Extension of the High Temperature Limit of Cooling Geospeedometry

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冷却地質速度計における高温限界の拡張

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Abstract: Geospeedometer proposed so far to estimate cooling history of rocks has a limit in terms of the maximum temperature above which we cannot deduce the history. The limit is governed by kinetic processes for geospeedometry and cooling rates; for example the olivine-spinel geospeedometry based on kinetics of Mg-Fe^{2+} exchange between olivine and spinel with the maximum grain size of a few millimeters cannot record any cooling history above 800°C if the cooling rate is $<10^{-4}^{\circ}\text{C/year}$. In order to extend the limit, a larger distance scale for geospeedometry is needed. By using mineralogical variations forming rock structures, whose distance scale is up to a meter order or more, we can in principle estimate thermal history of rocks up to their solidus temperatures, if effects of polycrystalline and multi-phase nature and the initial conditions for a large scale rock system are correctly assessed. The olivine-spinel geospeedometry was extended to deduce high temperature thermal history of a dunite-chromitite layer sampled from the Iwanai-dake peridotite mass, Hokkaido. The Fe-Mg variation over 6 cm in dunite from the contact is analyzed by a 1-D diffusion model with a composition-dependent diffusivity and a changeable cooling rate. The dunite-chromitite geospeedometry indicates that the Iwanai-dake mass was cooled from $\sim 1000^{\circ}\text{C}$ to 900°C with increasing cooling rate from $<0.01^{\circ}\text{C/year}$ to $\sim 0.3^{\circ}\text{C/year}$. This suggests that the slower cooling after the melting event was followed by the ascent of the mass that resulted in the inferred rapid cooling at $\sim 900^{\circ}\text{C}$.

1. Introduction

For better understanding of transportation processes within the earth, temperature and pressure history of rocks that brought up to the earth's surface by various processes provides useful information. P-T history of rocks can be obtained by applying geospeedometry¹⁾⁻³⁾, which utilizes kinetics of various reactions that proceed responding to changes in pressure and temperature conditions at a certain rate. For each geospeedometry, we have to know the mechanism of reaction and how fast the reaction proceeds in a given range of temperature. In this paper, one of the simplest types of geospeedometry, which is based on a diffusion-controlled cation exchange reaction between two coexisting minerals without boundary

migration is discussed⁴⁾⁻⁶⁾.

Geospeedometry based on cation exchange reactions has a limit in the inferable maximum temperature for a given range of size of minerals and a cooling rate. For example, application of the olivine-spinel geospeedometry²⁾ to slowly cooled rocks does not give thermal history above 800°C , because the size of isolated spinel grains is smaller than a few millimeters in general. The aim of this paper is to propose a way to extend the upper limit for slowly cooled rocks, ideally up to the solidus temperature by simply extending the size of reaction space up to 10 cm $\sim$ 1 m. The way to overcome difficulties in extending the distance scale is discussed and the method is applied to a dunite-chromitite composite sample.

2. Closure Temperature

Closure temperature (T_c), which is defined as the temperature of the system at the time when the composition involved in a reaction does not change

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any more during cooling, was formulated by Dodson⁷⁾ as follows,

$$\frac{E}{RT_c} = \ln \left(-\frac{ART_c^2 D_0 / a^2}{E\dot{T}} \right) \quad (1)$$

where D_0 is the diffusion pre-exponential factor, E is the activation energy for the diffusion process, $\dot{T}$ is the cooling rate (negative value for cooling), a is a characteristic dimension of the system (e.g., grain size), and A is a numerical constant depending on geometry (e.g., 55 for sphere⁷⁾).

Dodson's equation was formulated for a diffusional exchange of minor components between a mineral and a faster diffusing infinite reservoir, which could be a grain boundary phase or adjacent minerals. Ehlers and Powell⁸⁾ empirically modified Dodson's equation for a exchange reaction of major components between two minerals with finite sizes. They proposed the following expression for the closure temperature,

$$\frac{E}{RT_c} = \ln \left(-\alpha \frac{ART_c^2 D_0 / a^2}{E\dot{T}} + \beta \left(1 + \frac{1}{rk} \right) \right) \quad (2)$$

where r is the ratio of size of two minerals, k is the apparent distribution coefficient calculated by core-core pair of the two minerals. The parameters α and β were determined by numerical experiments to be 2.56 and 1.72, respectively.

3. Possible Methods for Maximization of Closure Temperature

In this section, ways to increase T_c for diffusion-controlled exchange reactions with cooling rate as low as $\sim 10^{-4}$ C/year, which is the slower estimated cooling rate of intrusive peridotites by olivine-spinel geospeedometry²⁾, are considered. Equation (1) shows that parameters adjustable to increase the closure temperature are D_0 , E , and a . The variation of parameter A is confined between 2 to 60⁹⁾. Because there is the compensation law^{10),11)}, D_0 (m²/sec) and E (kJ/mole) are not independently adjustable and are related by the equation

$$\log D_0 = a_1 E + a_2, \quad (3)$$

where a_1 and a_2 are constants.

Under such constraints, relationship between cooling rate and closure temperature is schematically illustrated in Fig. 1. Due to the common grain size of natural rocks (1 μ m–1 mm) and the com-

Fig. 1 Schematic illustration of relationship between closure temperature and cooling rate. The dotted region represents the window through which we can know cooling history of rocks by common geospeedometry utilizing a reaction with a normal activation energy and distance scale. By decreasing the distance scale as small as the TEM scale, high cooling rate at low temperatures can be detected. Low cooling rate at high temperatures can be estimated by increasing the distance scale.

ensation law with ordinary range of activation energy (40–800 kJ/mole^{12),13)}), a region where we can estimate a cooling rate for a given closure temperature is limited (dotted region in Fig. 1). Unless there is a reaction with anomalously high activation energy, we have to increase or decrease the distance scale to infer thermal history above or beneath this region. By decreasing the distance scale to submicrons, large cooling rates at low temperature (lower right region in Fig. 1) can be estimated. This can be done by transmission electron microscopy (TEM; e.g., Fujino et al.¹⁴⁾). By increasing the distance scale up to a meter or more, small cooling rates at high temperature (upper left corner in Fig. 1) may be estimated. This extension of the distance scale has not yet established as a useful geospeedometry for high temperature thermal history at low rate, in contrast to the successful application of the TEM technique to low temperature geospeedometry.

High temperature thermal history of slowly cooled rocks is examined quantitatively in Fig. 2, which shows the effect of activation energy on the

Fig. 2 Relationship between cooling rate and closure temperature for different activation energies and a 1 mm distance scale (a) and for various characteristic distance scale and Mg-Fe diffusion in olivine (b). The obliquely ruled areas show the range of the possible activation energy in (a) and that of common grain size in natural rocks in (b). Dotted areas show the ranges of temperature and cooling rate that are targeted in this paper. In (a) the compensation law is assumed (see text). In (b) two thick curves are for two extreme cases of thermal history with changing rate of cooling. The Mg-Fe interdiffusion coefficient in olivine is after Misener¹⁵⁾. If the diffusivity by Chakraborty¹⁶⁾ is used, closure temperatures are higher by 100°C than shown in (b) for cooling rate of 10^{-6} °C/year and grain size of 1 m - 1 cm.

relationship between closure temperature and cooling rate. The two constants $a_1 = 3.46 \times 10^{-2}$ and $a_2 = -9.94^{10)}$ are used in eq. (3). In order to increase closure temperature up to 1000°C for cooling rate less than 10^{-4} °C/year and for a grain with 1 mm size (dotted region at the upper left corner of Fig. 2a), the activation energy should be higher than 1600 kJ/mole, which is anomalously large for diffusion in oxide and silicate minerals^{12),13)}. Therefore, it will be necessary to increase the distance scale in order to obtain information at high temperatures for slowly cooled rocks.

Figure 2b shows the relationship between cooling rate and closure temperature for Mg-Fe olivine with various sizes. If the grain size is less than 1 mm (obliquely ruled area), then the maximum inferable temperature is as high as 700°C at cooling rate of 10^{-3} °C/year for path II, but it is 400°C for path I. For slowly cooled rocks represented by path I, the maximum grain size of 1 mm is a tremendous obstacle to deduce the thermal history. It is clear that if the distance scale is several tens centimeters, then we may be able to detect cooling rate of $\sim 10^{-4}$ °C/year at temperatures as high as 1000°C. Because the Mg-Fe diffusion in olivine is relatively fast compared to diffusion of other cations in major rock forming minerals, we can reduce the size to the order of a few to several tens centimeters if we use other reactions.

4. Problems in Extending Distance Scale for Diffusional Geospeedometry

Because common minerals with a meter or even centimeter size are very rare, there are several obstacles to increase the distance scale in slowly cooled rocks. At first, a polycrystalline and/or multi-phase rock system has to be treated. Polycrystals introduce grain boundaries, which can be neglected only if one mineral is completely included in another mineral. As far as the inter-phase boundaries between contacting two minerals are connected from a grain boundary network, there is a possibility of material influx from the fast path network. This effect on the contacting mineral pair can be evaluated by carefully examining zoning profiles of the minerals and larger scale structures (veins, layering, schistosity, etc.) and associated heterogeneities in the rock. By contrast, the distance scale of diffusion is inevitably larger than the grain size in the extension of the distance scale for geospeedometry, and diffusion through polycrystalline aggregate with grain boundaries and inter-phase boundaries has to be correctly evaluated. Polycrystalline nature also introduces either random or preferred orientation of mineral grains with diffusional anisotropy. For a grain size scale, the orientation of each grain can be specified and a suitable diffusivity along the direction of the measurement can be used. In the case of polycrystalline minerals with diffusional anisotropy, however, there are many possible paths with various diffusivities.

In addition to the aforementioned difficulties for a single phase system, a multi-phase system has other complexities such as, inter-phase boundary, variable diffusion coefficients and the anisotropy depending on minerals, elemental partitioning among minerals, variable molar concentration of a diffusing component (component density¹⁷⁾), modal change due to net-transfer reactions, and complex microstructures. In polycrystalline and multi-phase rocks, grain boundaries or inter-phase boundaries may be partially filled with fluid, such as silicate melt or H₂O or CO₂-rich fluid. The presence of such fluid phase not only adds the aforementioned complexities as in the case of addition of a new mineral phase but also plays a significant role in mass transport, because they can advect along the pressure gradient if their connectivity is attained. Furthermore, grain or inter-phase boundaries are not unique path for fluid migration, but cracks, whose orientation and number density could dynamically change, may be more effective.

Finally, the initial condition, which we need to know in order to extract P-T history, becomes more ambiguous if the distance scale is increased. In the case of distance scale less than a millimeter, higher temperature stage usually erases most of the heterogeneity before the closure temperature is approached. Thus, homogeneous initial condition at a certain temperature can be assumed. Dodson⁷⁾ noted that geospeedometry is independent of the starting temperature if it is sufficiently high to reach complete homogenization and equilibrium (also see Ozawa²⁾). However, complete homogenization of more than 10 cm scale *usually* cannot be expected because it requires very long time (up to ~0.1 Ga) to attain the homogeneity. The initial mineralogical variation in rocks, therefore, should be estimated by additional information from the rocks.

5. Qualitative Evaluation of the Problems in Geospeedometry

As shown above, there are many problems that should be solved before successful extension of the distance scale for a geospeedometry. All these problems cannot be evaluated in this paper, but several critical points are discussed.

5.1 Grain boundary and inter-phase boundaries

Grain boundary is an important path for mass transportation, of which role in diffusive mass

Fig. 3 Three diffusion regimes in polycrystals after Harrison²⁰⁾. Harrison's model was illustrated for cation exchange reactions between a single crystal and surrounding polycrystals of another mineral. The shaded area represents the region where the concentration of an exchange component is higher (or lower) than a certain value. The boundary values (time and lattice diffusivity) of regimes A and B and that between regimes B and C are after Joesten¹⁸⁾.

transfer has been discussed and reviewed by several authors in the earth science field^{17),18)} and in the material science field¹⁹⁾. Brady¹⁷⁾ regarded a mono-mineralic rock as a two-phase system by treating grain boundary as the secondary phase. Effective diffusivities can be expressed as a function of diffusivities of the two phases, the volume ratio (very small volume fraction for grain boundary), and configuration of grain boundaries (e.g., parallel or series). He stressed that the grain size of a rock is the most important textural parameter that affects intergranular diffusion because smaller crystals generate more intergranular paths per unit cross section. He also pointed out the importance of width of the intergranular region.

Joesten¹⁸⁾ reviewed grain-boundary diffusion in silicate and oxide minerals. He introduced the Harrison model²⁰⁾, which defined the three regimes for grain boundary and lattice diffusions in a polycrystal system with grain boundary net-

work (Fig. 3). Figure 3 illustrates the three regimes of Harrison²⁰) for a diffusion controlled exchange reaction between an isolated mineral grain and its surroundings (e.g., spinel in dunite). In regime A the diffusion length in the lattice is large compared with the grain size; in regime B the diffusion length in the lattice is smaller than the grain size; in regime C the diffusion length in the lattice is negligible, and diffusion occurs only along the grain boundary network. Joesten¹⁸) pointed out the importance of time (for isothermal conditions) in addition to the length scale of lattice diffusion and delineated the region for three types of diffusion kinetics in the diagram of time vs. lattice diffusivity.

In these reviews and previous work cited therein, constant diffusivity and thus a constant temperature were assumed. In order to evaluate the role of grain boundary diffusion for geospeedometry, the temperature-dependent (i.e., time-dependent) diffusivity has to be taken into consideration. A problem to be addressed is how elemental distribution in a rock with a macro-structure, as shown in Fig. 4a as an example, is frozen in during cooling. This problem is simplified as shown in Fig. 4b. Diffusion equations and boundary conditions in two dimensions are derived as follows,

$$\frac{\partial C^A}{\partial t} = D^A(t) \left\{ \frac{\partial^2 C^A}{\partial x^2} + \frac{\partial^2 C^A}{\partial y^2} \right\} \quad (4)$$

$$\frac{\partial C^{gb}}{\partial t} = D^{gb}(t) \frac{\partial^2 C^{gb}}{\partial y^2} - \frac{2D^A(t)}{\delta} \left(\frac{\partial C^A}{\partial x} \right)_{x=0} \quad (5)$$

$$C^A(x, 0, t) = C^{gb}(0, t) = C^B \quad (6)$$

$$C^A(x, \infty, t) = C^{gb}(\infty, t) = C^0 \quad (7)$$

$$\left(\frac{\partial C^A}{\partial x} \right)_{x=\frac{L}{2}} = 0 \quad (8)$$

where C^A and D^A are concentration and diffusivity in the crystal A, C^{gb} and D^{gb} are the concentration and diffusivity along the grain boundary, δ is the thickness of the grain boundary, L is the width of the crystal, C^0 is the initial concentration in A, and C^B is the fixed concentration at $y=0$. Eq. (5) is the diffusion equation along the grain boundary^{19), 21)} and can be regarded as a boundary condition for lattice diffusion in crystal A at $x=0$. The grain boundary thickness is supposed to be negli-

Fig. 4 Two dimensional grain boundary and inter-phase boundary model for elemental redistribution in a two-phase rock with a layer structure. (a) Banded two-phase rocks with sharp modal change at the layer boundary, and (b) extreme simplification of the two-phase model. In (b) thickness of the grain boundary is assumed to be significantly small as compared with the size of the grain. See text for the notations in (b).

gibly small as compared to the size of crystal, which is usually the case. The last term of the right hand side of (5) represents the sink term due to leaking from the boundary region to the crystal.

The boundary condition (6) assumes; (1) mineral B (or a fluid phase) has very large diffusivity of the component and is large enough as an infinite reservoir, and (2) partition coefficient of the component between A and B is constant. If diffusivity in mineral B is not so large and the partition coefficient between A and B is time dependent, a diffusion equation has to be solved for mineral B with appropriate boundary conditions along the A-B interphase boundary.

After introducing compressed time τ^1 ,

$$\tau = \int_0^t D^A(t) dt / D^A(0), \quad (9)$$

where is the initial diffusion coefficient, the diffusion equation and boundary conditions (4) - (8) are nondimensionalized. Because the effect of grain boundary diffusion in a coarse-grained rock is examined in this paper ($\delta^2/D^{gb} \ll L^2/D^A$), the problem may be regarded semi-infinite in both x and y directions. Therefore, the maximum compressed time $\tau_{\max}$ and the maximum diffusion distance $l_{\max}$,

$$\tau_{\max} = \int_0^\infty D^A(t) dt / D^A(0), \quad l_{\max} = \sqrt{\int_0^\infty D^A(t) dt}, \quad (10)$$

are chosen as time and distance scales. The composition is scaled by C^0-C^B . The nondimensionalized equations are obtained as follows after dropping prim,

$$\frac{\partial C^A}{\partial \tau} = \frac{\partial^2 C^A}{\partial x^2} + \frac{\partial^2 C^A}{\partial y^2} \quad (4')$$

$$\frac{\partial C^{gb}}{\partial \tau} = \Delta^{gb}(\tau) \frac{\partial^2 C^{gb}}{\partial y^2} - \zeta \Delta^A(\tau) \left(\frac{\partial C^A}{\partial x} \right)_{x=0} \quad (5')$$

$$C^A(x, 0, \tau) = C^{gb}(0, \tau) = 1 \quad (6')$$

$$C^A(x, \infty, \tau) = C^{gb}(\infty, \tau) = 0 \quad (7')$$

$$C^A(-\infty, y, \tau) = C^{gb}(+\infty, y, \tau) = 0 \quad (8')$$

where $\zeta = 2l_{\max}/\delta$, $\Delta^A(t) = D^A(t)/D^A(0)$, and $\Delta^{gb}(t) = D^{gb}(t)/D^A(0)$ are dimensionless parameters. The last two dimensionless parameters are time-dependent and represent the change of diffusivities during cooling.

Because the boundary condition (5') for the two dimensional diffusion problem in mineral A is a diffusion equation in itself, the equations (4') - (8') may not have a simple analytic solution, and they were solved numerically by implicit alternating-direction method (IAD²²). The results are shown in Figs. 5 and 6. In Fig. 5, development of zoning near a grain boundary during isothermal heating at 1000°C and cooling from 1000°C at 0.1°C/sec is compared. In the isothermal condition, the zoning becomes less pronounced after long duration and the profile becomes less steep with time (Fig. 5a; see also Fig. 4 of Joesten¹⁸ based on Fisher solution²¹). By contrast, the gra-

Fig. 5 Development of chemical zoning near a grain boundary during isothermal heating at 1000°C (a) and cooling from 1000°C with a rate of 0.1°C/sec (b). Contours of constant concentration (0.02) are drawn for several elapsed time steps indicated by numbers on each contour. The used parameters for activation energy and pre-exponential term for grain boundary diffusion are shown in (a).

dient near the grain boundary does not change much during cooling until it is completely frozen (Fig. 5b). For a given ζ value, a frozen zoning profile near grain boundary becomes more remarkable as $\Delta^{gb}(t)$ becomes large (compare Figs. 6b and 6d). On the contrary, for a given $\Delta^{gb}(t)$, $\Delta^A(t)$, and grain boundary width, the zoning is more pronounced as cooling rate increases (as ζ value decreases) (compare Figs. 6a, b, and c).

Fig. 6 Frozen elemental distribution near a grain boundary during cooling at various rates from $1.0^\circ\text{C}/\text{sec}$ to $10^{-4}^\circ\text{C}/\text{sec}$ (a, b, and c). Parameters used in the calculation are shown in the panel (c). In (d), effect of grain boundary diffusion is shown under the same conditions as used in (b) except for the pre-exponential term for grain boundary diffusion. Both axes are normalized to the maximum diffusion distance, which depends on cooling rate, thus the actual scale of each panel decreases from (a) to (c).

Such behavior of lattice diffusion near grain boundaries is governed by the relative importance of the grain boundary diffusion term and leakage term in (5'), which is characterized by the parameter $\zeta' = \zeta \Delta^A(\tau) / \Delta^{gb}(\tau) = \zeta D^A(\tau) / D^{gb}(\tau)$.

If ζ' is small, then there is no leakage from the grain boundary and only grain boundary diffusion takes place (Fig. 6d). This corresponds to Harrison's grain boundary diffusion kinetic regime C. By contrast, if ζ' is significantly large, extensive

leakage takes place and the grain boundary region is always buffered by the diffusive flux from the surrounding crystal (Figs. 6a). This is Harrison's kinetic regime A. If ζ' is close to unity, then the leakage and diffusion along grain boundary are competing (Figs. 6b and c), which is the situation of Harrison's regime B. During cooling, ζ' decreases because the activation energy of grain boundary diffusion is much smaller than that of the lattice diffusion. This is the reason why the gradient near grain boundary does not change significantly during cooling (Fig. 5b).

Figure 6 shows that if grain boundary width is a few nm and $\Delta^{gb}(t)$ is $\sim 10^5$ (as in the case of olivine), grain boundary diffusion does not affect diffusional mass transport in a polycrystalline material during a cooling process unless the grain size is significantly smaller than $\sim l_{\text{max}}/5$. If the cooling rate is $0.01^\circ\text{C}/\text{year}$, then $l_{\text{max}}/5$ is $539\mu\text{m}$, which is still as large as the naturally observed grain size in peridotite ($\sim 1\text{mm}$). Furthermore, as cooling rate decreases, leakage to the adjacent crystal dominates over grain boundary diffusion due to large ζ

value, which results in the diffusion kinetics of regime A (Fig. 6). It is summarized that as far as the average grain size of olivine is larger than a few hundreds nm, grain boundary diffusion does not play an important role in diffusive mass transfer in slowly cooled peridotites.

5.2 Multi-phase problems

The problems in application of geospeedometry to a multi-phase system are rather classical and have been studied as diffusion problems in hetero-

geneous media^{23),24)}. Even in a two-phase system the effective diffusivity is strongly dependent on mineral mode, grain size, and morphology of the interface¹⁷⁾. Therefore, there is a limitation in application of the effective diffusivity because microstructures of natural rocks are very complicated and the number of phases present in those rocks are usually more than two. Numerical approach may be the unique method to precisely evaluate diffusion in a multi-phase system²⁴⁾. Presence of phases with zero or very low concentration of a component used for geospeedometry, such as plagioclase in mafic rocks for Mg-Fe components, makes the geospeedometry complicated for application, but has also an advantage to increase tortuosity²⁵⁾, which can increase the effective distance scale and thus the closure temperature.

5. 3 Initial condition problems

Initial condition is the most difficult problem, which should be properly treated for each case considering processes by which the rock had formed before it started to cool. In the following section, geospeedometry for a multi-phase system will be applied to peridotites and the initial condition needed for the application is briefly mentioned here. For the initial condition of a peridotite, we cannot simply assume homogeneity in mineral phases at a certain high temperature. The real initial conditions should be the stage when magmatic processes had come to the end and the rock started to cool. Therefore, we have to invert magmatic processes that formed the structure used for geospeedometry and cooling process simultaneously.

6. Application

Geospeedometry using macro-structures is applied to a chromitite-dunite composite sample from the Iwanai-dake peridotite mass, Hokkaido. This unrooted sample is 10 cm in size consisting of 1/4 of chromitite and 3/4 of dunite (Fig. 7). Chromitite contains more than 90 vol% chromite and interstitial olivine with minor chlorite. Dunite consists mostly of olivine with minor spinel grains and secondary phases such as tremolite and diopside along veins. The sample is suitable for a macro scale geospeedometry because chromite and dunite can be regarded as monomineralic, which greatly simplifies the procedure for geospeedometry.

Fig. 7 Photograph of the studied sample from the Iwanai-dake mass, Hokkaido. The black portion on the right is chromitite with interstitial olivine and the gray part on the left is dunite with minor spinel. The profile shown in Fig. 8a is along A-B.

Figure 8 shows variations of Fo mol.% and NiO wt.% in olivine across the boundary of the chromitite and dunite layers (Fig. 7). Olivine in the dunite becomes strongly rich in Fo mol.% and NiO wt.% toward the boundary with the chromitite. The variation is observed over the distance scale of 6 centimeters, which is significantly large as compared with the zoning in olivine around a millimeter size chromite²⁶⁾. The remarkable enrichment of Mg and Ni in olivine in and near the chromitite (Figs. 8) indicates that their variation is principally due to the Mg-Fe-Ni exchange between the dunite and chromitite layers during cooling. This is because Mg and Ni are preferentially partitioned into olivine at low temperature as compared to Fe^{27),28)}. Therefore, the zoning can be used to estimate high temperature thermal history. Locally, very Fo-rich and NiO-rich vein-like regions are present, which is attributable to the late stage modification along fractures (at very low temperature possibly with fluid influx). This is consistent with the occurrence of diopside and tremolite along such Mg-rich veins.

Figure 9a shows modeled zonings with the observed Fo variation shown in Fig. 8. The model is one dimensional and assumes two monomineralic layers contacting with flat interface. The model further assumes rapid diffusion in chromitite, kinetic regime A, Fo 92.4 as initial olivine composition, 1000°C initial temperature. These assumptions are assessed or explained below.

The assumption of rapid diffusion in the chromitite may not be completely satisfied because of the smaller diffusivity in Cr-rich spinel²⁾, but

Fig. 8 Variation of Fo mole% (a) and NiO wt% (b) in olivine across the dunite-chromitite contact from the Iwanai-dake mass, Hokkaido, Japan (along A-B in Fig. 7). The contact is located at 20 mm. The data clearly related to the secondary process forming hydrous veins are omitted.

gives the maximum cooling rate estimation. The regime A assumption is not correct, but the late stage low-temperature disturbance is spiky, suggesting that the smoothed lower bound give the frozen A regime profile (Fig. 8). The assumed initial value of Fo 92.4 dunite has no clear supporting evidence, but the minimum Fo value in the dunite layer was taken. The initial value could be lower than 92.4, and thus the assumption gives the maximum estimate for the cooling rate. The initial homogeneity is suggested by the convex downward positive correlation between Fo and NiO content in olivine, which may be attributable to the slower diffusivity of Ni in olivine³⁰. The initial temperature is the maximum calculated temperature with a pair of large spinel in chromitite and the most Fe-rich olivine in dunite.

The overall misfit between any model profiles assuming a constant cooling rate and the observation is large (Fig. 9a), suggesting an increase in

Fig. 9 Cooling models (I and II shown in (b)) with changeable rate to fit the Fo variation. The models assume rapid diffusion in the chromitite layer and the homogeneous initial condition Fo=92.4. The composition dependent Fe-Mg interdiffusion coefficient after Misener¹⁵ and the Mg-Fe partition coefficient between olivine and spinel after Fabriès²⁹ were used. Note that any cooling models with constant rate does not reproduce the observation.

the cooling rate by more than one order of magnitude. This is because the decrease in cooling rate produces much gentler zoning profile. If the assumption of the initial Fo=92.4 is correct, the Fo profile can be reproduced by slower cooling rate as low as 0.001–0.01 °C/year at ~1000 °C and increasing rate by one or two orders of magnitude during ~200 °C temperature drop (Fig. 9b). The tendency of the increasing cooling rate is consistent with the dunite-chromitite geospeedometry².

The increasing cooling rate as cooling proceeds is contrasting to the thermal history inferred for a contact aureole³, where the cooling rate gradually decreases. The inferred increase of cooling rate may be explained by two scenarios. Cooling of the Iwanai-dake mass was accelerated in the shallower level probably by nearly constant uplift of the mantle material. Alternatively, the initial slow cooling represents static cooling after the melting event,

which was followed by an ascent of the complex that caused rapid cooling at lower temperatures.

7. Conclusion

In order to estimate the high temperature thermal history that cannot be obtained by conventional geospeedometry, there are two possible ways; the first is to find a mineral that has an extraordinary high activation energy for diffusion of a component and the second is to increase a distance scale for the geospeedometry. The first approach fails because the activation energy, which is related to the frequency factor of Arrhenius relations for diffusion by the compensation law, is usually less than 800 kJ/mole. The second method is more promising but gives rise to many difficulties that have to be overcome before the successful application of this method.

Among these difficulties, the role of grain boundary diffusion, along which material transportation may be significant, is evaluated by a simple 2-D model. Analysis of the model shows that the grain boundary diffusion is not important for slowly cooled rocks if the grain size is larger than a few hundreds nm and if diffusion along grain boundary with ~1 nm thickness is not faster than lattice diffusion by 5 orders of magnitude.

The method of increasing distance scale for geospeedometry is applied to a dunite-chromitite contact from the Iwanai-dake mass, Hokkaido. The distance scale is ~10 cm, which is almost 100 times larger than the maximum size of spinel grain used for olivine-spinel geospeedometry. The maximum temperature calculated for a pair of spinel in chromitite and the most Fe-rich olivine in dunite gives 1000°C, suggesting the initial temperature higher than this value. The estimated cooling rate decreases from ~0.001°C/year to 0.3°C/year during cooling from 1000 to 900°C.

Further studies needed to devise useful high temperature geospeedometry for slowly cooled rocks are to find suitable approximation of diffusion in a polycrystalline and multi-phase system and simultaneous inversion of cooling history and magmatic processes.

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冷却地質速度計における高温限界の拡張

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要旨：岩石の冷却速度を推定するために今まで提案された冷却地質速度計には、冷却史を推定することのできない最高温度が必ず存在する。この高温限界は、地質速度計に関わるカインेटイクスと冷却速度によって決まってくる。例えば、かんらん石とスピネル間でのMg-Feの交換反応のカインेटイクスを利用したかんらん石-スピネル地質速度計では、スピネルの一般的最大粒径が数mmであるので、かんらん岩の冷却速度としてごく普通の 10^{-4} °/年というゆっくりした冷却の場合には、高々800°C以下の冷却史しか推定できない。このように低い高温限界をより高くする方法で最も有力なものは、速度計の距離スケールを大きくすることである。鉱物の粒子の大きさには限界があるが、鉱物の量比の変化によってできる岩石のマクロな構造には、このような限界がなく、原理的にはソリダス温度までの冷却史を推定できるはずである。ただし、このような

マクロ構造を冷却速度計として用いるためには、岩石という多粒子・多相系に伴う様々な複雑さや初期条件の不明確さという困難を乗り越えなくてはならない。この論文では、多粒子系の問題を検討した後、かんらん石-スピネル地質速度計を拡張し、北海道岩内岳かんらん岩体産のダナイトとクロミタイト層の境界について、カンラン石のFe-Mg比の変化を利用してより高温の冷却史推定を試みた。6 cmにも及ぶそのFe-Mg比の変化を一次元の拡散係数の組成依存性と冷却速度の時間依存性を考慮した拡散モデルで解析した。このダナイト-クロミタイト地質速度計によって、岩内岳かんらん岩体は約1000°Cから900°Cまで冷却速度が 0.01 °/年以下から約 0.3 °/年程度まで増加したことがわかった。この冷却史から、かんらん岩体は融解過程終了後の冷却に引き続き急速に上昇をしたと考えられる。