# Exsolution in titanomagnetites as an indicator of cooling rates

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ABSTRACT. The scale and nature of the exsolution textures developed in some titanomagnetites have been used to calculate the rate at which the oxides were cooling at the time of exsolution. The cooling rates were calculated by evaluating a kinetic model, which describes the growth of an ulvöspinel-rich lamella in titanomagnetite during exsolution. The model was evaluated both by numerical techniques and by an approximate analytical method.

The cooling rates during titanomagnetite exsolution of the Taberg, Skaergaard and part of the Mt. Yamaska intrusions were calculated to be approximately 130, 12 and 6000 °C per 1000 years respectively. These values are in good agreement with cooling rates calculated from heat flow models of the intrusions.

THE scale of the exsolution textures developed in materials has been traditionally used as a qualitative indicator of the rate at which the materials bearing the microstructures cooled. More recently, however, efforts have been made to quantify the cooling rates which were prevalent during the growth of these exsolution microstructures (e.g. Goldstein and Short, 1967; McConnell, 1975; Yund et al., 1974). In order to achieve this quantification a model for microstructural development must be established, and data on the parameters controlling the formation of the exsolution textures must be available. In previous papers (Price, 1980, 1981a, b) the mechanisms of formation of the exsolution-derived microstructures in titanomagnetites, and the pertinent phase and kinetic data, have been outlined. In this paper, a mathematical kinetic model, intended to describe the growth of the titanomagnetite exsolution texture, will be advanced. This model will be used to obtain quantitative, or at least semi-quantitative, values for the cooling rates of several igneous intrusions from the scale of the exsolution texture developed in their titanomagnetites.

Perhaps the most important of the recent attempts to obtain quantitative cooling rate data from mineral microstructures are those of Wood (1964), Goldstein and Ogilvie (1965), Goldstein and Short (1967) and later authors (see Moren (1978) for a full bibliography), in which the authors have used the available diffusion and phase data for the Fe–Ni–P system to obtain cooling rates of iron meteorites, by solving an equation describing the diffusional development of the kamacite lamellae, usually by numerical methods. Recently Miyamoto and Takeda (1977) have also modelled the development of exsolution lamellae in some clinopyroxenes, and have obtained cooling rates for several stony meteorites. They did not solve their model entirely numerically, however, but used various approximations to obtain a semi-analytical solution to their diffusion-based kinetic model.

In this present paper, both numerical solutions and approximate analytical solutions to the diffusion equation will be used to evaluate the cooling rates of titanomagnetites from the scale of their exsolution microstructures. The specific examples employed to illustrate the use of titanomagnetite exsolution microstructures as indicators of cooling rates will be taken from the Skaergaard intrusion of E. Greenland, the Mt. Yamaska intrusion of Quebec and the Taberg intrusion of S. Sweden. In order to ensure that the values of the cooling rates calculated for these bodies are physically reasonable, the calculated cooling rates will be compared with cooling rates calculated by modelling the heat flow from the intrusions, as they cooled. Norton and Taylor (1979) have carried out detailed heat flow (with ground-water convection) studies of the Skaergaard intrusion, while the smaller and simpler Taberg and Mt. Yamaska intrusions will be modelled by the heat flow solutions for simple bodies, given by Carslaw and Jaeger (1959) and Crank (1956).

### The intrusions studied

The Taberg intrusion is a body of elliptical cross-section (0.9 × 0.6 km), situated to the south of Lake Vatten, Sweden, and has been previously described by Hjelmquist (1950). The intrusion is
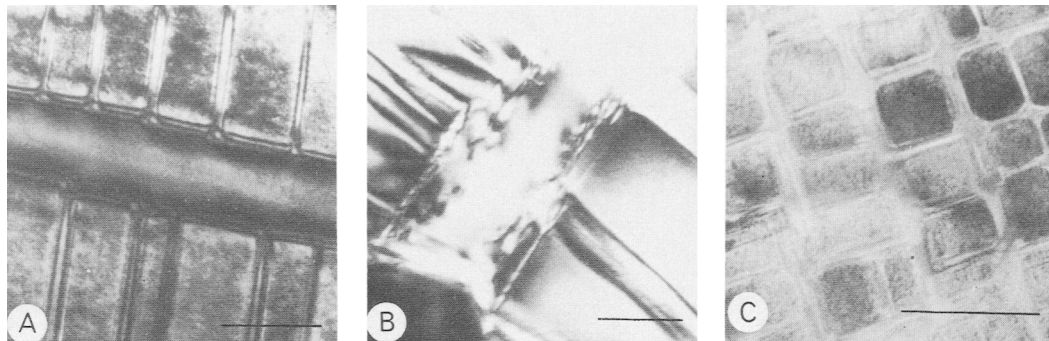
FIG. 1. Electron micrographs of exsolution textures developed in some titanomagnetites (scale bar = 200 nm). (a) A typical ulvöspinel-rich lamella in titanomagnetites from the Taberg intrusion. Minor lamellae, in the process of resorption, subdivide the magnetite-rich regions into blocks. The magnetite-rich regions have developed a characteristic mottling, while the ulvöspinel-rich lamellae are free of such contrast. (b) An ulvöspinel-rich lamella developed in a titanomagnetite from the Skaergaard intrusion. The lamella shows signs of alteration. (c) Blocks of magnetite are separated from each other by lamellae of ulvöspinel in this titanomagnetite from Mt. Yamaska.

largely composed of a feldspathic magnetite-peridotite, which appears to have been intruded into the gneissic country rock in a single igneous event. A small hornfels contact aurole, of width less than 150 m, is exposed around part of the intrusion. The titanomagnetites (no. 54252 in the Harker collection) studied were taken from the centre of the intrusion and have a composition with an ulvöspinel:magnetite ratio of 47:53 (Price, 1980), it being assumed that all other spinel phases have been partitioned into the pleonaste lamellae, which have also developed in this oxide). The oxides show a well-developed exsolution texture (fig. 1a), the detailed nature of which has been discussed by Price (1980).

The titanomagnetites studied from the Skaergaard intrusion came from an olivine-poor gabbro (no. 118792) from the Lower Zone of the intrusion, on Kraemer's Island. The titanomagnetite showed a relatively coarsely developed cloth-texture, and showed slight signs of low temperature titano-maghemitization. From an extensive study of the specimen, by TEM and optically, the median lamellar half-width of the exsolved ulvöspinel-rich phase, appeared to be 0.15 $\mu$m (fig. 1b). The analysis of the oxide indicated a bulk $Fe_2RO_4:FeX_2O_4$ ratio of 42:58. Since there were no exsolution lamellae of pleonaste visible in this specimen this ratio was taken as the 'ulvöspinel:magnetite' ratio.

The microstructure developed in the Skaergaard titanomagnetites shows no interaction with the grain boundaries, and it is therefore thought to have resulted from the coarsening of a spinodal texture (Price, 1980). Similarly the microstructure (fig. 1c) developed in pleonaste-bearing titanomagnetites from Mt. Yamaska (no. 92966), is

thought to have formed by spinodal processes. The samples studied came from a yamaskite rock, which formed part of a dyke associated with this small, complex intrusion in Quebec. The titanomagnetites have an ulvöspinel:magnetite ratio of 48:52 (Price, 1980), and a typical ulvöspinel lamellar half-width of 0.015 $\mu$m.

### The kinetic model

The development of a coarse microstructure is a complex process involving variations in the growth rates of particles, as some particles impinge on each other and some are resorbed. It is currently not possible to outline a detailed kinetic model to describe all of these processes in three-dimensional microstructures. Graham and Kraft (1966) and Lifshitz and Slyozov (1961) have developed models to describe the isothermal coarsening of linear, eutectic intergrowths and particle arrays. However, it is far from clear whether their models can be extended to describe the development of three-dimensional, interconnecting lamellar microstructures, similar to those developed by titanomagnetites. In cooling systems, the rate of development of microstructures is a complicated function of both surface and chemical-free energy changes, but it is generally assumed that the chemical-free energy changes play the dominant role, except perhaps for very slowly cooled systems. This assumption is based upon the relative magnitudes of the energies involved in chemical and surface energy driven processes (e.g. Martin and Doherty, 1976). Following the treatment used by Goldstein and Short (1967), therefore, the model used in this paper to describe the development of exsolution microstruc-

tures in titanomagnetites as a whole will be based simply on the growth of ulvöspinel lamellae. This model ignores the resorption and surface energy effects, and simply describes the diffusion-controlled, isobaric growth of a plane fronted precipitate, with time-dependent boundary conditions. In addition it is assumed that:

(i) the ulvöspinel lamellae grow along a plane front (and not by ledge migration).

(ii) the interface compositions of the ulvöspinel and magnetite-rich phase are given by the equilibrium phase diagram.

(iii) the molar volume difference between ulvöspinel and magnetite can be neglected.

Compared with some of the features of microstructural development indicated above, a model of this type is extremely naïve. However, such a model has been used by Goldstein and Short (1967) and others, with some success, in the no less complex Fe–Ni–P system, and so it is suggested that this model should give at least semiquantitative cooling rate data in this present study of titanomagnetites microstructures.

Initially, an ulvöspinel lamella such as the one described above is expected to have a small finite width, and to be set within a virtually homogeneous matrix. With time, the concentration gradients within the lamella and matrix change as the lamella grows. The evolution of the concentration gradients is a function of the increasing diffusion distance and of the changing equilibrium composition of the lamella-matrix interface, as the system cools. At low temperatures, the gradients within the lamella and the matrix cannot equilibrate, because of the slowness of diffusion at these temperatures, and stranded profiles are retained in both phases. The growth of ulvöspinel lamellae can be described in terms of composition ($C$) and diffusion coefficient ($\tilde{D}$), by Fick's second law of diffusion:

$$\frac{\delta C}{\delta t} = \frac{\delta}{\delta x}\left(\tilde{D}\frac{\delta C}{\delta x}\right) \qquad (1)$$

Analytical solutions to Fick's second law are available for many sets of boundary conditions. However, no analytical solution is available for non-isothermal, lamellar growth, which requires a moving interface and a diffusion coefficient which varies as a function of time (for non-isothermal growth, $\tilde{D}$ is a function of temperature ($T$), and hence time). However, a solution to equation (1) with the above boundary conditions may be obtained numerically, or, by making suitable approximations, the equation and boundary conditions can be modified so that an analytical solution is possible. Both these techniques will be discussed below.

*Numerical solutions.* Numerical solutions to the diffusion equation describing lamellar growth have been obtained by using a computer program kindly provided by Professor J. I. Goldstein. The program, originally written to model Fe–Ni interdiffusion and the development of Widmanstatten structure in meteorites, has been modified in this present study to model Fe–Ti interdiffusion in titanomagnetites during the growth of ulvöspinel-rich lamellae. The essential nature of the program has been described in some detail in Goldstein and Short (1967).

In order to evaluate the program, the following input parameters are required:

(i) the phase relations, in a parameterized form, as a function of $T$ and composition.

(ii) the parameterized form of the diffusion coefficient, as a function of $T$ (i.e. $D_0$ and $\Delta E$, the pre-exponential factor and the activation energy respectively).

(iii) the bulk composition of the system.

(iv) the spacing between adjacent ulvöspinel lamellae ($L$).

(v) the temperature ($T_N$), at which unmixing started.

(vi) the cooling rate, ($s$), of the system.

In the study performed by Goldstein and Short (1967), neither the initial temperature of exsolution ($T_N$), nor the cooling rate ($s$) of the systems were known. Consequently, the values of both of these parameters had to be estimated by a series of trial and error calculations. This technique, however, could not be fully adopted in the calculation of the cooling rates of the titanomagnetites from their exsolution microstructures, because, although composition profiles were available from analytical transmission electron microscopy (TEM), the phase data are not sufficiently accurate to justify a profile-fitting technique, similar to that used by Goldstein and Short (1967). Instead, the temperature $T_N$ was assumed to be the temperature of the coherent spinodal for the bulk system, and was calculated by the method discussed by Price (1981b). From this calculated value of $T_N$ and known or estimated diffusion and phase relations (Price, 1981a, b) a series of calculations were performed with varying values of $s$, the cooling rate, until a good agreement between the calculated and observed lamellar widths was obtained.

*Analytical solutions.* Jost (1952) outlined the exact solutions of the diffusion equation for the isothermal growth of a lamella into an infinite matrix phase so that the lamellar half-width ($W$), after a time $t$, can be expressed as:

$$W = 2\beta(\tilde{D}t)^{0.5} \qquad (2)$$

where $\beta$ is the solution of:

$$\frac{C_m - C_o}{C_1 - C_m} = \pi^{\frac{1}{2}} \beta \exp[\beta^2]\mathrm{erfc}[\beta] \qquad (3)$$

where $C_m$ is the composition of the matrix phase at the planar interface, $C_1$ is the interfacial composition of the lamellar phase, and $C_o$ is the bulk composition of the oxide.

For a non-isothermal system, however, $\tilde{D}$ is a function of $t$, and the above solution is no longer valid. As pointed out by Miyake and Goldstein (1974), Armstrong (1958) has suggested that for systems which have $C_1$ and $C_m$ independent of $T$, the lamellar half-width can be expressed as:

$$W^2 = 4\beta^2 \int_0^t \tilde{D}\, dt \qquad (4)$$

The evaluation of the above integral involves yet another assumption, however, concerning the dependence of $T$ on $t$ during the cooling process. For mathematical convenience, Goldstein and Short (1967) assumed an exponential cooling relationship, $T = T_N \exp\{-ct\}$, over the temperature range of interest. Although such a cooling relationship may not be physically realistic over a large temperature range, its use in cooling-rate calculations does not introduce significant errors, since most ($> 80\%$) microstructural growth occurs within $50\,^\circ\mathrm{C}$ of $T_N$, and, over this range, the difference between an exponential (or even linear) cooling relationship and the probable, natural $T$–$t$ relationship is small. In fact, Elphick (1977, and pers. comm.) has shown that it is virtually impossible to distinguish between microstructures which have formed during exponential cooling and those which formed during linear cooling. $T = T_N - st$, or even when a reciprocal relationship exists between $T$ and $t$, $1/T = 1/T_N + ct$.

On this basis, therefore, a linear cooling relationship was adopted in the evaluation (4), since its use produces a mathematically tractable integral, while the use of the other $T$–$t$ relationships produces less convenient integrals. It is important to note that, since the lamellar half-width in equation (4) is dependent upon the integral of the diffusion coefficient with respect to time, it is not possible to deduce the exact thermal history of materials which have undergone a complex $T$–$t$ path, and only average thermal histories can be obtained for these materials.

By adopting the linear cooling $T$–$t$ relationship and using the approximations discussed by Armstrong (1958), the lamellar half-width can be conveniently expressed in terms of the cooling rate, $s$:

$$W^2 = \frac{4\beta^2 RT_N^2 D_0}{s\Delta E} \exp\{-\Delta E/RT_N\} \qquad (5)$$

Therefore, from known or measured values of $\beta$, $T_N$, $D_0$, $\Delta E$, and $W$, a value of $s$ (in units of $^\circ\mathrm{C}$ per sec) can be calculated.

As pointed out above, this approach is only strictly valid if $\beta$ is not a function of $T$. In a system with a symmetrical solvus, this condition is only true at the centre of the solid solution (i.e. at $C_o = 0.5$, where $C$ is expressed in terms of mole fractions). However, $\beta$ is only a slowly varying function of $T$ in the range $0.3 < C < 0.7$, and so the errors introduced by making the approximation that $\beta$ is independent of $T$, are small.

*Results*

*Numerical solution.* The values of the parameters used to calculate the cooling rates of the Taberg and Skaergaard intrusions and the yamaskite dyke are given in Table I, where cooling rates have been calculated for a range of lamellar half-widths. The average cooling rates calculated from these parameters correspond to a cooling rate for the Taberg intrusion, at 652K, of $120\,^\circ\mathrm{C}$ per 1000 years; to a cooling rate for the Skaergaard intrusion, at 638.5K, of $14\,^\circ\mathrm{C}$ per 1000 years; and to a cooling rate for the yamaskite dyke of $6700\,^\circ\mathrm{C}$ per 1000 years.

The composition profile measured within an ulvöspinel-rich lamella from the Taberg specimen is shown in fig. 2. The analyses were made with a Philips EM400 electron microscope, with EDAX analytical facilities, and the compositions were calculated, from the measured X-ray intensities, by the usual ratio method (Cliff and Lorimer, 1972). The relative positions of the analysed points were obtained from the contamination spots which developed on the lamella during analysis. The indifferent agreement between the calculated and measured profiles (fig. 2) is thought to reflect the uncertainties in the titanomagnetite phase and

TABLE I. *Values used in the numerical evaluation of the diffusion model*

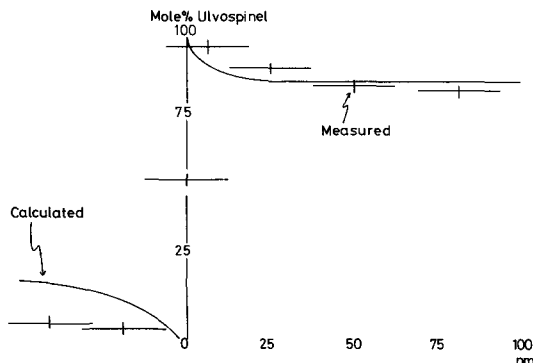|  | Taberg | Skaergaard | Yamaskite |
|---|---|---|---|
| $C_o$, mole fraction ratio, $U:M$ | 47:53 | 42:58 | 48:52 |
| $T_n$, initiation temperature (K) | 652 | 638 | 652 |
| $W$, half width (cm) | $0.9 \times 10^{-5}$ | $1.5 \times 10^{-5}$ | $0.15 \times 10^{-5}$ |
| $L$, interlamellar spacing (cm) | $2.5 \times 10^{-5}$ | $4.5 \times 10^{-5}$ | $0.41 \times 10^{-5}$ |
| $s$, cooling rate ($^\circ\mathrm{C}$ per 1000 y) | 140 | 10 | 6000 |
| $W$, half width (cm) | $1.0 \times 10^{-5}$ | $1.2 \times 10^{-5}$ | $0.12 \times 10^{-5}$ |
| $L$, interlamellar spacing (cm) | $3.0 \times 10^{-5}$ | $3.7 \times 10^{-5}$ | $0.30 \times 10^{-5}$ |
| $s$, cooling rate ($^\circ\mathrm{C}$ per 1000 y) | 100 | 17 | 7500 |

Mole% Ulvospinel



FIG. 2. A plot of the calculated composition profile within an ulvöspinel-rich lamella from the Taberg intrusion is compared with the compositions measured by analytical TEM. The relatively coarse-scale diameter of the electron beam used in the analysis means that a definitive comparison between the calculated and measured profiles cannot be made. The results are, however, in fair overall agreement within the lamellar phase, although the agreement within the magnetite phase is less good.

**TABLE II.** *Values of the parameters used to calculate s*

|  | Taberg | | Skaergaard | | Yamaskite | |
|---|---|---|---|---|---|---|
| $\beta$ | 0.35 | $\pm 0.03$ | 0.25 | $\pm 0.03$ | 0.35 | $\pm 0.03$ |
| $\ln(\beta^2)$ | $-2.10$ | $\pm 0.17$ | $-2.77$ | $\pm 0.21$ | $-2.10$ | $\pm 0.17$ |
| $\Delta E$ (kcal mole$^{-1}$) | 49.8 | $\pm 1.5$ | 49.8 | $\pm 1.5$ | 49.8 | $\pm 1.5$ |
| $\ln(\Delta E)$ | 10.8 | $\pm 0.05$ | 10.8 | $\pm 0.05$ | 10.8 | $\pm 0.05$ |
| $\ln(D)$ | $-44.6$ | $\pm 0.06$ | $-45.4$ | $\pm 0.07$ | $-44.6$ | $\pm 0.06$ |
| $\ln(W^2)$ | $-23.2$ | $\pm 0.3$ | $-22.2$ | $\pm 0.3$ | $-26.8$ | $\pm 0.3$ |
| $\ln(s)$ | $-19.3$ | $\pm 0.58$ | $-21.8$ | $\pm 0.63$ | $-15.7$ | $\pm 0.58$ |
| $s_{MIN}$ (°C per 1000 y) | 75.5 | | 5.72 | | 2700 | |
| $s_{MAX}$ | 241.0 | | 20.2 | | 8700 | |
| $\bar{s}$ | 135.0 | | 10.7 | | 4870 | |

The units of the parameters quoted in logarithmic form are $\Delta E$ in kcal mole$^{-1}$, $D$ in cm$^2$s$^{-1}$, $W$ in cm and $s$ in °C per sec.; $\beta$ is dimensionless. The calculated variation in $s$ is based only on the numerical uncertainties in $\beta$, $\Delta E$, $D_0$ and $W$. The uncertainty in $s$ is probably larger (see text for details).

kinetic data used in the calculations. The mismatch between the calculated and measured profile within the magnetite-rich phase may reflect the effect of another ulvöspinel-rich lamella upon the magnetite-rich region.

*Analytical evaluation.* The rates of cooling of the three intrusions were calculated by evaluating $s$ from equation (5), using the values of $T_N$, $D_0$ and $\Delta E$ used in the evaluation of the numerical solution, and median values of $W$, obtained from several measurements of electron and optical micrographs. Values of $\beta$ were obtained from the bulk composition of the oxides and the equilibrium composition of the coexisting oxides at the temperature of unmixing. (Values used in these calculations, and their estimated uncertainties, are given in Table II.)

The cooling rates of the Taberg, Skaergaard and yamaskite intrusions were calculated to be 135 °C per 1000 years, 10.7 °C per 1000 years and 4870 °C per 1000 years respectively. Considering the uncertainties in the calculations (see below), the agreement between the results of the approximation and numerical techniques is excellent. It is consequently suggested that the approximations made in the derivation of equation (5) are valid, at least for the examples considered here.

*Assessment of errors.* The errors associated with the calculations outlined above, arise from two main sources:

(i) The magnitude of the errors resulting from the uncertainties involved in the measurement of the parameters used to calculate the cooling rates of the Taberg, Skaergaard and yamaskite intrusions are shown in Table II. Errors in the term $\beta$

arise from the variation in the composition of the oxides as measured by the electron microprobe, errors in $W$ arise from the range of measured lamellar widths, and the error in $D_0$ and $\Delta E$ are those found from experiment (Price, 1981a).

These errors propagate through the above calculations, so that the estimated errors in the value of the logarithm of $s$ (the cooling rate in °C per sec.), calculated from the approximation technique, is $\pm 0.58$, for the Taberg and the yamaskite intrusions, and $\pm 0.63$ for the Skaergaard intrusion. Thus, the expected range in the calculated cooling rate for the Taberg intrusion is between 230 and 80 °C per 1000 years; for the yamaskite dyke it is between 8700 and 2700 °C per 1000 years; and for the Skaergaard intrusion the expected range is between 20.2 and 5.7 °C per 1000 years. A similar range of uncertainty is expected for the cooling rates obtained from the numerical evaluation of the diffusion model.

(ii) The second source of error, and doubtless the most significant, arises from the possible inapplicability of the values of $D_0$, $\Delta E$ and $T_N$ used in the calculations.

The $D_0$ and $\Delta E$ values used in the calculations were those obtained by Price (1981a) from homogenization experiments performed on naturally exsolved titanomagnetites. Although they are the only currently available data for Fe–Ti interdiffusion in moderately ulvöspinel-rich titanomagnetites (ulvöspinel content > 25%), they have several shortcomings when applied to exsolution modelling in natural titanomagnetites. These include the facts that they (i) were performed 200–300 °C above the temperature of exsolution, (ii) were unable to take into account the effect of $P_{O_2}$ on diffusion rates, and (iii) were unable to take into account the role of pressure on diffusion rates.

Although none of these factors are expected to have a major effect on the results obtained from the materials studied above, they must add considerably to the uncertainties in the results, but to an unquantifiable extent.

As concluded by Price (1981b), the value of the consolute temperature of the titanomagnetite solvus is less than 455 °C and, from thermodynamic data, may be approximately 440 °C. However, as this temperature has not been strictly defined, it must also add to the uncertainty in the calculated cooling rate values. On this basis, the values of the cooling rates calculated above are likely to be maximum cooling rates, since if the solvus crest is at a temperature lower than 450–440 °C the calculated cooling rates would all be smaller than those values quoted above. A lowering of the temperature of the solvus crest by 10 °C produces a decrease in the calculated cooling rate of a factor of two.

*Heat flow models*

Norton and Taylor (1979) have studied several models of the magma-hydrothermal system of the Skaergaard intrusion, and have obtained quantitative predictions of the variations of temperature with time within the intrusion, as well as reproducing the likely oxygen isotope variation within the intrusion and country rock. They found that for their model (S1), the average cooling rate of the intrusion, at temperatures of 400 °C, was 2.2 °C per 1000 years. However, for a region in the Middle Zone of the intrusion, near the margins of the intrusion (a similar location to that of the Skaergaard specimen studied above), they calculated that the cooling rate varied from 15 to 3 °C per 1000 years, in the temperature range 550 to 375 °C. Applying another model (S2) to the system, they found that the cooling rates in this region were, however, uniformly 2–3 °C per 1000 years. Considering the uncertainties in the microstructurally-based kinetic model outlined above, the cooling rate of the Skaergaard intrusion calculated from the scale of the titanomagnetite microstructure is in fair agreement with that calculated by Norton and Taylor (1979).

The thermal history of the Taberg intrusion can be modelled (but with less accuracy than that of the Skaergaard) by solving the heat-flow equation for a cylindrical body. Although the Taberg is not perfectly circular in cross-section, the heat-flow solution for a cylinder will at least be a reasonable approximation to the conductive heat loss of the Taberg intrusion as it cooled from magmatic temperatures. This model does not take into account the loss of heat by hydrothermal convection, which may cause a body to cool at a rate

which is about twice as fast as it would be if it had cooled simply by convective heat loss (Norton and Taylor, 1979).

The solution to the heat flow equation from the core of a cylinder, is given by Crank (1956) as:

$$T = T_0(1 - \exp\{-a^2/4Kt\}) \qquad (6)$$

where $T$ is the temperature at the centre of the cylinder, after time $t$, $T_0$ is the initial temperature difference between the cylinder and its surroundings, $a$ is the radius of the cylinder and $K$ is the diffusivity, which typically for rock is equal to 0.012 $cm^2s^{-1}$ (Carslaw and Jaeger, 1959). From equation (6), the cooling rate of the centre of a cylinder can be calculated.

Assuming that the initial temperature of the intrusion was 1100 °C and that of the country rock was 100 °C, then for cylindrical intrusions of radii 0.3 and 0.45 km (the limiting radii of the Taberg intrusion), the cooling rates at 380 °C ($T_N$ for exsolution) are 233 and 104 °C per 1000 years respectively.

Similar calculations to those above can be made to estimate the expected cooling rate of the yamaskite dyke from Mt. Yamaska. Unfortunately, the exact size of the dyke from which the specimen was taken is unknown. However, dykes in this area are generally less than 50 m wide. Jaeger (1959) has calculated the likely cooling curves for dykes of various thicknesses and, from his graphs, it is expected that the cooling rate of a dyke, at about 500–300 °C, is given by:

$$dT/dt = -8.3 \times 10^6/d^2 \qquad (7)$$

where $d$ is the dyke thickness, in metres. For a dyke of 50 m width, the cooling rate, at $\sim 400$ °C, is likely to be approximately 3300 °C per 1000 years; again a result in good agreement with the cooling rates calculated from the titanomagnetite microstructures.

Although the above cooling calculations, involving heat flow modelling, are of varying sophistication, it appears that they are in broad agreement with the cooling rates calculated from the scale of titanomagnetite microstructures. This agreement may be to some extent fortuitous, considering the approximations made in both types of calculations. Nevertheless, it has been shown that the cooling rates calculated from titanomagnetite microstructures are at least semiquantitative. Perhaps further progress could be made in the field of modelling microstructural development if a detailed systematic study of the titanomagnetite microstructures developed in oxides 'from a specific, well-characterized intrusion (e.g. the Skaergaard) was performed, and the variation of the microstructures observed correlated with the expected variations in the cooling rates within the intrusion.

*Assessment of the kinetic model and its solutions*

As suggested above, the model proposed, namely that the evolution of a complex three-dimensional microstructure can be described by the growth of a simple lamella into a matrix phase, is highly approximate. However, it is currently not obvious how a more sophisticated model could be developed. The major problems in developing a more accurate model lie in (i) modelling three-dimensional diffusion fields and (ii) determining the relative importance of chemical and surface-energy driving forces in cooling systems. As discussed above, it would seem reasonable that the chemical free energy would serve as the major driving force for microstructural change, when cooling rates were relatively rapid and overall chemical equilibrium was never approached. Surface energy, however, would be expected to be more important in the later stages of growth, in more slowly cooled systems. It is not currently possible to quantify the relative importance of these effects. However, their role should always be borne in mind when the kinetic model is applied to oxides from more slowly cooled systems.

In addition to the shortcoming of ignoring surface energy effects, a major assumption, made in this model, is that one-dimensional lamellar growth proceeds at similar rates to that of three-dimensional microstructural development. In theory, the growth of three, mutually orthogonal planar lamella should be modelled, in order to reproduce more accurately the development of the titanomagnetite microstructures (this would still ignore the effect of lamellar resorption during coarsening). A calculation of this sort would, however, be mathematically very complex. Thus, it is concluded that the model adopted in this study is not entirely satisfactory, yet from the results of previous studies and from the findings of this study, it appears that this simple model can produce reasonably accurate results.

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