GEOPHYSICAL RESEARCH LETTERS, VOL. 31, L13605, doi:10.1029/2004GL019950, 2004

Crystallization and layering induced by heating a reactive porous medium

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Received 11 March 2004; revised 1 June 2004; accepted 8 June 2004; published 2 July 2004.

[1] Normally heating causes melting and not solidification. Here we describe a fundamental series of experiments in which heating a reactive porous medium from above leads to crystallization in the interior. As the porous matrix near the heated boundary dissolves, the resulting dense interstitial liquid sinks into the cooler porous matrix, becomes supersaturated and recrystallizes. We present a theoretical model that quantifies how this vertical redistribution of composition leads to the formation of layers in an initially homogeneous porous medium. We propose that this is a fundamental and naturally occurring process in a variety of different situations in permeable rocks. *INDEX TERMS:* 3210 Mathematical Geophysics: Modeling; 3230 Mathematical Geophysics: Numerical solutions; 3640 Mineralogy and Petrology: Igneous petrology; 5114 Physical Properties of Rocks: Permeability and porosity; 5112 Physical Properties of Rocks: Microstructure. **Citation:** Hallworth, M. A., H. E. Huppert, and A. W. Woods (2004), Crystallization and layering induced by heating a reactive porous medium, *Geophys. Res. Lett.*, *31*, L13605, doi:10.1029/2004GL019950.

1. Introduction

[2] Porous media are frameworks of solid grains bathed in interstitial liquid, and exist in many natural situations [*Bear*, 1979; *Phillips*, 1991; *Dullien*, 1992]. We report a fundamental mechanism by which a homogeneous porous medium becomes stratified into compositionally distinct layers. The mechanism requires partial dissolution of the solid framework into the interstitial liquid, and subsequent redistribution of the heavier dissolved component by compositional convection [*Huppert*, 1990]. We describe laboratory experiments, backed up by theoretical analysis, in which a homogeneous assemblage of solid crystals, saturated liquid and a non-reactive phase of small glass spheres (ballotini) is heated from above. Crystals at the top of the layer dissolve, forming relatively dense melt which drives compositional convection below, and leaves behind a layer of compacted ballotini overlain by a layer of pure melt. The homogeneous porous medium thus develops into a three-layer stratified system. Recrystallization of dissolved crystals occurs in the lowest layer. Thus, paradoxically, even though the system is heated, convective processes cause solidification in a remote region. These concepts suggest novel post-depositional mechanisms to induce compositional layering in both sedimentary and igneous rocks prior to lithification.

2. The Experiments

[3] To test these ideas we conducted a series of experiments in a Perspex tank with internal horizontal dimensions of 2 cm by 30 cm, and a depth of 43 cm. Each experiment began by filling the tank with a homogeneous porous medium composed of a self-supporting matrix of solid crystals of KNO_3 mixed with varying proportions of a non-reactive phase of 3 mm diameter glass ballotini, bathed in interstitial liquid of aqueous KNO_3 saturated at room temperature. Heating at the top of the porous medium was supplied by a steel tube, centred at a height of 39.5 cm from the base, through which we continuously circulated water maintained at 50.0°C. Heat losses to the laboratory were reduced by insulating the tank on all sides with expanded polystyrene 5 cm thick.

[4] During the experiments the heights of the top of the solid matrix and any internal interfaces were recorded to within 1 mm, along with temperature measurements with an accuracy of ±0.1°C from a vertical array of eight thermistors. At the end of each experiment, the concentration of interstitial fluid at various heights was determined by measuring the refractive index of withdrawn samples, and the residual solid matrix was sectioned into 2 cm wide sample strips from which the volume fractions of solid crystals and ballotini could be determined as functions of height.

[5] As a control on the thermal characteristics of the experimental system, we carried out a simple test experiment using a porous bed composed entirely of ballotini immersed in pure water. The resulting temperature profile was in excellent agreement with that determined theoretically based purely on thermal conduction, as presented in *Carslaw and Jaeger* [1959]. In order to develop our initial understanding, we then performed some preliminary experiments using a porous bed composed of just KNO_3 crystals and interstitial liquid (i.e., no ballotini). These developed into a two-layer stratified system, but otherwise showed the general features of the more sophisticated three-component system which we shall now describe. Various experiments were performed using loosely-packed mixtures of KNO_3 crystals and ballotini with initial solid volume fraction $\phi_0 \approx 0.6$, immersed in saturated aqueous KNO_3 at room temperature. Upon heating, the interstitial melt at the top of the layer immedi-

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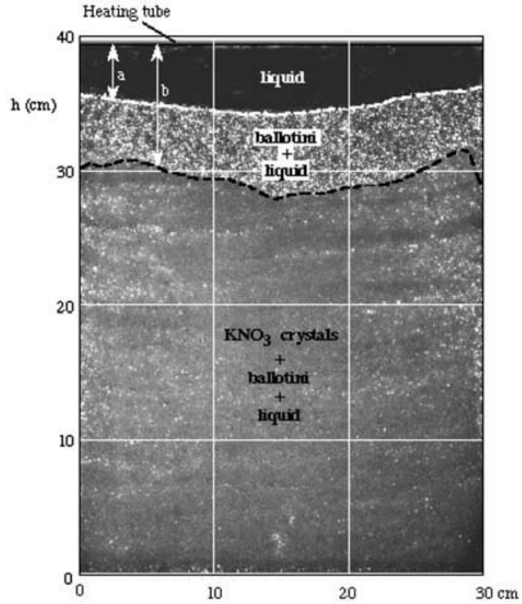

Figure 1. Photograph of an experiment showing the development of three distinct layers. See color version of this figure in the HTML.

ately began to dissolve the enveloped solid crystals, increasing both the KNO_3 concentration and density of the melt, which thereby became gravitationally unstable. This initiated compositional convection in the form of descending plumes of relatively warm, dense melt along with an equivalent upflow of cooler, saturated interstitial liquid which replenished the interfacial region. With the use of potassium permanganate dye streaks, the plumes were observed to percolate throughout the entire porous medium. As the KNO_3 crystals dissolved, two descending interfaces formed, as seen in Figure 1. The lower interface defined the top of the KNO_3 crystal layer. The upper interface separated a layer of closely-packed ballotini bathed in pure liquid from an overlying pure liquid layer. This intermediate layer formed by the settling of ballotini into a close-packed structure following dissolution of the solid KNO_3 crystals. The interfaces were not strictly horizontal but took up an undulating shape owing to the time-dependent nature of the motion in the plumes. Temperature profiles as functions of time and height (Figure 2a) indicate the existence of a thermal gradient in the crystal-free region, and a gradual increase in temperature of the lowest layer with time, which remains essentially uniform throughout its depth. Despite the increasing temperature, the volume fraction of solid KNO_3 increases in the lower layer (Figure 2b). This increase in solid fraction represents the crystallization from the melt that convected downwards from the upper dissolving interface and became supersaturated in the colder lower layer.

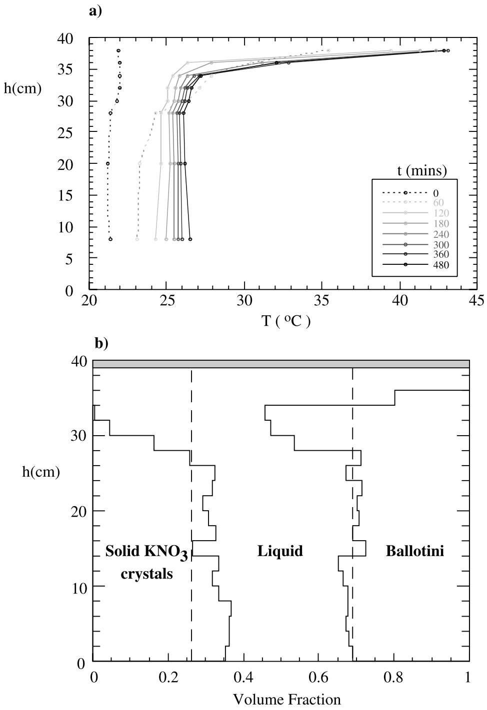

Figure 2. a) the temperature as a function of height at eight different times; and b) the final volume fraction of KNO_3 crystals, ballotini and aqueous melt as a function of height, for an experiment commencing with a matrix of 26% (by volume) of KNO_3, 31% of ballotini and 43% of aqueous melt, as indicated by the vertical dashed lines.

[6] We conducted another series of experiments, in which the porous medium was heated from below. In this situation the dense melt produced cannot convect away from the zone of melting and remains ponded at the base. The interstitial fluid becomes more (stably) stratified with time and does not redistribute the dissolved species into layers.

3. The Theory

[7] We have constructed a mathematical model to describe many of the important features of the main experiments. While the convecting plumes give a three-dimensional structure to the experiments, the main properties can be well described by a one-dimensional model which varies only in height and time as sketched in Figure 3. There are then six unknowns: $T(z, t)$, the (horizontal mean of the) temperature as a function of the distance z from the heating plate and time t; $C(t)$, the spatially uniform concentration of the interstitial fluid in the convecting

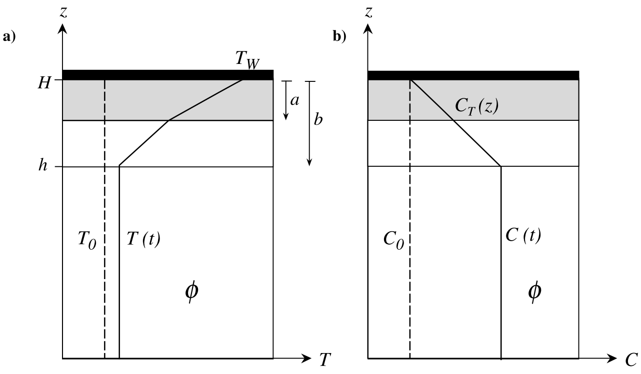

Figure 3. A sketch of the vertical profiles of a) temperature and b) concentration as functions of height showing the three-layer system which develops due to the maintenance of T_w at the height of H.

reactive porous medium; $C_T(z, t)$, the concentration of the interstitial fluid above the reactive porous medium; $\phi(t)$, the volume fraction of (solid) reactive crystals; $a(t)$, the thickness of the clear fluid layer; and $b(t)$, the distance of the top of the reactive porous medium from the heating plate.

[8] Conservation of nonreactive material (the glass ballotini) requires that the volume of compacted ballotini in the middle layer, following the dissolution of the salt, $\chi_1(b - a)A$, where χ_1 is the volume fraction of the compacted ballotini and A is the horizontal cross-sectional area, equals the initial volume of ballotini in the two uppermost layers, $\chi_0 bA$, where χ_0 is the initial volume fraction of the ballotini in the system. Thus $a = rb$, where $r = 1 - (\chi_0/\chi_1)$.

[9] In the model we assume that the temperature and composition profiles are continuous functions of height and that within the porous lower layer the system remains in chemical and thermodynamic equilibrium and so the concentration and temperature of the interstitial liquid are linked by the liquidus [*Huppert*, 1990]. Since the density of the liquid is much more strongly controlled by composition than temperature, and the composition of the liquid within the reactive porous layer increases with time, the liquid which is released above the reactive porous layer is stably stratified. The depth of each surface of fluid released from the reactive porous layer may then be followed. As the lower interface moves downwards into the reactive porous layer through dissolution, the dissolved solid from the interface is redistributed throughout the porous layer by the convective transport through saturated liquid. As this supersaturated liquid migrates into the porous layer from the interface, it reprecipitates a fraction of the solute, releasing latent heat in the process, in order to restore the liquid within the matrix to chemical and thermodynamic equilibrium. The total flux of solute supplied to the lower layer through dissolution at the interface is given by

$$F_s = \phi C_s \frac{db}{dt}, \tag{1}$$

where C_s is the concentration of solute in the solid (for KNO_3, $C_s = 1$). This flux changes the total liquid composition within the lower porous layer by an amount $(1 - \phi - \chi_0)$ $(H - b)dC/dt$ and the total solid composition by $C_s(H - b)$ $d\phi/dt$. In order that the system remain in equilibrium, and the temperature and concentration in the lower porous layer be related by the liquidus, the heat flux F_H released by crystallisation, and given by

$$F_H = \rho L(H - b)\frac{d\phi}{dt}, \tag{2}$$

equals that taken up by the increase in temperature, given by

$$F_H = \rho c_p (H - b)\frac{dT}{dt}. \tag{3}$$

The model is closed by assuming that the conductive heat flux supplied from the top of the system

$$Q = \rho c_p \kappa (T_w - T)/b, \tag{4}$$

where κ is the thermal diffusivity and T_w the constantly maintained temperature at the heating plate, matches the heat required to dissolve the porous layer, given by

$$Q = \rho\phi L \frac{db}{dt}. \tag{5}$$

[10] The solutions to (1–5), which need to be determined numerically, are primarily governed by the two nondimensional parameters Γ and S, which (on the simplifying assumption that the physical properties of liquid and solid are equal) are given by $\Gamma = m\Delta T/(C_s - C_0))$ and $S = L\phi_0/(c_p\Lambda T)$, where $\Delta T = T_w - T_0$ is the temperature difference between the top boundary and the initial system and m is the assumed constant slope of the liquidus curve, dC/dT. The nondimensional parameter Γ represents the ratio of the change in concentration associated with heating the crystal pile from its initial temperature to the temperature at the upper boundary and the initial difference in concentration between solid crystals and interstitial melt, while S represents an augmented Stefan number [*Carslaw and Jaeger*, 1959; *Hill*, 1987] reflecting the ratio of the thermal energy input at the top of the layer to that required to dissolve all the crystals. The time scale of the dissolution process is given by $t_* = SH^2/\kappa$, which is thus the product of the Stefan number and the conductive time scale. It is of order 1,000 hours (~one month) for our experiments and ranges from between months and decades for H varying from 1 m to 10 m with geological values of the parameters. Comparisons between predictions of the theoretical model and our experimental observations are presented in Figure 4 and show very good agreement. Even though the duration of our experiments is somewhat less than the predicted timescale, the early agreement between the two results, without any adjustable parameters in the theory, lends a good degree of confidence to the validity of the model. The theory further suggests that for a different range of the parameters Γ and S, not easily attainable in the laboratory, but possibly valid in natural situations, recrystallization in the lowest layer can ultimately lead to its complete solidification ($\phi_0 = 1$). In practice, the porous medium is likely to become impermeable before this state is fully attained. However, the formation of physical barriers to fluid flow as a result of heating reactive porous media is a surprising result and has important implications in both natural and industrial situations.

4. Some Geological Implications

[11] These concepts indicate a fundamental mechanism that induces compositional layering from an initially homogeneous porous medium. The mechanism requires that the porous medium is initially permeable and allows interstitial liquid to move relative to the solid framework, which consists of at least two components: a reactive species capable of dissolving in response to changes to the system; and a non-reactive species which remains insoluble. An essential feature of the process is the change in fluid density that accompanies the dissolution, thereby driving compositional convection which redistributes the dissolved component. The dissolution of the matrix occurs in response to the local undersaturation of the interstitial fluid. This undersaturation may result from heating at the boundary of

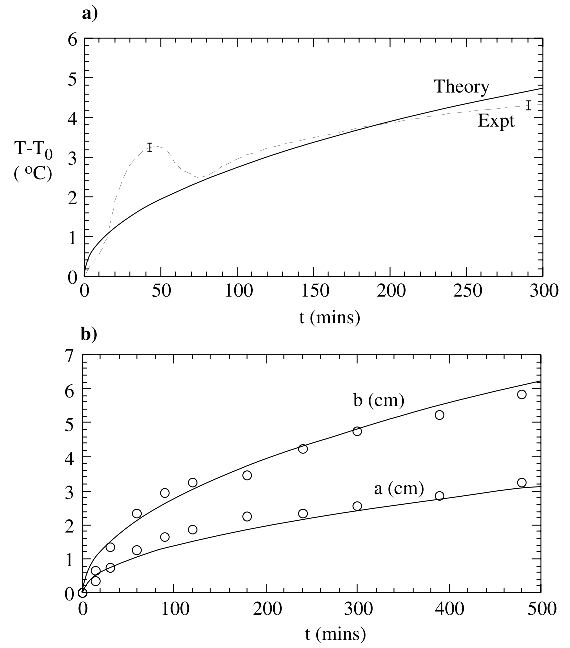

Figure 4. Graphs of the predictions of our theoretical model for a) the mean temperature excess in the crystal layer over the initial temperature, and b) the mean displacement of the descending interfaces, all as functions of time, compared to the experimental data displayed by the dashed curve (with error bars corresponding to ±0.1°C) in a) and by circles in b). The deviation in the experimental temperature profile at around 40 minutes is due to warm descending plumes, which are not accounted for in the theoretical model.

the porous medium, as described here, or it may also arise if the interstitial fluid is displaced by a second fluid of different composition which then reacts with the matrix. This opens up a rich and fascinating series of post-depositional mechanisms for generating compositional zonation in permeable rocks. For example, the process will contribute to the post cumulus development of phase layering in igneous cumulate rocks, which form as an accumulation of settled crystals at the base of basaltic magma chambers [*Wager and Brown*, 1968; *Irvine*, 1987]. Such chambers may be episodically replenished by the input of hotter, new magma, which is usually more dense than the melt in the chamber and thus ponds at its base above any existing (crystal) cumulate pile [*Huppert and Sparks*, 1980]. The juxtaposition of hot, primitive magma against a cooler, porous cumulate may lead to its partial dissolution, either by straightforward heat transfer, or by the hot reactive melt displacing the resident equilibrium melt [*Hallworth*, 1998]. An analogous situation with similar fluid dynamics is relevant to acidic groundwater percolating through calcareenaceous sediments, which would selectively dissolve the calcium carbonate grains but not the silica [*Phillips*, 1991].

[12] **Acknowledgments.** We are grateful to Professor R. S. J. Sparks for extensive comments on an early draft of the manuscript, which was prepared while one of us (*Huppert*) was a Visiting Gledden Fellow at the University of Western Australia. He is grateful to Professor J. Imberger and all the staff of the Centre of Water Resources for the friendly help they gave freely during his visit. The research was partially supported by awards from the EU RTN Euromelt project, the Isaac Newton Trust and the Royal Society small grants scheme.

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