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# Time-dependent Soret transport: Applications to brine and magma

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## ABSTRACT

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We have developed a numerical model which simulates the coupling of a compositional field to a time-dependent temperature field and have applied it to natural salt and magma systems. An implicit central difference numerical approach is used in which the coupling of mass and heat is taken into account by chemical and thermal diffusion mass fluxes and a conductive heat flux. Unique in this analysis is the time dependency of the thermal regime and the role of transient thermal gradients in enhancing mass transport. Zero mass flux at the two end boundaries of a Soret cell is required in modeling certain thermal diffusion experiments for deriving the Soret coefficients of brines. For the case of an evolving temperature field, the numerical analysis predicts a transient period where thermal diffusion creates an unexpected enrichment at the hot end of the Soret cell and a depletion at the cold end. For a fixed linear temperature gradient, all NaCl enrichment normally occurs at the cold end of the cell. In a second application, several initial and boundary conditions are incorporated in the one-dimensional model in order to evaluate a variety of magmatic boundary layer scenarios. The results of the magmatic system model indicate that minimal chemical fractionation will occur as the thermal field propagates through the boundary layer.

## 1. Introduction

The mass transport of chemical species in response to a temperature gradient, often referred to as thermal or Soret diffusion, can lead under certain conditions to the efficient separation of chemical constituents (Jones and Furry, 1946; Powers, 1962; Tyrell and Harris, 1984). Thermal diffusion processes have been observed in a variety of physicochemical conditions and materials: gases (Jones and Furry, 1946), aqueous solutions (Chipman, 1926; Agar and Turner, 1960; Snowdon and Turner, 1960a, b) and silicate melts (Walker et al., 1981; Leshner et al., 1982; Leshner, 1986; Leshner and Walker, 1991). The extent of chemical fractionation in any of these systems will be

primarily a function of thermal gradient, temperature, composition, geometry and, of course, time.

The coupling of heat transfer and mass transport processes is of considerable significance in the safe isolation of radioactive nuclear wastes in a geological repository (Carnahan, 1984). Thermal diffusion and, to a lesser extent, thermal migration are the principal mechanisms responsible for the migration of fluid inclusions in halite, one of the geologic host media currently under investigation. Transportation of corrosive brines up a thermal gradient may eventually result in the leaching of radioactive species from waste containers in response to a thermal gradient created by the decay and cooling of the radio-

active waste (Pigford, 1982). The hotter end of the fluid inclusion will become undersaturated with respect to sodium chloride and therefore will lead to the dissolution of the halite. Aqueous sodium chloride is transported by thermal diffusion to the cooler end of the inclusion where supersaturation and precipitation of halite occurs. The result of this sequence of thermodynamic and kinetic processes is the net migration of the brine inclusion towards the heat source. Chou (1982), Olander et al. (1982) and, more recently, Stein and McTigue (1992) provide details of this unique coupling of heat and mass fluxes.

The significance of thermal diffusion has also been recognized in the physicochemical processes associated with nuclear fusion reactors (Longhurst, 1985) and the compositional changes associated with seawater (Caldwell, 1973; Caldwell and Eide, 1981). Thornton and Seyfried (1983) have experimentally investigated the contribution of thermal diffusion to the transport of chemical species in the saturated solutions associated with pelagic clays. Cussler (1984) provides a comprehensive examination of the role of thermal diffusion in aqueous solutions and fluid systems and discusses the contribution of convective heat transfer in these systems.

Sizable temperature gradients are created at the margins of magmatic systems with the intrusion of magma into cooler host rock. The magnitude of these gradients and their residence time will determine the effective role of thermal diffusion in the fractionation of chemical species in the silicate melt within the boundary layer (see Carrigan and Cygan, 1986). Numerous researchers (Hildreth, 1979, 1981; Schott, 1983; Koyaguchi, 1989) have suggested that thermal diffusion (Soret fractionation) may be a significant process in contributing to the chemical zonation of magma bodies. However, experimental determinations of the Soret coefficients for a variety of silicate melt compositions (Ponander and Mahood, 1984; Leshner, 1986; Leshner and Walker,

1986; Pugin and Bagdasarov, 1987; Ponander, 1988) suggest the magnitude of the Soret terms to be extremely small and, moreover, the Soret coefficients are often of the opposite sign for what would be required for the chemical fractionations observed in the crystallized magmas. Walker and Delong (1982, 1984) determined that Soret fractionation is, at best, a small effect and would only be preserved in the gabbros associated with mid-ocean ridge basalts. Several researchers (Michael, 1983; Cameron, 1984; Stix et al., 1988) have indicated that crystal fractionation processes, and not Soret processes, can account for the observed chemical separations in rhyolitic magmas. Leshner and Walker (1988) and Pugin (1988) have examined the subtle contributions of Soret diffusion in conjunction with the crystallization of mafic magmas.

Recently, Carrigan and Cygan (1986) presented the results of several thermal diffusion models in their attempt to quantify the extent of fractionation associated with thermal diffusion processes. Their results indicate that even for extreme thermal gradients (on the order of  $100^{\circ}\text{C cm}^{-1}$ ) the magma residence times and chemical separation amounts were insufficient to contribute to chemical fractionation of magma. Additionally, the results of their model taking into account the convection of magma in thermal boundaries suggest an even smaller extent of chemical fractionation by thermal diffusion. Carrigan and Cygan (1986) briefly discuss the significance of an early transient period during evolution of a thermal field; thermal diffusion during the early stages of magma intrusion, when larger thermal gradients would exist, may possibly lead to greater chemical fractionation.

This broad range of thermal and chemical conditions for which Soret transport has been invoked suggests the need for a general model capable of evaluating the magnitude of the Soret effect. Therefore, we have developed a model to examine the transient nature of Soret diffusion. In this paper we present the results

of several numerical simulations of two unique coupled mass and heat transport processes using the generalized model. We first present a theoretical discussion of thermal diffusion and the basics of the general numerical model. We then apply the model to an aqueous system in order to simulate the conditions of an experiment designed to measure the Soret coefficients of brines. The model is then used to examine the transient state of a thermal boundary of a magma body and determine the extent of chemical separation.

## 2. Theory

Thermal diffusion processes are best analyzed using a phenomenological approach and the fundamental tenets of the theory of irreversible thermodynamics (see DeGroot and Mazur, 1962; Kreuzer, 1981). This general method of analyzing nonequilibrium processes examines the rate of entropy production for a chemical system by the bilinear combination of fluxes and forces. The total flux  $J_i$  of any particular physicochemical entity such as mass, heat, electrical charge, etc., is presented as a linear combination of all contributing forces  $X_j$ :

$$J_i = \sum_j L_{ij} X_j \quad (1)$$

The proportionality terms  $L_{ij}$  are the phenomenological coefficients. These terms contain the more familiar kinetic rate terms such as the chemical diffusion coefficients for mass flux and thermal diffusivities for heat flux.

In order to treat thermal diffusion processes in the formalism of nonequilibrium thermodynamics, it will be necessary to examine eq. 1 for the case of mass flux which results from the coupling of two forces, one involving mass and the other heat. The mass force is related to the gradient of chemical potential while the heat force is equivalent to the negative gradient of the temperature:

$$X_1 = -V\mu \quad (2)$$

$$X_2 = -VT \quad (3)$$

These two equations are similar to the usual flux equations of Fick and Fourier for mass and heat transfer processes, respectively. However, eq. 1 provides for the coupling of these two forces to produce the total mass flux or heat flux. Combining eqs. 2 and 3 into eq. 1 results in the following total flux for mass in a one-dimensional system:

$$J_{\text{mass}} = -D \frac{\partial C}{\partial x} - D\sigma C \frac{\partial T}{\partial x} \quad (4)$$

This mass flux equation is presented with the more familiar terms  $D$ , the chemical diffusion coefficient, and  $C$ , the molar concentration. A kinetic term  $\sigma$ , the Soret coefficient, is also introduced to define the extent of coupling of the thermal gradient to the mass flux. The Soret coefficient is formally defined as the ratio of the thermal diffusion coefficient  $D_T$  to the isothermal diffusion coefficient  $D$ :

$$\sigma = D_T/D \quad (5)$$

It is customary to use  $\sigma$  rather than  $D_T$  in evaluating thermal diffusion processes.

Analogous to the mass flux expressed by eq. 4 is the heat flux generated by coupling the mass and heat forces. Eq. 6 provides the resulting expression for heat flux generated by combining eqs. 2 and 3 into eq. 1:

$$J_{\text{heat}} = -D_D C T \frac{\partial C}{\partial x} - \kappa \frac{\partial T}{\partial x} \quad (6)$$

The phenomenological coefficients for the heat flux include the thermal diffusivity  $\kappa$  and the Dufour coefficient  $D_D$ . The latter term describes the Dufour process by defining the extent of coupling of the concentration gradient to the heat flux. The Dufour and Soret (thermal diffusion) effects are reciprocal processes. In the following discussion we will only be concerned with the coupling described by eq. 4; the Dufour effect will not be considered.

The mass flux associated with Soret diffusion presented by eq. 4 involves two terms, an isothermal diffusion term (ordinary diffusion) and a nonisothermal term (thermal diffusion). For steady-state conditions ( $J_{\text{mass}}=0$ ) these two terms can be equated to provide a simple differential equation that is readily solved. Therefore most previous analyses of thermal diffusion processes have utilized the steady-state solution. As a system approaches steady state, thermal diffusion will generate a compositional gradient which will tend to be homogenized by ordinary diffusion with an opposite mass flux. However, at steady state the opposing mass fluxes will be equivalent and the compositional gradient will remain fixed as long as the thermal field does not change. The steady-state concentration profile will be linear if the temperature profile is linear and the coefficients of eq. 4 remain constant. However, this situation is unlikely in real systems due to the temperature dependence of the chemical potential. Powers (1962) and Carrigan and Cygan (1986) provide discussions of the usefulness and limits of the steady-state approximation. However, for the present investigation we are concerned with the transient nature of mass flux and, in addition, the effect of nonlinear and transient temperature fields upon the limits of Soret fractionation and separation.

To examine the transient response of thermal diffusion, we require a solution to eq. 4 under the constraint of mass conservation for the chemical system. The following one-dimensional differential equation provides this requirement:

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} \quad (7)$$

where  $J$  is the mass flux associated with thermal diffusion given by eq. 4. Combining eq. 7 with eq. 4 provides the general one-dimensional partial differential equation for thermal diffusion:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} + D\sigma C \frac{\partial T}{\partial x} \right) \quad (8)$$

Several analytical non-steady-state solutions to eq. 8 are available (Jones and Furry, 1946; Bierlein, 1955; DeGroot and Mazur, 1962). However, these solutions are limited by the approximations and assumptions inherent in their derivation. More importantly, there is a limitation imposed by the constraint of a linear and static temperature gradient that is required in all of the analytical models.

To overcome the difficulties in applying these analytical solutions to magmatic (Schott, 1983; Carrigan and Cygan, 1986) and aqueous (Cygan and Jarrell, 1992) systems, we have developed a generalized one-dimensional numerical model that solves eq. 8 for a variety of initial and boundary conditions. External constraints on the temperature fields associated with the chemical system are readily incorporated. Therefore, the effects of nonlinear temperature gradients and evolving temperature fields upon thermal diffusion and Soret fractionation can be examined.

The numerical scheme uses implicit central differences to solve eq. 8 and utilizes a Gauss elimination method to solve for concentration as a function of time and position (see Smith, 1978; Press et al., 1986). Time-dependent temperature fields are determined by analytical solutions to the following parabolic partial differential equation describing conductive heat flow in a one-dimensional system:

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} \quad (9)$$

Several initial and boundary conditions are implemented for the temperature field in solving eq. 9, depending upon the geometry and thermal constraints in the application. These results are directly input into the numerical scheme for solving eq. 8 at each time step. The numerical model can easily accommodate the temperature dependency of the diffusion and Soret coefficients; however, these terms were

maintained at constant values in the present applications.

All calculations were performed using FORTRAN-77 code (IBM® Professional FORTRAN) and an IBM® PS/2 Model 80 personal computer. First, the appropriate thermal field model was selected and coded into a subroutine. Several checks on the time increment and spatial discretization were performed to ensure numerical stability and provide the appropriate resolution for the application. Numerical results obtained for static linear temperature fields were in agreement with earlier analytical and numerical calculations. Execution time varied for each application and was dependent upon time and spatial resolution. However, final results were usually obtained after < 5 min. of computational time.

### 3. Application to brine systems

The thermal diffusion of aqueous species, primarily NaCl, is of considerable concern for research on the migration of fluid inclusions in halite. The lack of appropriate experimental data for NaCl-H<sub>2</sub>O Soret coefficients has led to some uncertainty in evaluating migration models for fluid inclusions (Chou, 1982) and bears directly on the suitability of siting radioactive waste repositories in salt. Experimental determinations of Soret coefficients for concentrated aqueous solutions, polyelectrolytes, and brines have usually relied upon the measurement of concentration profiles of solutions in Soret cells by a conductimetric or an interferometric method (see Agar and Turner, 1960; Snowdon and Turner, 1960a, b; Caldwell, 1973; Hawksworth et al., 1977; Lobo and Teixeira, 1982; Cygan and Jarrell, 1992).

Normally, the Soret experiment involves imposing a thermal gradient upon a small enclosed volume (1 ml) of solution by two constant-temperature reservoirs on either side of the solution. This so-called Soret cell is maintained in a vertical position with the hot end on top and the cold end on the bottom in order

to maintain thermal stability and avoid thermal convection. Soret coefficients are derived from an analysis of the refractive index or electrical conductivity change of the cell as a function of time. Eliminating convection in the Soret cell is critical for deriving accurate Soret coefficients (see Henry and Roux, 1987).

An additional concern in the Soret experiment is the manner in which the thermal gradient evolves relative to the development of the concentration gradient of the chemical system. Normally, researchers have assumed that thermal conduction in the solution is so efficient that a linear temperature profile is quickly generated across the solution in the cell. Therefore, it is assumed that there is little or no time for thermal diffusion to create a compositional gradient within the solution while the linear thermal gradient is created. However, these assumptions are untested and have led to some ambiguity as to what is the appropriate zero time for a Soret experiment. Large thermal gradients do exist during the early period of thermal conduction as the solution evolves from a homogeneous temperature distribution to the steady-state linear thermal field. It is not known how much thermal diffusion occurs in the solution as the thermal field evolves.

We can respond to this question by examining the numerical solution to eq. 8 with the temperature field provided by the appropriate analytical solution of eq. 9. The boundary conditions for the thermal diffusion equation (eq. 8) are that of zero mass flux at either end of the system. These can be obtained by setting eq. 4 to zero at  $x=0$  and  $x=a$  ( $a$  is the length of the cell). We also assume a homogeneous initial distribution of NaCl in the solution, although the numerical model is generalized to accept any initial concentration distribution.

The analytical model of Carslaw and Jaeger (1959) [equation (III-1)] provides the temperature distribution of the Soret cell as a function of time. It is a solution to eq. 9 for a system with fixed end temperatures and an initially homogeneous temperature distribu-

tion. The temperature distribution is presented in Fig. 1 for selected times. In order to simulate the experimental conditions of Cygan and Jarrell (1992) we have constrained the end temperatures for the model to  $45^\circ$  and  $35^\circ\text{C}$  to produce a final linear thermal gradient of  $10^\circ\text{C cm}^{-1}$  for the 1-cm-long cell. A steady-state thermal profile is attained just 80 s after imposing the end temperature values. The results of the thermal conduction model indicate that substantial, symmetrical thermal gradients at the cell margins tend to decrease in magnitude as the thermal system tends towards steady state. In fact, the earliest stage of the thermal transfer process can be characterized by infinite temperature gradients at the ends of the cell. In order to determine the extent of thermal diffusion for these gradients, which occur over fairly short time periods, we must now examine the coupling of the thermal field to eq. 8 and the resulting numerical solution.

The results of the numerical calculations for an initially homogeneous 0.5 N NaCl brine are provided in Fig. 2. Soret and isothermal diffusion coefficients were set at  $3.0 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$  and  $3.0 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , respectively (Cygan and Jarrell, 1992). The early-stage calculations were obtained with a time step of 1 s, while the later stages were determined with a time step

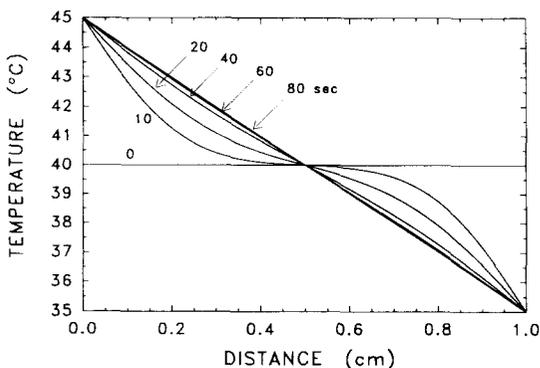


Fig. 1. Evolution of temperature field for an aqueous sodium chloride solution in a Soret cell with fixed end temperatures. The analytical results are derived using equation (III-1) from Carslaw and Jaeger (1959).

of 5 s. A spatial resolution of 0.01 cm was used for all of the calculations. Several different time and spatial steps were used to determine the numerical stability of the solutions; all of the results were in good agreement. The numerical model, when examined with a constant linear thermal gradient, was in agreement with the analytical solution provided by Bierlein (1955) for times greater than  $t_{ss}/5$  ( $t_{ss}$  is the time to reach steady state); only approximate analytical solutions are available for the early-stage thermal diffusion process (see Cygan and Jarrell, 1992).

Fig. 2 exhibits three stages of the evolution of the concentration profile of the NaCl brine. The late-stage results depict the typical response of thermal diffusion in reaching a steady state; the thermal profile has attained a steady-state linear value of  $10^\circ\text{C cm}^{-1}$ . The positive value for the Soret coefficient indicates mass transport down the thermal gradient. There-

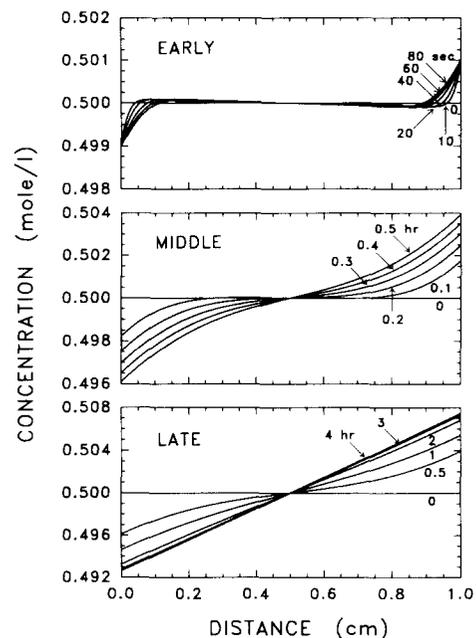


Fig. 2. Evolution of compositional field for an aqueous sodium chloride solution in a Soret cell for three different stages of development as induced by the time-dependent temperature field with fixed end temperatures presented in Fig. 1. Note that each stage is plotted with a different concentration scale.

fore we observe enrichment of the NaCl at the cold end and depletion at the hot end. The thermal diffusive flux is greater than that of ordinary (isothermal) diffusion and therefore the compositional gradients increase with time as noted for the time intervals from 0.5 to 2 hr. Ultimately, a steady state is approached at  $\sim 4$  hr. where the ordinary diffusive flux is equivalent to the thermal diffusive flux. As long as the thermal gradients remains constant this steady-state compositional field will not change.

The early-stage results depicted in Fig. 2 are somewhat more interesting than the later stages and represent the unique behavior of the compositional field in response to the thermal field evolution depicted in Fig. 1. As opposed to the fixed linear thermal field associated with the late stage, the initial response of the system is characterized by large, transient and nonlinear temperature gradients. This results in a large flux of material near the margins, which is however restricted from advancing across the interior of the cell where the smaller temperature gradients occur. The result is a temporary reversal of enrichment/depletion from that which would be expected for a fixed linear temperature profile. After 80 s the temperature profile reaches its steady state and the concentration profile continues to evolve. The enrichment/depletion reversal dissipates after 0.1 hr. as shown in the middle stage of Fig. 2. Artifacts of the transient thermal profiles are completely removed after 0.4 hr.; solutions of the numerical models for both fixed linear and transient thermal fields agree after this time.

These results emphasize the importance of examining Soret experiments throughout the entire thermal diffusion process. The effects of minor thermal perturbations leading to nonlinear thermal fields may ultimately affect the net directional flux of material. However, the extent of enhanced enrichment/depletion of the NaCl content of the brine as predicted by this numerical model is beyond the sensitivity

of the conductimetric method used by Cygan and Jarrell (1992).

#### 4. Application to magmatic systems

The possibility of enhanced Soret fractionation of silicate melt in a stable thermal boundary layer has been examined by Carrigan and Cygan (1986) for steady-state conditions. However, no complete analysis has been performed for the transient stage, especially during the development of the thermal field at the magma margin. A transient, or non-steady state, model would simulate the propagation of the thermal field through the hot magma parcel as it cools in contact with the host rock. In order to quantify the attainable limits of chemical separation in this magma, we use the previous numerical scheme to solve the thermal diffusion equation (eq. 8) coupled with the appropriate analytical solution of eq. 9. By examining the evolution of a non-convective regime where residence times of magma are significant, we hope to determine the maximum possible amount of Soret fractionation. As with the previous study (Carrigan and Cygan, 1986) the model will incorporate the most liberal estimates for the input parameters in order to provide the most conducive conditions for Soret separation.

The thermal boundary layer is defined as the volume of magma that is located at the margin of the magma body near the host rock and characterized by compressed isotherms and large thermal gradients. Two thermal models were chosen to describe the thermal boundary layer at the vertical margin for the intrusion of magma of rhyolite rheology and composition. The magma is characterized by a density of  $2.6 \text{ g cm}^{-3}$  and a thermal diffusivity of  $3.8 \cdot 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ . The thermal models are semi-infinite solutions of eq. 9: the first maintains a constant boundary temperature [equation (4-58) of Eckert and Drake, 1972]; the second maintains a constant heat flux at the

boundary [equation (4-93) of Eckert and Drake, 1972].

Fig. 3 presents the results of the first thermal model where the temperature of the magma at the boundary with the host rock has been fixed at 700°C. The magma, initially at a homogeneous temperature of 1000°C, intrudes the host rock at time zero then conductively cools through the thermal boundary layer. Isochrons are provided for times up to 5000 hr. after intrusion. The thermal gradients at the margin vary from an infinite value at zero time, via 12°C cm<sup>-1</sup> at 10 hr., to 0.65°C cm<sup>-1</sup> at 5000 hr.

The extent of Soret fractionation that accompanies the transient thermal field is obtained by coupling the thermal model with the thermal diffusion equation. The numerical scheme for the magmatic applications requires a slightly different set of boundary conditions compared to those used to model the aqueous solution in the Soret cell. The boundary with the host rock is characterized by zero mass flux and, therefore, indicates a magma system with no host rock infiltration or assimilation; the magma and host rock are unreactive with one another. The other boundary, toward the interior of the magma body, is characterized by a boundary condition that has been modified to

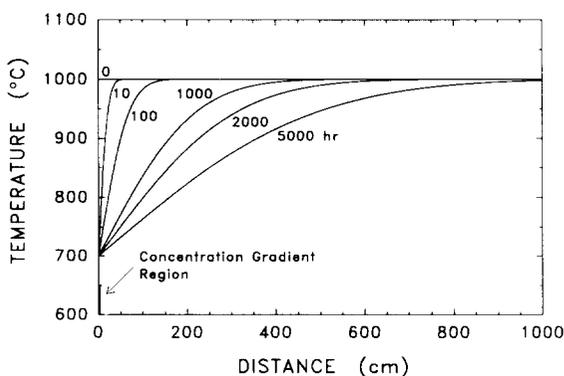


Fig. 3. Evolution of temperature field at a magma chamber margin with a fixed temperature boundary. The analytical results are derived using equation (4-58) from Eckert and Drake (1972). The bar in the lower left hand plotted at 600–650°C denotes the full distance associated with Fig. 4.

allow a nonzero mass flux. This allows the chemical system to be unbounded with respect to mass and, therefore, simulate a semi-infinite medium as used in the analytical thermal models.

An idealized chemical component at 5 wt.% is homogeneously distributed in the boundary layer at the initial time of intrusion. The thermal diffusion model assumes a pseudo-binary chemical system such that the mass transport behavior of a single component can be examined relative to the remaining components of the melt. Values for the Soret and isothermal diffusion coefficients of  $1 \cdot 10^{-3} \text{ }^\circ\text{C}^{-1}$  (Leshner and Walker, 1986) and  $1 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  (Hofmann, 1980), respectively, were obtained from experimental studies. The positive value for the Soret coefficient indicates that the idealized component will migrate down the temperature gradient and enrich the magma margin at the host rock boundary.

The numerical results of the thermal diffusion model for the fixed boundary temperature thermal model are provided in Fig. 4 for times corresponding to those in Fig. 3. Note that the distance axis in Fig. 4 represents a significantly smaller distance than that exhibited for the thermal field evolution in Fig. 3. A time step of 1 hr. and a spatial step of 0.03 cm were used to obtain all of the final compositional

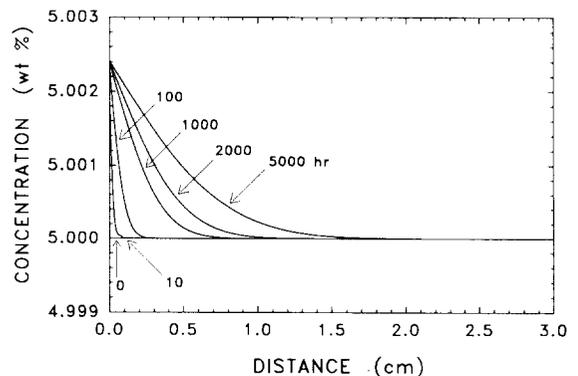


Fig. 4. Evolution of compositional field at the extreme edge of a magma chamber as induced by Soret diffusion and corresponding to the time-dependent temperature field for fixed temperature at the boundary presented in Fig. 3.

field results. As with the brine calculations, several time and spatial steps were incorporated to evaluate the numerical stability of the solutions.

The numerical results indicate some enrichment at the boundary of the magma body, but limited to a distance of  $\sim 1$  cm. For the same period of time,  $\sim 0.6$  yr., the thermal boundary layer has evolved to a distance of  $\sim 500$  cm. However, only during the very early stage of development is the system characterized by steep temperature gradients. The concentration of the component at the magma/host rock interface ( $x=0$ ) increases initially until at  $\sim 100$  hr. it reaches an approximate "steady-state" value of 5.0024 wt.% corresponding to an enrichment factor of 1.0005. This interface concentration appears to be the maximum attainable amount of separation for this system. As time increases, and the thermal gradients decrease, the compositional profile begins to flatten and extend further into the thermal boundary layer of the magma.

The thermal diffusion model assumes the magma to be a static and non-convective medium; mass transport occurs within a stationary volume of silicate melt at the margin. However, at the upper horizontal margin of a magma body the thermal boundary layers will develop instabilities after a characteristic period of time (Carrigan and Cygan, 1986). The thermal boundary layer will eventually collapse and sink into the interior of the convecting magma body. The residence time of a magma parcel in the boundary layer can be determined using a statistical model for high Rayleigh number convection. A rhyolite magma, 5000 hr. after intrusion, would have a thermal boundary layer characterized by a residence time of  $\sim 100$  hr. (Carrigan and Cygan, 1986). Fig. 4 indicates that the maximum concentration enhancement due to thermal diffusion for this short time period is  $<0.004\%$ . This value must be interpreted as an upper limit on any possible Soret enhancements for

magma in a "dynamic" thermal boundary layer.

The results of the second analytical model for the evolution of the thermal field are presented in Fig. 5. The temperature profiles result from the conductive cooling of magma, initially at  $1000^\circ\text{C}$ , through a boundary layer with constant heat flux corresponding to a thermal gradient of  $1^\circ\text{C cm}^{-1}$ . Isochrons are provided for times up to 5000 hr. since the intrusion of the magma body. All of the thermal curves are parallel to each other at the boundary due to the constant heat flux condition. The thermal field extends further into the magma body with time and after 5000 hr. is similar to the temperature profile obtained for the fixed boundary temperature model (see Fig. 3).

The corresponding compositional profiles for this thermal model as obtained by the numerical scheme are presented in Fig. 6. Boundary and initial conditions for the thermal diffusion equation and numerical steps are identical to those of the previous magma application. Again the distance axis of the compositional plot is significantly smaller than that used for presenting the thermal model results. The magnitude of Soret enhancement of the component in the thermal boundary layer is

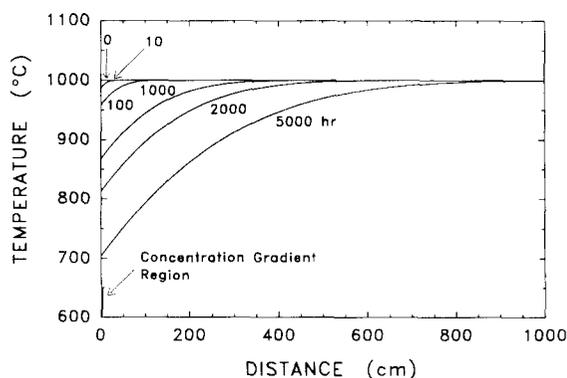


Fig. 5. Evolution of temperature field at a magma chamber margin with a constant heat flux at the boundary corresponding to a thermal gradient of  $100^\circ\text{C m}^{-1}$ . The analytical results are derived using equation (4-93) from Eckert and Drake (1972). The bar in the lower left hand of the figure plotted at  $600\text{--}650^\circ\text{C}$  denotes the full distance associated with Fig. 6.

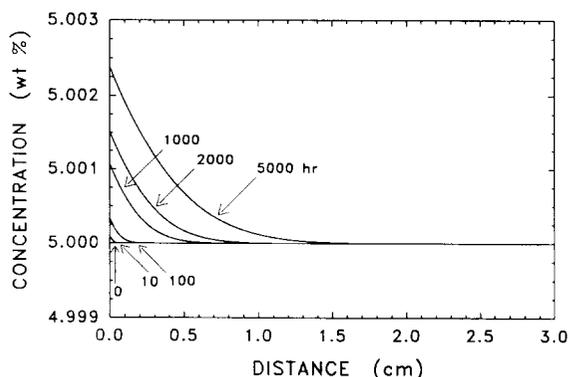


Fig. 6. Evolution of compositional field at the extreme edge of a magma chamber as induced by Soret diffusion and corresponding to the time-dependent temperature field for constant heat flux at the boundary presented in Fig. 5.

equivalent to that observed for the first thermal model; after 5000 hr. the interface concentration of the component is 5.0024, and enrichment is limited to  $\sim 1$  cm from the boundary. *Both models suggest that transient nonlinear thermal gradients contribute little to enhancing the Soret separation of silicate melt in thermal boundary layers.* Nonetheless, the compositional profiles of the two models evolve in somewhat different fashions. Fig. 6 exhibits a parallel evolution of the concentration profiles with time, which represents a fixed flux of material based on eq. 4 for a constant thermal gradient. In fact, the entire thermal diffusion process is limited to a region that experiences a fixed linear temperature gradient.

As long as the thermal gradient remains fixed at the magma–host rock boundary, the thermal diffusive flux will be greater than that obtained using the fixed-temperature model. However, the compositional fields are limited in their development to the extreme margin of the thermal boundary layer. Further evolution of the curves in Fig. 6 indicated a slow convergence of the composition fields to an insignificant level. Practical limits will also prevent the increase of concentration to a meaningful or measurable amount. The residence times of magma parcels in the thermal boundary layer are much too short to provide the time for fur-

ther chemical separation. In addition, continued cooling of the magma within the boundary layer will lead to temperatures low enough for crystallization to occur and, therefore, to halt thermal diffusion of the melt. We also assume constant values for the thermal and isothermal diffusion coefficients (see eq. 5). These values will most likely decrease with decreasing temperature and, therefore, will contribute to lessening the effect of thermal diffusion upon chemical fractionation.

## 5. Conclusions

The numerical model developed here allows for an evaluation of coupled transport processes. We have examined the effect of nonlinear and time-dependent temperature fields upon the mass flux associated with thermal diffusion. In applying the equations to model aqueous sodium chloride solutions used in Soret experiments, we have recognized an anomalous compositional response. The evolving thermal field induces a temporary reversal of the usual compositional zoning that is observed. This complex behavior is in response to the balance of heat and mass fluxes as dictated by thermal and compositional gradients in a closed system. The same governing equations can be used to model the thermal diffusion transport of silicate melt systems. The results suggest that thermal diffusion (Soret separation) of magma in a time-dependent thermal field is minimal and cannot be considered a significant chemical fractionation process. The changes in composition of a silicate melt as induced by thermal diffusion in a thermal boundary layer are orders of magnitude below those observed in experimental (Walker et al., 1981; Leshner, 1986) and field (Hildreth, 1979) studies.

The success of the model in simulating thermal diffusion processes lies in its ability to carefully evaluate disequilibrium processes in nonisothermal systems. It overcomes the constraints of analytical solutions to the thermal

diffusion equation and their limiting assumptions. The role of transient thermal conditions in modifying the mass transport of chemical species can therefore be identified and treated in a realistic manner.

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