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MULTICOMPONENT CRYSTALLIZATION AND CONVECTION BENEATH VOLCANOES

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Some recent experiments and theoretical calculations of the effects of cooling and crystallizing multicomponent systems are briefly reviewed. The research has been motivated mainly by a desire to understand phenomena which occur in magma chambers beneath volcanoes. However, the results can be applied to a large variety of other natural and industrial situations.

1. Introduction

Beneath all volcanoes there are storage reservoirs of liquid rock known as magma chambers. Their size varies from a small fraction to a few hundreds of cubic kilometres. During eruption the chamber is tapped, while at other times it may be replenished by the introduction of hot magma from greater depths. Between these episodes the magma cools, crystallizes and evolves chemically and physically. Convective processes, on a variety of scales, accompany the crystallization because the solid product selectively extracts components from the melt to leave residual melt of a different density. The convection influences the solidification rate and the distribution of components within the solid rocks.

There has been a great deal of recent research in this field by fluid dynamicists, often in collaboration with geologists. The investigations have ranged widely over theoretical contributions, laboratory experiments and confirmatory field observations. Many experiments have used aqueous solutions and have led to a better understanding of the crystallization of binary and higher-order systems. There exist numerous applications of the results to areas of crystal growth, geology and metallurgy.

This paper presents a brief review of a number of different situations all based on the fact that when crystals grow from a multicomponent melt, important convective effects occur that influence both the rate of crystal growth and the development of chemical and thermal gradients in the melt. The next section discusses the cooling, crystallization and resultant evolution of a two-layer binary system, in which the lower layer is both hotter and heavier than the upper layer because of a compositional difference between the two layers. Section 3 discusses the crystallization and resulting convection in an initially homogeneous binary system which is cooled at a horizontal boundary. Section 4 considers the effect of cooling at a vertical side wall, and Section 5 describes some recent experiments in which the cooling takes place at an inclined slope.

The geological applications will be described only very briefly. These are discussed in the original papers, to which references are given. Reviews of the new subject, known as *Geological Fluid Mechanics*, which is concerned primarily with the various motions of the fluid material that upon solidification become the rocks that make up the earth, appear in refs. [1–4].

Fluid motions, driven by double-diffusive connection, underlie much of the work. Such convection readily occurs wherever there are two (or more) components, of different molecular diffusivities, that contribute to the fluid density. For example, the components might be heat and composition or two different compositions. The structure of double-diffusive convection can be very different from that of single-component convection, such as purely thermal convection. Vigorous motions can take place even when the total density is everywhere increasing with depth. This is because the motion can selectively draw on the potential energy stored in just one of the compo-

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nents, even though the contribution of the other component to the overall vertical density gradient is larger. The hallmark of double-diffusive convection is the formation of a series of vigorously convecting layers separated by thin, horizontal interfaces across which there are relatively large compositional gradients. For example, application of heat to the base of a uniform body of water, as in a kettle, causes the resultant light fluid particles to rise all the way to the surface. If the water has a salinity profile which increases with depth, however, hot fluid particles are restricted in their rise by the ambient density gradient. This restriction causes the convection to evolve into a series of layers. Comprehensive reviews of many of the basic phenomena of double-diffusive convection are contained in refs. [5–7].

2. Evolution of a two-layer system

The geological motivation behind this study is as follows. Magma chambers are occasionally replenished by a small fraction of new, relatively hot ($\approx 1400\,^\circ$C) magma which is rich in magnesium oxide (≈ 18 wt%). Yet the lavas which are erupted from the chamber, whose mean temperature $\approx 1200\,^\circ$C, have a much lower MgO content.

The paradox, which puzzled geologists for decades, was resolved by a theoretical analysis of the fluid mechanics and crystallization which occur in the chamber [8,9]. The validity of the main ideas of the model were then tested by a laboratory experiment [10] which is now described. A hot, heavy layer of an aqueous KNO_3 solution was rapidly injected beneath a cooler, less dense layer, made up of aqueous $NaNO_3$. The lower layer cooled, by transferring heat across the paper-thin interface separating the two layers. It is known [5,10] that under such circumstances there is a negligibly small mass transfer across the interface. After a time, the fluid in the lower layer became slightly supersaturated and crystallized. The density of residual liquid then decreased due to the changing composition as the temperature decreased, until the density difference across the interface became zero. The fluid of the lower layer then rose and the two fluids mixed intimately, as seen in fig. 1, which reproduces a photograph taken during one of the experiments. A significant amount of the KNO_3 input originally into the container was deposited as crystals, while some remained in solution and was, upon the overturn, dispersed throughout the container. It should be noted that if the initial KNO_3 solution and $NaNO_3$ solution were mixed mechanically no crystallization would occur; the resultant fluid would be undersaturated in both components. It is the separation of the two layers due to their density difference (and the negligible mass transfer) that allows the lower layer to evolve independently.

The geological implication of this experiment is that the new hot, heavy magma ponds at the base of the chamber and forms a separate layer. As this lower layer cools, the MgO content of the fluid magma decreases as crystals of magnesium silicate are formed. Concurrently, the density of the melt decreases. After some time, which can be calculated quantitatively [9], the residual liquid, depleted of approximately half its original MgO content, mixes with the older magma in the chamber. At a number of sites throughout the world, these ideas have been found to be in good agreement with field observations.

Fig. 1. The residual liquid of an initially hot and heavy lower layer of aqueous KNO_3 has just reached the same density as the fluid in the upper layer and is mixing with it.

3. Crystallization at a horizontal boundary

Between eruptions, replenishments and the evolution episodes just described, magma in a chamber cools by transferring heat to the surrounding rocks and to the strong hydrothermal circulations above some magma chambers. This effect suggested the need for an investigation of the result of cooling a melt at the roof, floor or walls (possibly slanted) of a confined chamber. There is, of course, a large literature in the fields of metallurgy and crystal growth bearing on this subject. Here we constrain ourselves to discuss merely a part of the work, carried out with the geological application in mind. The essential concept to include in any investigation is that crystallization selectively withdraws various components from the melt. This can induce compositional convection because the composition, and hence also the density, of the melt adjacent to the forming crystals are generally different from the far-field values.

In a study aimed at elucidating some of the fundamental principles of the dynamics of solidification, Huppert and Worster [11] delineated the different flows which can occur when an initially homogeneous fluid with a simple phase diagram, such as a binary alloy, is cooled at a horizontal boundary. There are six different cases because the cooling can be either from above or below, and the released liquid can be either relatively heavy (initial composition below the eutectic value), relatively light (initial composition above the eutectic value) or of the same density, and composition, as the melt (of eutectic composition). Because of the different roles of the resulting thermal and compositional fields, each case involves different fluid mechanical effects and a separate analysis. Huppert and Worster show how quantitative results for the rate of growth of the resultant crystal block can be obtained by the straightforward use of relationships for the conservation of heat and composition. They confined their particular calculations to the cases of cooling from below either a eutectic melt or a melt whose initial composition was less than eutectic and obtained excellent agreement between their theoretical results and those obtained from laboratory experiments with aqueous solutions. Their general method has now been applied to the other cases [12–14].

The cooling from above of an initially homogeneous solution whose composition exceeds the eutectic may be of particular interest. Turner et al. [13] carried out a series of experiments with aqueous solutions of Na_2CO_3, Na_2SO_4 and KNO_3. Initially, vigorous thermal convection occurred and small dendritic crystals nucleated at the roof of

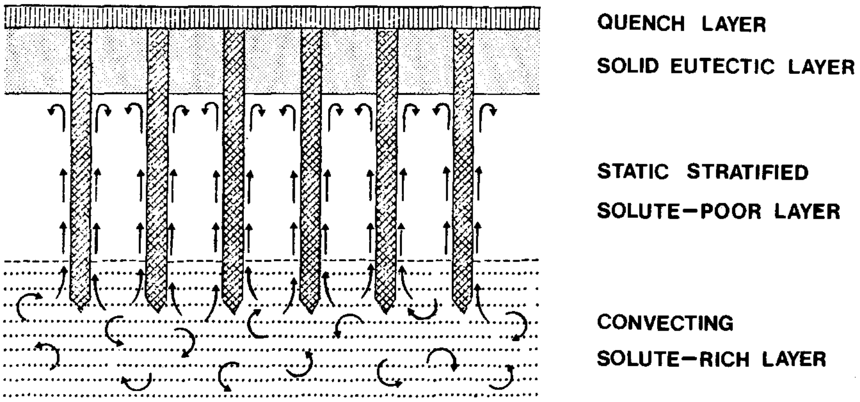

Fig. 2. A schematic sketch of the result of strongly cooling from above an initially homogeneous solution of composition greater than the eutectic. The ends of the predominantly vertical crystals extend into a convecting layer where further crystallization releases light liquid. This rises along the dendrite faces to form a compositionally stable layer.

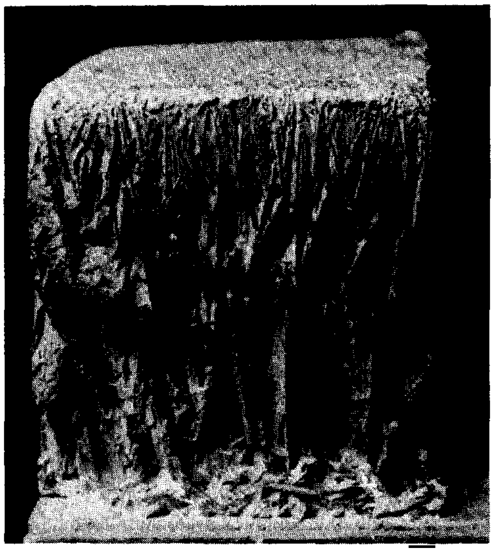

Fig. 3. The resultant crystal block formed on strongly cooling from above an initially homogeneous aqueous solution of Na_2CO_3 of composition greater than eutectic. The ice has been allowed to melt and run out of the block and partial dehydration had occurred before the photograph was taken.

the experimental container. At first the crystals had a wide range of orientations with respect to the roof. As each experiment progressed, the crystals increasingly became oriented perpendicular to the roof. Concurrently, a stagnant pool of less dense, released fluid formed between the growing crystals. The tips of the crystals extended beyond this layer into the saturated, convecting fluid beneath, as schematically sketched in fig. 2. Part of the resultant crystal field is seen in fig. 3 which is a photograph taken upon completion of an experiment after the ice had melted and the $Na_2CO_3 \cdot 10H_2O$ crystals had partially dehydrated.

The geological application of these experiments is to a structure known as "spinifex texture", which is ubiquitous in low-viscosity lava flows which were prevalent on the earth 3000 million years ago. Fig. 4 shows a typical thin section of one such flow and the skeletal crystal morphologies are clearly seen. These were formed, it is suggested, during the post-emplacement cooling of lava ponds by overlying seawater [13].

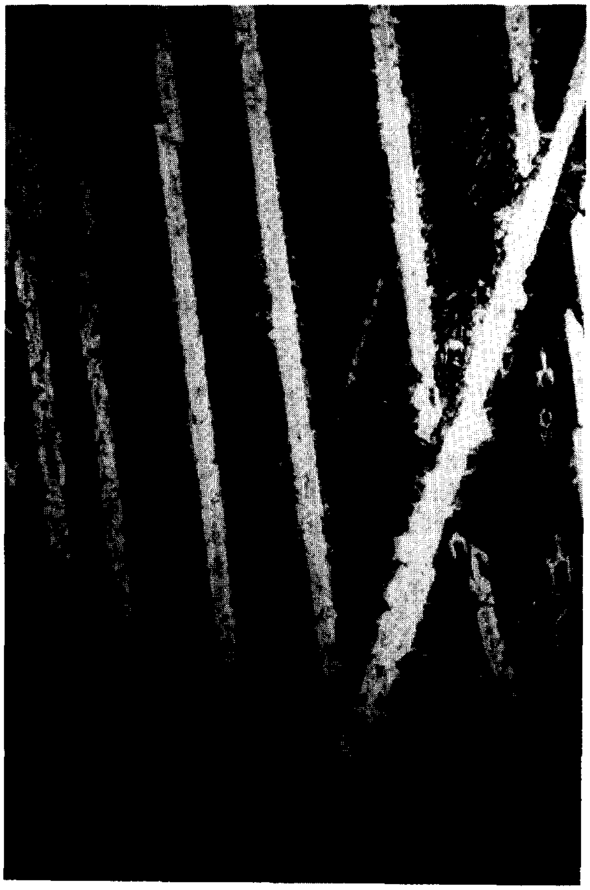

Fig. 4. A thin section of dendrite olivines (Mg_2SiO_4) grown in a cooling lava in Western Australia 3000 million years ago.

4. Crystallization at a vertical boundary

When the cooling is applied at a vertical boundary, there are necessarily horizontal temperature and compositional gradients which couple into the predominantly vertical flow of the cold, released fluid. A detailed boundary-layer analysis has been conducted of the flow induced by a prescribed temperature and composition anomaly at a fixed vertical wall in an unbounded fluid [15–18]. The analysis was confined to the case of positive density anomaly due to temperature, which would tend to induce downward motion, and negative density anomaly due to composition, which would tend to induce upward motion. On the assumption that the compositional diffusivity $D \ll \kappa_T \ll \nu$, where κ_T is the thermal diffusivity and ν is the kinematic viscosity, three regions can be discerned. In the inner region, closest to the wall, compositional buoyancy forces balance viscous forces. Beyond this, in the outer region, thermal buoyancy forces balance viscous forces. Finally, in the furthest region, the inner and outer motions are responded to by viscous coupling with the inertia forces. For given Prandtl number $\mathrm{Pr} = \nu/\kappa_T$ and diffusivity ratio $\tau = D/\kappa_T$, the flow depends only on the ratio $\Gamma = \Delta\rho_T/\Delta\rho_c > 0$, where $\Delta\rho_T$ and $\Delta\rho_c$ are the magnitudes of the prescribed density anomalies due to temperature and composition respectively.

For sufficiently small Γ, compositional effects overpower thermal effects and the entire flow is upwards and takes place in a boundary layer whose width increases like $x^{1/4}$, where x is the coordinate axis in the direction of flow. For sufficiently large Γ, thermal effects dominate and the entire flow is downwards. For intermediate values of Γ, a bi-directional motion results, with an upwards inner flow and downwards outer flow. In the limit of large Pr, this occurs when $0.627\ \tau < \Gamma < 1.09\ \tau^{1/3}$ [17]. Assuming that $\tau \ll 1$, Nilson [17] matches an inner, upflowing boundary layer, whose width increases up the wall, to a very much thicker outer, downflowing boundary layer, whose width increases down the wall. A typical example of the resulting flow field, with physical parameters according to magmatic values, is presented in fig. 5.

Effects due to a moving crystal front and the finite volume of the container have only begun to be investigated. For example, fig. 6 reproduces a photograph taken during an experiment conducted by J.S. Turner at ANU, Canberra. A small central rod was positioned in a solution of Na_2CO_3 which was initially almost saturated, and the rod was then cooled uniformly along its length. Crystals of $Na_2CO_3 \cdot 10H_2O$ grew and released light liquid, which induced strong double-diffusive layering in the interior. Unanswered questions include: how can the rate of growth of the crystals be calculated; why is the thickness of the solid such a variable function of position along the rod; what govers the size of the double-diffusive layers formed; and why are there many thin ones at the top and thicker ones below?

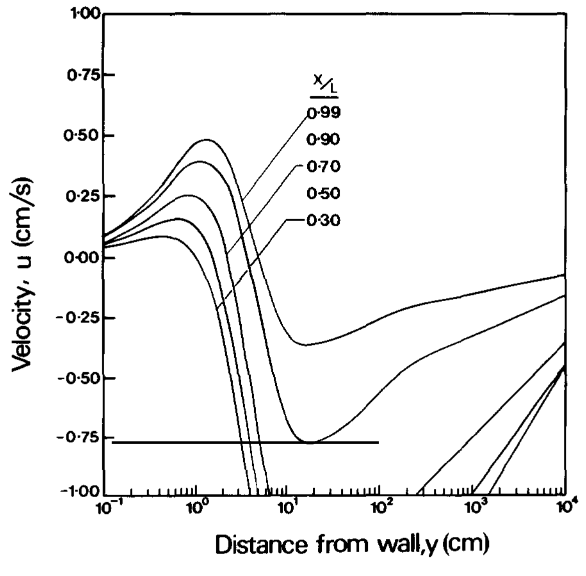

Fig. 5. The vertical velocity as a function of distance from a wall of height L which maintains an increased composition and a decreased temperature over the far-field value. The profiles at five positions up the wall were calculated in ref. [15] using typical magmatic parameter values.

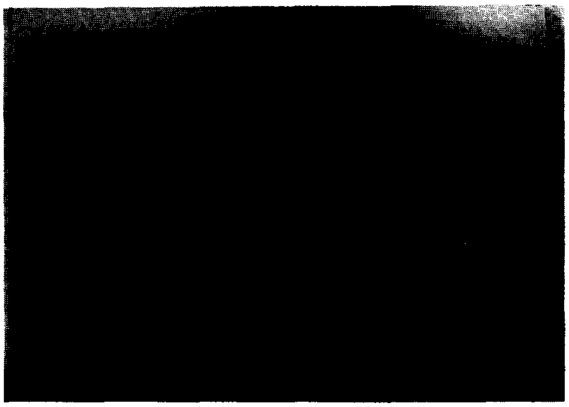

Fig. 6. The result of cooling a large body of an initially homogeneous, almost saturated solution of Na_2CO_3 at a small central rod for 21 h 38 min. Experiment and photograph executed by J.S. Turner of the ANU, Canberra.

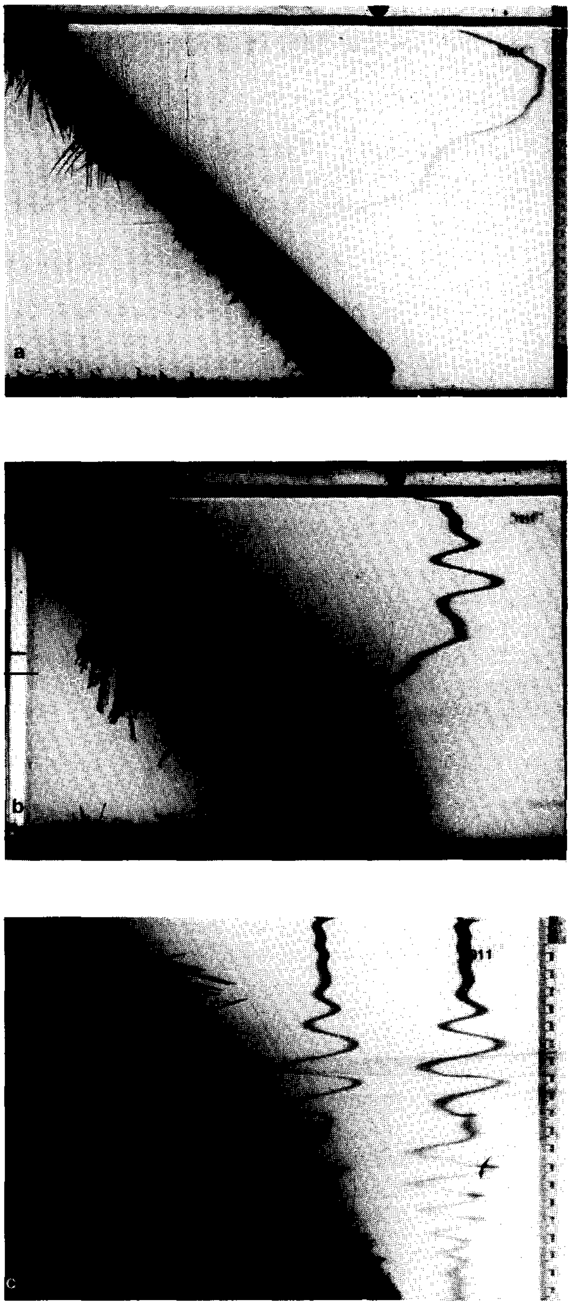

Fig. 7. The result of cooling an initially homogeneous, almost saturated aqueous solution of Na_2CO_3 at a 45° slope, (a) after 65 min, (b) after $3\frac{1}{2}$ h, and (c) after $23\frac{1}{2}$ h. Note the very different forms of motion above and below the slope – strong compositional convection above and virtually stagnant below – and the complex velocity structure which developes with time above the slope.

5. Crystallization at a sloping boundary

A number of the phenomena connected with crystallization can be interestingly displayed by allowing the cooling to take place at a sloping boundary. Experimentally, the upward and downward surface can be investigated simultaneously and the differences easily conveyed [19]. Fig. 7 presents a sequence of photographs from one experiment using an initially homogeneous aqueous solution of 13 wt% Na_2CO_3 (whose eutectic composition is 6 wt%). On both sides of the cooling plate, crystallization releases light liquid. On the upper surface, this rises from where it was formed as a series of plumes which mix with the environment and drive a large-scale flow, whose structure becomes more complicated with time. On the lower surface, the released liquid winds its way up through the crystal mush and is deposited at the top of the layer. As the temperature decreases so does the density of the released liquid and it thus displaces fluid at the top of the layer downwards as in the familiar "filling-box" problem [5,20]. As time proceeds, all the fluid in the region bounded by the downward-facing cooling surface finally reaches the eutectic composition. On the other side, double-diffusive layering with strong velocity gradients emerge.

If the ambient fluid incorporates a (stable) composition, and hence density gradient, two competing forces operate. Released fluid will, if the geometry permits it, rise vertically (on the assumption that it is less dense; relatively heavy released fluid would *fall* vertically). But its movement is constrained by the density gradient. The amount of rise of fluid parcels will vary directly with the density anomaly and inversely with the magnitude of the gradient. Experiments investigating these effects are being conducted at the time of writing.

6. Summary

There are many new convective phenomena, of great potential interest to crystal growers, fluid dynamicists, geologists and metallurgists, which occur upon crystallization of a multi-component melt. Significant progress cam be made by investigating the crystallizing of aqueous solutions, which are useful representatives of binary alloys. Scientists who have contributed to other areas in the discipline of crystal growth could undoubtedly make useful contributions to the field and share in the current excitement which the field is creating.

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