} - \bar{c}_{Si})V, \qquad (III.7b)$$

where $\bar{c}_i$ and V represent the constant (i.e., time-independent) overall concentration of component i and net volume change of wollastonite by diffusion per unit time in the lamina, respectively. A physical meaning of (III.7a and b) is that increments of both components are consumed in the precipitation (or dissolution) of wollastonite and conservation of composition of a pore solution.

Using the above mass balance equations, (III. 5a and b') and (III.6a and b), the following equation can be obtained:

$$V = -k_1 k_2 \frac{(c_{Si}/c_{Ca})_{x=\tau+d\tau} - (c_{Si}/c_{Ca})_{x=\tau}}{k_1 + k_2(c_{Si}/c_{Ca})_{x=\tau+d\tau}} \left(\beta^n \frac{\partial c_{Ca}}{\partial x}\right)_{x=\tau},$$
$$(III.8)$$

where

$$k_1 = \bar{D}_{Ca}(n_{wol} - \bar{c}_{Ca})^{-1} \text{ and } k_2 = \bar{D}_{Si}(n_{wol} - \bar{c}_{Si})^{-1}.$$

Note that k_1 and k_2 are positive because the molar density of wollastonite (n_{wol}) is always larger than the saturated concentrations ($\bar{c}_{Ca}$ and $\bar{c}_{Si}$) by more than three orders of magnitude (Table 1). Since the concentration gradient of Ca is positive ($\partial c_{Ca}/\partial x > 0$) until the steady state ($\partial c_{Ca}/\partial x = 0$) is achieved through the zone, the saturation curve is convex toward the origin in

Fig. 1,

$$(c_{Si}/c_{Ca})_{x=\tau} > (c_{Si}/c_{Ca})_{x=\tau+d\tau}.$$

Hence,

$$V > 0, \qquad (III.9)$$

that is, wollastonite continues to precipitate through the zone. Because of the constant porosity at the replacement front by (III.2), as the fissure is approached, the porosity in the zone becomes small.

3. Impossibility of column development — The fundamental transport equation (II.1) can be rewritten as follows:

$$\frac{\partial \rho_i}{\partial t} = D_i \beta^n \frac{\partial^2 c_i}{\partial x^2} + \left(D_i \frac{\partial \beta^n}{\partial x} - \bar{v}\right)\frac{\partial c_i}{\partial x}. \qquad (III.10)$$

As can be supposed by the above equation, when the porosity decreases toward the fissure ($\partial \beta^n/\partial x > 0$) as discussed above, the effect of varying porosity on metasomatism is the same as that of reverse-infiltration ($\bar{v} < 0$, that is, a pore solution migrate toward the fissure) on it. Consequently, concentration profiles of the components Ca and Si may tend to be convex away from and toward the distance axis, respectively. In other words, the decrease in porosity through the zone brings about the steady state profiles ($\partial c_i/\partial x = 0$) near the replacement front.

Numerical analyses of the column (see App. A) show that even when the porosity at the front is extremely large, the porosity is reduced to almost zero at the second slab ($x = \Delta x$) after replacement of a few slabs. Hence, the composition of a pore solution in the wollastonite zone becomes almost the same as that at the front (Fig. 4). In other words, the true steady state (III.4a and b) is achieved. Note that the thickness of the slab (Δx) can be chosen arbitrarily. For example, if one choose the value as 0.1, the computed time is reduced by a factor of 100. Therefore, the above results suggest that the front cannot proceed in fact under the analyzed conditions and assumptions.
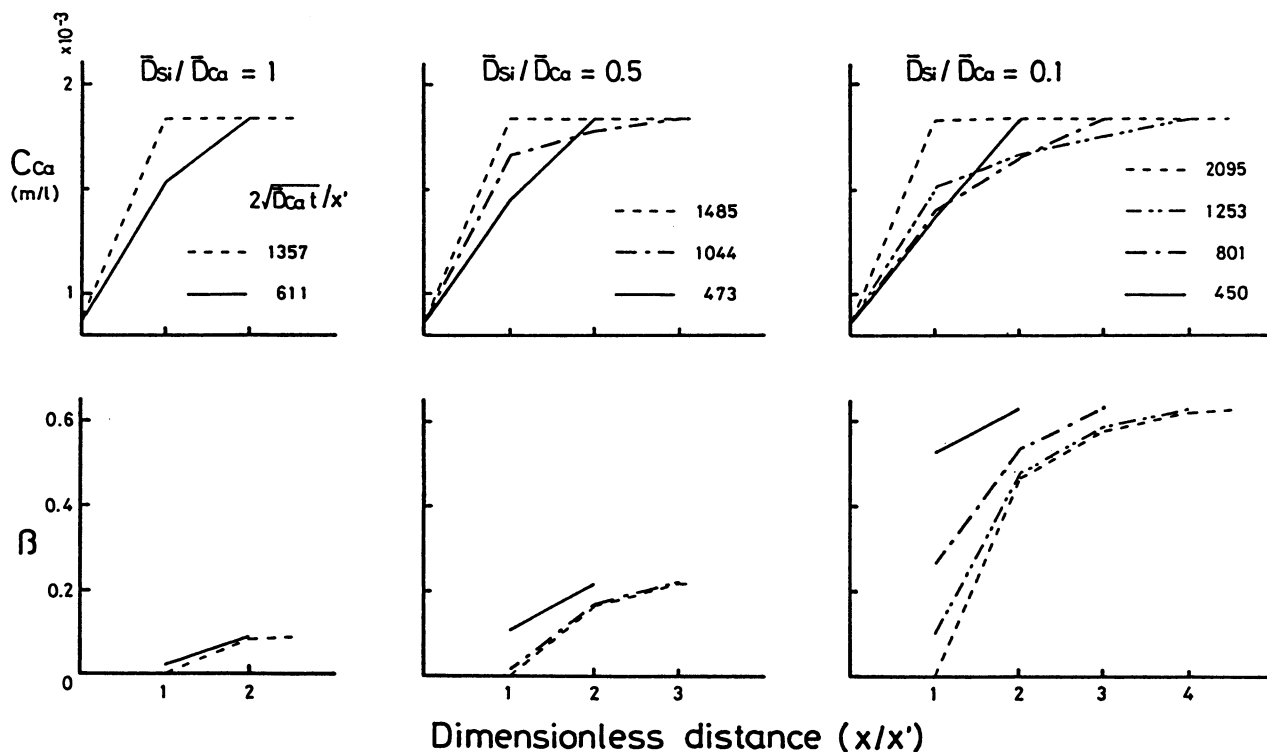
Fig. 4   Diffusion replacement of calcite by wollastonite. Profiles of concentration (c_{ca}) and porosity (β) are shown as functions of dimensionless distance (x/x', where x' represents characteristic length, for example, 1 cm). $D_i = \beta^n D_i$ ($n=1$), and $D_{si}/D_{ca}=1$, 0.5 and 0.1. Note that columns have been analyzed after replacement of the first slab (see app. A). Computed time is represented in dimensionless unit ($2(D_{ca}t)^{1/2}/x'$). Broken lines show the profiles when a diference in concentration between slabs at the replacement front and behind it becomes less than 10^{-6} m/l.

C. Infiltration effect

In the case of wall rock alterations around a fissure, pore solutions should migrate *toward* the fissure, since reduction in pressure is typical of fissure-zones (Korzhinskii, 1970). Namely, the wall rock alteration is a process of combined diffusion and *reverse*-infiltration matasomatism.

Let us consider an effect of volume flux on porosity change in the wollastonite zone. A net volume change of wollastonite in the lamina of thickness $d\zeta$ of the zone due to the volume flux (V') can be obtained by the same way as was used in the previous section. That is,

$$V' = \bar{v}k_1'k_2' \frac{(c_{si}/c_{ca})_{x=\tau}-(c_{si}/c_{ca})_{x=\tau+d\tau}}{k_1'-k_2'(c_{si}/c_{ca})_{x=\tau+d\tau}}$$

$$x \ (c_{ca})_{x=\tau} \ , \qquad\qquad (III.11)$$

where,

$$k_1' = (n_{wol}-\bar{c}_{ca})^{-1} \quad \text{and} \quad k_2' = (n_{wol}-\bar{c}_{si})^{-1}.$$

As shown in Fig. 1, the following inequality holds through the zone:

$$k_1' < k_2'(c_{si}/c_{ca})$$

Consequently, in this case ($\bar{v}<0$),

$$V' > 0 \ . \qquad\qquad (III.12)$$

This means that the reverse-infiltration also causes the porosity to decrease through the zone. As a result, a steady state may be achieved even in the combined diffusion and reverse-infiltraion metasomatism.

According to the above analysis, it may be said that the reverse-infiltration metasomatism can not play an important role in the process, but may act as an obstacle to the developement of the skarn.

IV. Application to metasomatic replacement in a solid solution mineral

Variation in composition of solid solution minerals by infiltration and combined infiltration and diffusion metasomatism was analyzed by Hofmann (1972) and Fletcher and Hofmann (1973), respectively. After a close examination of the assumptions made by them, metasomatism of a solid solution mineral and the resultant variation in porosity will be analayzed in the following sections.

A. Isotherm and concentration diagram

A S-shaped isotherm is shown in the inset of Fig. 5. The above studies have taken the solution composition at the isotherm as dimensionless *concnetration*, and put it into the transport equation directly. Note that the composition at an isotherm is described usually as *relative concentration* (C_A) such as:

$$C_A = c_A / (c_A + c_B) , \qquad (IV.1)$$

where A and B represent an endmember's component of the solid solution mineral. Since, however, the transport equation is based on mass balance,
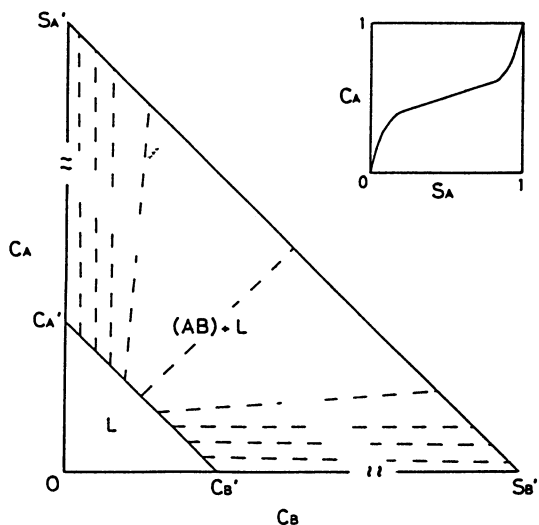
the concentration in the equation should be described as quantities per unit volume (for example, mole/cc). Accordingly, we may use the *relative concentration* in the equation only when the total concentration $(c_A + c_B)$ is constant through the column as assumed below.

For comparing analytical results with those of Fletcher and Hofmann (1973), the following assumptions with respect to the concentartion diagram (Fig. 5) are used: the saturated concentration of the components A and B are equal $(c'_A = c'_B)$, $c'_A-c'_B$ is linear, and the molar volume of both components are the same $(s'_A = s'_B)$. The ratio c'/s' is tentatively assumed to be 10^{-3}.

The initial and boundary conditions are

$$c_A = c_A', \quad c_B = 0 \qquad \text{at } x>0, \ t=0,$$
$$c_A = 0, \quad c_B = c_B' \qquad \text{at } x=0.$$

B. Possibility of porosity change

For the simple model being analyzed, the transport equation for both replacing and replaced components A and B can be written as follows:

$$\frac{\partial \rho_A}{\partial t} = D_A \frac{\partial}{\partial x}\left(\beta^n \frac{\partial c_A}{\partial x}\right) - \bar{v} \frac{\partial c_A}{\partial x} \qquad (IV.2a)$$

and

$$\frac{\partial \rho_B}{\partial t} = D_B \frac{\partial}{\partial x}\left(\beta^n \frac{\partial c_B}{\partial x}\right) - \bar{v} \frac{\partial c_B}{\partial x}$$

$$= -D_B \frac{\partial}{\partial x}\left(\beta^n \frac{\partial c_A}{\partial x}\right) + \bar{v} \frac{\partial c_A}{\partial x} . \qquad (IV.2b)$$

On the other hand, from the above assumptions,

$$\rho_A + \rho_B = s'V_{AB} + c'(1-V_{AB}). \qquad (IV.3)$$

Hence,

$$\frac{\partial V_{AB}}{\partial t} = \frac{1}{(s'-c')} \frac{\partial(\rho_A+\rho_B)}{\partial t}$$

$$= \frac{c'}{(s'-c')} (D_A-D_B) \frac{\partial}{\partial x}\left(\beta^n \frac{\partial c_A}{\partial x}\right). \qquad (IV.4)$$

Note that as far as the process proceeds, the

Fig. 5 Concentration diagram for the system H_2O-A-B containing a solid solution phase (AB). An equilibrium isotherm is shown in the inset.

following inequality should be satisfied through the column:

$$\frac{\partial}{\partial x}\left(\beta^n \frac{\partial C_A}{\partial x}\right) > 0 . \qquad (IV.5)$$

Therefore, if a ratio between the intrinsic diffusion coefficients of replaced and replacing components $(\bar{D}_B /\bar{D}_A)$ is less than (or more than) unity, the mineral may precipitate (or dissolve) throughout the column with a resultant decrease (or increase) in the porosity toward the fissure.

C. Diffusion replacement

As discussed in the preceding section, when the intrinsic diffusion coefficients differ from each other, the porosity may vary through the column. In other words, only when the coefficients are equal, can an analyzed column become the same as that of Fletcher and Hoffmann (1973). Following their work, $\bar{\beta}$ is set equal to 10^{-3} and D_i is set equal to $\beta^n D_i$ (n=1). Fig. 6 shows the concentration profiles of solid and liquid phases when the ratio $(\bar{D}_B /\bar{D}_A)$ is unity (see App. B).

If the ratio exceeds unity $(\bar{D}_B > \bar{D}_A)$, an increase of porosity results in an increase of effective diffusion coefficients, which in turn causes a concentration profile to "stub its toe" (Fig. 7). For example, when the ratio is 1.1,
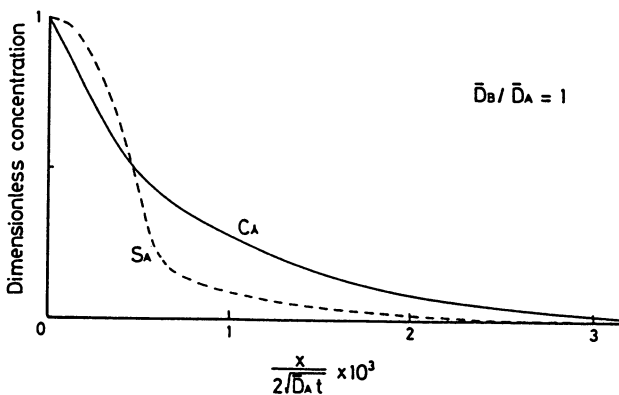

Fig. 6   Diffusion metasomatism in a solid solution mineral. $\bar{D}_B /\bar{D}_A =1$. Concentration profiles of liquid (solid line) and solid (broken line) are shown as functions of dimensionless distance $(x/2(\bar{D}_B t)^{1/2})$.
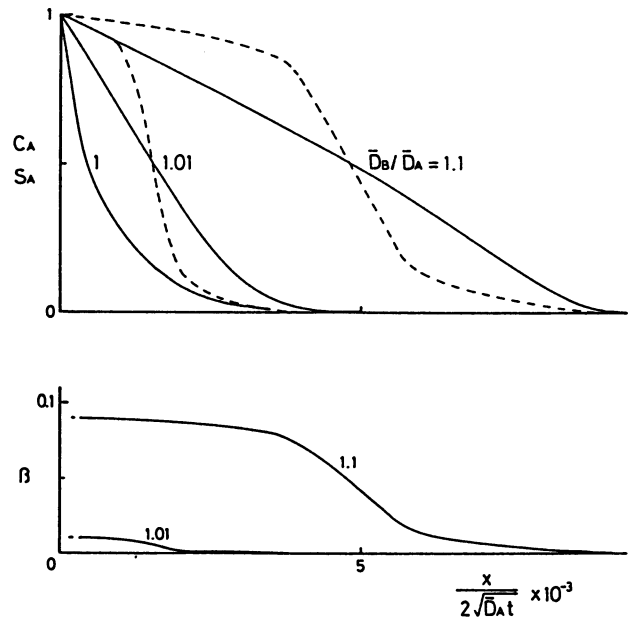

Fig. 7   Diffusion metasomatism in a solid solution mineral. $\bar{D}_B /\bar{D}_A =1.01$.
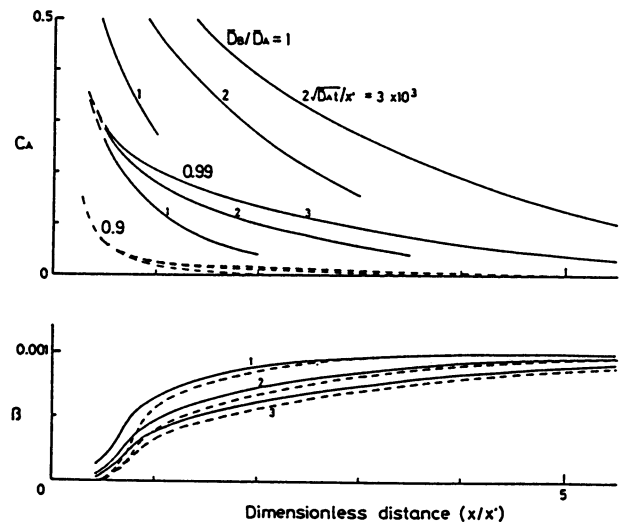

Fig. 8   Diffusion metasomatism in a solid solution mineral. $\bar{D}_B /\bar{D}_A =0.99$ and 0.9. For explanations of distance and time units, see caption of Fig. 4.

penetration depth at the composition $C_A =0.5$ becomes almost ten times as long as that of the ratio is unity, while the depth at $C_A =0.1$ becomes only about four times. When the ratio is less than unity $(\bar{D}_B < \bar{D}_A)$, a decrease in the coefficients retards the alteration process (Fig. 8). In this case, only a low concentration profile can proceed because the porosity near the bound-

ary becomes almost zero.   As can be seen in Fig. 7, the porosity varies at a rate proportional to the slope of the isotherm (dS_A/dC_A).   The reason is in that when the slope is greater, larger increment is needed to alter the composition of the mineral.

D. Infiltration effect

According to (IV.3), an infiltration of pore solution may not directly act on porosity change. Therefore, even if the ratio of the coefficients $(\bar{D}_B/\bar{D}_A)$ is not unity, a steady state will be achieved when the pore solution migrates toward a fissure.

Let the intrinsic diffusion coefficients of both components be 10^{-4} cm²/s, and the volume flux of solution migrating through pores be -1cm³/cm² per year, that is, about -1.6×10^{-5} cm/s for fluid velocity at $\beta=0.002$.   The values taken may be reasonable for processes of geological interest (Fletcher and Hofmann, 1973; Fujimoto, 1987).

When the ratio is unity, the computed concentration profile of a pore solution with an S-shaped isotherm in the steady state is the same as an anlytical one with a linear isotherm $(dS_i/dC_i=1)$ in the state (Fig. 9).   That is:

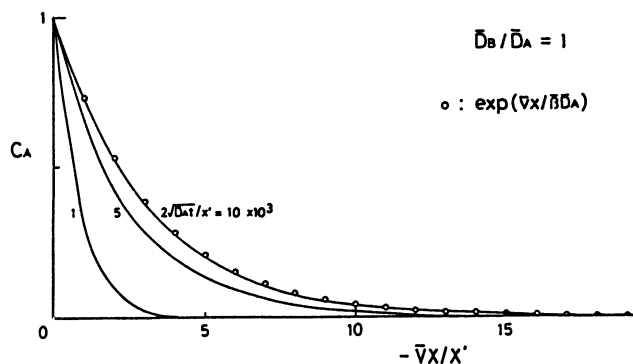$$C_i = \exp(x\bar{v}/\beta^n \bar{D}_i) .   \qquad (IV.3)$$

Fig. 9   Combined diffusion and reverse-infil tration metasomatism in a solid solu tion mineral. $\bar{D}_B/\bar{D}_A=1$. The concentra tion profile for each time level is shown as a function of relative dis tance $(-\bar{v}x/x')$. Open circle corre sponds to an analytical solution for a linear isotherm (see text).
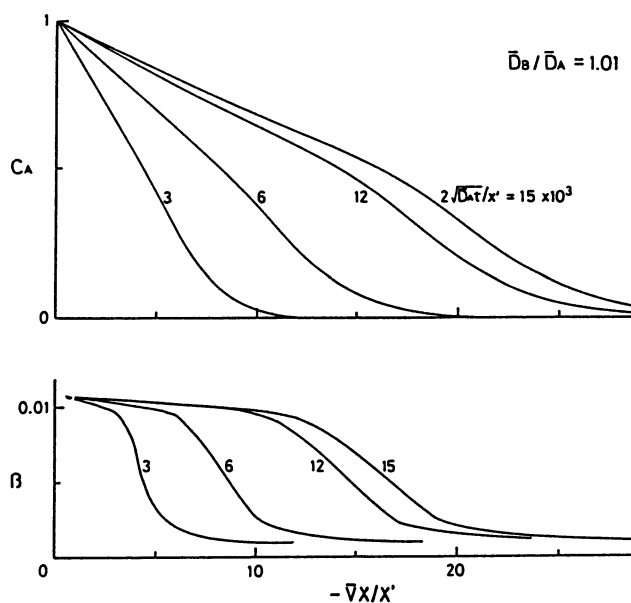
Fig. 10   Combined diffusion and reverse-infil tration metasomatism in a solid solu tion mineral. $\bar{D}_B/\bar{D}_A=1.01$.   Time and distance are the same as in Fig. 9.
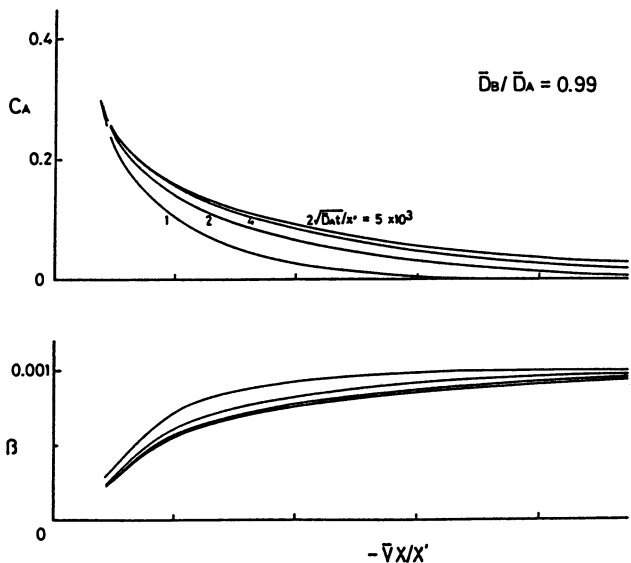
Fig. 11   Combined diffusion and reverse-infil tration metasomatism in a solid solu tion mineral. $\bar{D}_B/\bar{D}_A=0.99$.   Time and distance are the same as in Fig. 9.

Accordingly, it may be applicable to any isotherm whenever the ratio is unity.

As can be seen intuitively by (III.10), when the ratio exceeds unity, the steady state may be achieved more slowly than the above case (Fig. 10).   When the ratio is less than unity, the

state may be achieved more rapidly (Fig. 11).

V. Discussion and conclusions

The metasomatic process has been reexamined, considering the effect of varying porosity on the process itself using the thermodynamic assumptions. These consist mainly of constant volume and local equilibrium assumptions, essential in analyzing metasomatism. It has been concluded that the zone replaced by wollastonite around the fissure in limestone, a typical "wall-rock alteration", cannot be developed because of the "salting out" effect.

This may also be true for metasomatic replacement of any reaction mineral. The reason for this statement lies in the fact that so far as local equilibrium is achieved, the mineral should be precipitated by the "salting out" effect unless the reaction constant is negative. The result may also be applicable even when the fissure solution is somewhat undersaturated with the reaction mineral. Suppose that the replaced zone of a certain length and the dissolution front of the reaction mineral could be formed as discussed by Korzhinskii (1970). Even in this case, since the inequalities (III.9 and 12) should hold throughout the zone, a sharp dissolution front might be developed without preliminary dissolution of the mineral in the zone. Hence, the steady state ($\partial c_i/\partial x=0$) might also be achieved near the replacement front.

This conclusion may also be relevant to bimetsomatic replacement of a reaction mineral. Although they assumed a constant effective diffusion coefficients to calculate contributions of internal production in the zone to the total growth of the zone, Franz and Mao (1976) pointed out the possibility that the mineral could precipitate through the replaced zone. Fisher and Lasaga (1981) also calculated the growth rate of the wollastonite rim formed between chert and limestone while neglecting the internal production under the assumptions of a constant porosity and a constant diffusion coefficient. However, since (III.9) still holds in the replaced zone,

the diffusion coefficient varies throughout the zone (see Fig. A-2 in App. A). Therefore, the steady state may be achieved near both replacement fronts.

The above discussions allow us to emphasize that the porosity change, acting as a "braking mechanism", is an essential feature of metasomatism by reaction mineral. In other words, the metasomatic replacement is a "self-controlled" process.

On the other hand, in nature, a monomineralic replaced zone does occur around fissure such as the wollastonite skarn in the Fujigatani mine. However, this is impossible to achieve under the conditions analyzed in this paper. Therefore, to accurately understand naturally-occurring metasomatism, we must reexamine the assumptions used since Korzhinskii (1970).

In addition, the effect of changing porosity on the metasomatism in a solid solution mineral has been evaluated. It has been proven that only a small difference of intrinsic diffusion coefficients of both replacing and replaced components brings about a large variation of porosity, resulting in quite different concentration profiles as compared with those calculated under the constant porosity. Interestingly, it has been revealed that when the intrinsic diffusion coefficient of a replacing component exceeds that of replaced one, composition of the mineral shows very limited variation.

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Appendix A

Finite-difference equation and porosity
at the replacement front

For diffusion metasomatism, an explicit dif-
ference equation of the fundamental transport
equation (II.11) for component i at the distance
($x=j\Delta x$) and time ($t=h\Delta t$) can be written as
(Smith, 1985):

$$\Delta_t \rho_{i,j} = r_D D_i \{ \beta^n_{j+1/2} (c_{i,j+1} - c_{i,j})$$
$$- \beta^n_{j-1/2} (c_{i,j} - c_{i,j-1}) \}, \qquad (A.1)$$

where

$$r_D = \Delta t / (\Delta x)^2 .$$

Hereafter, subscript indicating time (h) is omit-
ted in all variables as in (A.1).

At the replacement front,

$$\Delta_t \rho_{ca,j} = \alpha_d{}' \Delta_t V_{wol,j} + \alpha_b{}' \Delta_t V_{cal,j}$$
$$= -r_D D_{ca} \beta^n_{j-1/2} (c_{ca}{}^a - c_{ca,j-1}) , \quad (A.2a)$$

and

$$\Delta_t \rho_{si,j} = \alpha_c{}' \Delta_t V_{wol,j} - c_{si}{}^a \Delta_t V_{cal,j}$$
$$= -r_D D_{si} \beta^n_{j-1/2} (c_{si}{}^a - c_{si,j-1})$$
$$= r_D D_{si} \beta^n_{j-1/2} (K/c_{ca}{}^a c_{ca,j-1})(c_{ca}{}^a$$
$$-c_{ca,j-1}), \qquad (A.2b)$$

where

$$\alpha_d{}' = (n_{wol} - c_{ca}{}^a),$$
$$\alpha_b{}' = (n_{cal} - c_{ca}{}^a),$$
$$\alpha_c{}' = (n_{wol} - c_{si}{}^a).$$

Hence,

$$\frac{\Delta_t V_{wol,j}}{\Delta_t V_{cal,j}} = \frac{-c_{si}{}^a D_{ca} + \alpha_b{}'(K/c_{ca}{}^a c_{ca,j-1}) D_{si}}{-\alpha_c{}' D_{ca} - \alpha_d{}'(K/c_{ca}{}^a c_{ca,j-1}) D_{si}} .$$
$$(A.3)$$

At $\Delta x \to 0$, $c_{ca,j-1} \to c_{ca}{}^a$, then,

$$\frac{\Delta_t V_{wol,j}}{\Delta_t V_{cal,j}} = \frac{-c_{si}{}^a c_{ca}{}^a D_{ca} + \alpha_b{}' c_{si}{}^a D_{si}}{-\alpha_c{}' c_{ca}{}^a D_{ca} - \alpha_d{}' c_{si}{}^a D_{si}} . \quad (A.3')$$

On the other hand, if β_f represents porosity at
the replacement front,

$$\beta_f = 1 + (1-\bar{\beta}) \frac{\Delta_t V_{wol,j}}{\Delta_t V_{cal,j}} . \qquad (A.4)$$
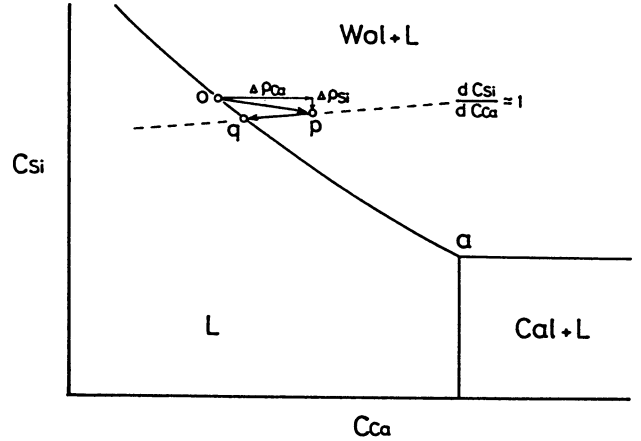
An analytical procedure for the wollastonite zone

Fig. A-1 A procedure to analyze compositional
change in the wollastonite zone (see
text).

is summarized in Fig. A-1. Let the composition
of the pore solution at a certain distance
($x=j\Delta x$) and time ($t=h\Delta t$) be represented as the
point o (on the saturation curve) in the figure.
Then, as discussed previously, the composition
may become slightly oversaturated (point p) after
infinite time Δt, which in turn decreases insta-
ntaneously to the point q (on the curve), result-
ing in corresponding precipitation of wollaston-
ite by the assumption d). In this process, the
left-hand side of (A.1) can be written as

$$\Delta_t \rho_i = (1-V_{wol})(c_i{}^p - c_i{}^o)$$
$$= n_{wol} \Delta_t V_{wol} + (1-V_{wol} - \Delta_t V_{wol}) c_i{}^q$$
$$- (1-V_{wol}) c_i{}^o , \qquad (A.5)$$

where the subscript j is also omitted and (1-
V_{wol}) represents the porosity at $x=j\Delta x$ and
$t=h\Delta t$. From (A.5),

$$(c_{ca}{}^p - c_{ca}{}^q)/(c_{si}{}^p - c_{si}{}^q) = (n_{wol} - c_{ca}{}^q)/(n_{wol} - c_{si}{}^q)$$
$$\simeq 1 . \qquad (A.6)$$

Thus, an increment of volume of wollastonite and
concentration of both components can be obtained
by the above equations (A.1, 5 and 6).

Since it is impossible to obtain the porosity
gradient in the analysis of the first slab
($x=\Delta x$), columns have been analyzed from the
second slab ($x=2\Delta x$), taking the initial porosity
of the first slab as β_f from (A.4). In the
analyses, the porosity at the replacement front
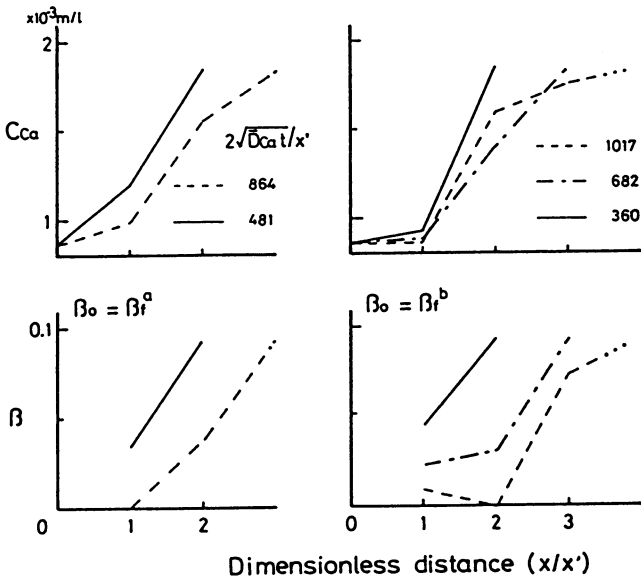
Fig. A-2 Diffusion replacement of calcite by wollastonite for constant porosity at the boundary. $D_{S_i}/D_{C_a}=1$. The boundary porosity (β_B) is set equal to $\beta_f{}^a$ (=0.94, the same as that of replacement front (β_f)) in the left figure, while set equal to $\beta_f{}^b$ (=0.930, an estimated porosity of a replacement front of quartz by wollastonite at the point b in Fig. 1b) in the right figure. Broken lines represent the profiles of concentration and porosity when the porosity is reduced to zero at the first slab (in the left figure) and the second slab (in the right figure).

is fixed as β_f, and the value $\beta^n{}_{1/2}$ is approximated as $\beta^n{}_1-(\beta^n{}_2-\beta^n{}_1)/2$ (>0). Note that even if the porosity at the boundary is fixed at a certain value, the steady state ($\partial c_i/\partial x=0$) may be achieved near the replacement front because the porosity of a certain slab is reduced to zero (Fig. A-2).

Appendix B
Analytical procedure of alteration processes by solid solution minerals

For the model being analyzed, (II.11) can be approximated as

$$\Delta_t \rho_{i.j} = s'\{(V_{AB.j}+\Delta_t V_{AB.j})(S_{i.j}+\Delta_t S_{i.j})- V_{AB.j}S_{i.j}\} + c'\{(1-V_{AB.j}-\Delta_t V_{AB.j})$$

$$x\ (C_{i.j}+\Delta_t C_{i.j})-(1-V_{AB.j})C_{i.j}\}$$
$$= c'\Delta_t P_{i.j}\ ,\qquad\qquad (B.1)$$

where

$$\Delta_t P_{i.j} = r_D D_i\{\beta^n{}_{j+1/2}(C_{i.j+1}-C_{i.j})$$
$$-\beta^n{}_{j-1/2}(C_{i.j}-C_{i.j-1})\}$$
$$-r_1\bar{v}(C_{i.j+1}-C_{i.j-1})\ ,\qquad (B.2)$$

and

$$r_1 = \Delta t/(2\Delta x).$$

Thus, (IV.4) becomes

$$\Delta_t V_{AB.j} = r_D(D_A-D_B)\{\beta^n{}_{j+1/2}(C_{A.j+1}-C_{A.j})$$
$$-\beta^n{}_{j-1/2}(C_{A.j}-C_{A.j-1})\}/(s'/c'-1).(B.3)$$

On the other hand, $C_{i.j}$ is a function of $S_{i.j}$ by the assumption d), $\Delta_t C_{i.j}$ can be obtained from (B.1) and (B.2), that is,

$$\Delta_t C_i = \frac{(c'/s')\Delta_t P_i-\Delta_t V_{AB}(S_i-(c'/s')C_i)}{(V_{AB}+\Delta_t V_{AB})(\Delta_t S_i/\Delta_t C_i)+(c'/s')(1-V_{AB}+\Delta_t V_{AB})}$$
$$(B.4)$$

where the subscript j is omitted. The value, $\Delta_t S_i/\Delta_t C_i$, is approximated as dS_i/dC_i at $t=h\Delta t$ in the analyses.

Appendix C
Occurrence of wollastonite skarn

"Vein-type" skarns, up to 2m wide, occur around a fissure in a lenticular limestone in the scheelite deposits of the Fujigatani mine, SW Japan (Fig. C-1). Among them, small-scaled skarn ranging in width from a few millimeters to a few centimeters, usually composed of wollastonite only, is sometimes observed (Fig. C-2(a)). Hoshino et al.(1982) reported the zonal arrangements in a well-developed skarn as follows: from the limestone side toward the center, coarse-grained calcite zone, wollastonite zone, garnet-clinopyroxene zone, clinopyroxene-garnet zone, and central zone (Fig. C-2(b)). Zone boundaries are usually sharp, where the modal ratio of early skarn minerals and chemical composition of clinopyroxene change abruptly (Fig. C-3). Based on
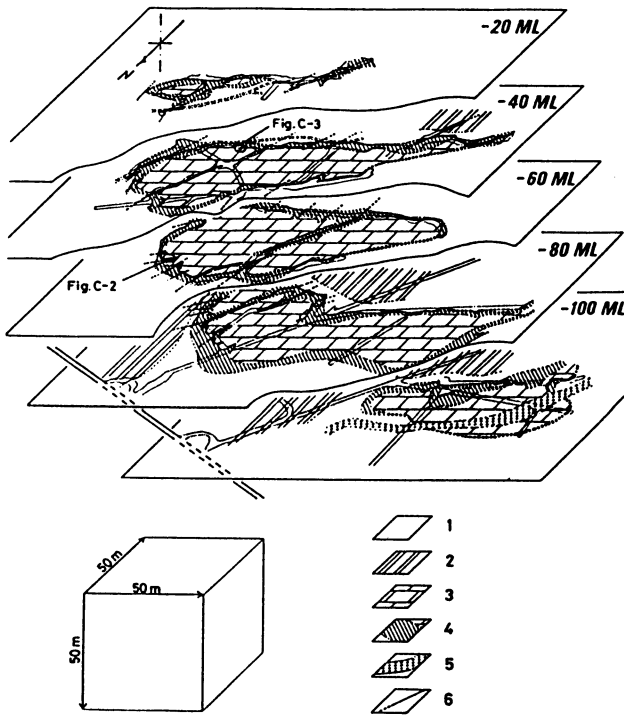
Fig. C-1 Occurrence of skarn in the Akemidani
No. 5 orebody of the Fujigatani mine,
SW Japan (partly modified from
Hoshino et al., 1982).
1. slate, 2. chert, 3. limestone, 4.
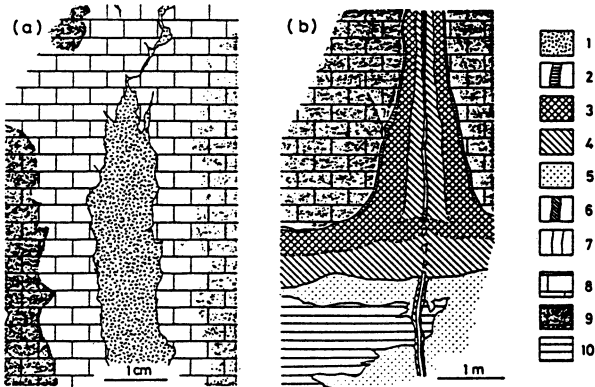skarn, 5. aplitic dike, 6. quartz
vein.

Fig. C-2 Occurrence of "vein-type" skarn.
(a) wollastonite monomineralic skarn.
(b) zoned skarn (partly modified from
Hoshino et al., 1982).
1 and 2. wollastonite zone, 3.
garnet-clinopyroxene zone, 4. clino-
pyroxene garnet zone, 5. epidote-
clinopyroxene zone, 6. central zone
composed of coarse-grained clino-
pyroxene, 7. central zone (quartz
vein), 8. recrystallized limestone,
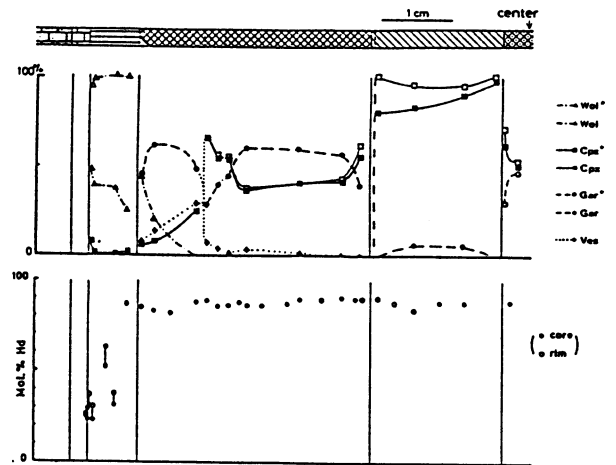9. crystalline limestone with
graphhitic matters, 10. slate.

Fig. C-3 Characteristics of zoned skarn (modi-
fied from Hoshino et al., 1982).
Sampling locality is shown in Fig.
C-1.
(a) Modal ratios of Wo*, Cpc*, Gar*,
and Ves.
(b) Compositional variation of clino-
pyroxene.
Abbreviations: Wol: wollastonite,
Cpx: clinopyroxene, Gar: garnet, Ves:
vesvianite. Star (*) indicates each
mineral with its alteration products.

field and detailed microscopic observations, they
concluded that the central zone was originally a
fracture, into which solution invaded to yield
the skarn andthat the inner zone replaced the
outer zone toward the limestone side.

Using scanning electron microscope observa-
tions, porosity of the recrystalline limestone
around the thin vein-type wollastonite skarn is
estimated to be about 2×10^{-3}. The value is
essentially the same as the effective porosity
(1.4×10^{-3}) of the recrystalline limestone used
for the diffusion experiments of iodine ion
(Nishiyama and Nakashima pers. comm.).

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