EVOLUTION OF THE QUATERNARY MAGMATIC SYSTEM,
MINERAL MOUNTAINS, UTAH:
INTERPRETATIONS FROM CHEMICAL AND EXPERIMENTAL MODELING

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Abstract

The evolution of silicic magmas in the upper crust is characterized by the establishment of chemical and thermal gradients in the upper portion of magma chambers. The chemical changes observed in rhyolite magmas erupted over a period of 300,000 years in the Mineral Mountains are similar to those recorded at Twin Peaks, Utah, and in the spatially zoned Bishop Tuff from Long Valley, California. Chemical and fluid dynamic models indicate that cooling of a silicic magma body from the top and sides can result in the formation of a roof zone above a convecting region which is chemically and thermally stratified, as well as highly fractionated and water rich. Crystallization experiments have been performed with sodium carbonate solutions as an analog to crystallization in magmatic systems. Top and side cooling of a homogeneous sodium carbonate solution results in crystallization along the top and sides and upward convection of sodium carbonate-depleted fluid. A stably stratified roof zone, which is increasingly water rich and cooler upwards, develops over a thermally and chemically homogeneous convecting region. Crystallization at the top ultimately ceases, and continued upward convection of water-rich fluid causes a slight undersaturation adjacent to the roof despite cooler temperatures. By analogy, crystallization at the margins of a magma chamber and buoyant rise of the fractionated boundary layer into the roof zone can account for the chemical evolution of the magma system at the Mineral Mountains.

To produce compositionally stratified silicic magmas requires thermal input to a silicic system via mafic magmas. The small volume, phenocryst-poor rhyolite magma which persisted for at least 300,000 years in the Mineral Mountains requires the presence of a continued thermal input from a mafic

magma source. The presence of silicic lavas signifies that there is a substantial thermal anomaly both in the crust and upper mantle. The production of silicic lavas requires 1) the heating of the lower crust to near the solidus for silicic melts, 2) partial fusion by the additional convective transfer of heat from the mantle by injection of the basaltic magma, 3) continued input of heat in excess of the conductive and convective heat loss to allow the crustal melt to grow to some critical size so that it can rise buoyantly into the upper crust. In the Mineral Mountains there has been an inadequate prolonged thermal flux to produce caldera-forming eruptions. Moreover, the distributed extension in the Basin and Range allows for the propagation of small volumes of magma upward probably in dike-like bodies parallel to the direction of maximum horizontal compressive stress. The erupted lavas represent a highly differentiated and presumably small fraction of the total volume of silicic magma which is contained at considerable depth.

Introduction

Major geothermal resources are associated with large silicic volcanic systems in the western United States. Among these are the Valles Caldera, New Mexico, Long Valley and the Coso Mountains, California, and, on a smaller scale, the Mineral Mountains in Utah. Quaternary volcanism in the Mineral Mountains of west-central Utah shares many common characteristics with other centers of silicic volcanism in the western United States, and its chemical evolution over time is similar to chemical variations exhibited in compositionally zoned ash-flow tuffs. Compositionally zoned ash-flow tuffs have been widely recognized in the western United States (Williams, 1942; Lipman et al., 1966; Hildreth, 1979) and are thought to have erupted from roof zones of compositionally stratified high-silica magmas. As an ash-flow tuff erupts, it taps progressively deeper levels of a zoned magma, and hence, it represents an instantaneous, inverted record of gradients in the upper portion of the magma chamber. The most thoroughly documented study of a zoned ash-flow tuff is that of Hildreth (1977, 1979) on the Bishop tuff of Long Valley, California, which has served as a model of comparison for other areas. More recently, Crecraft et al. (1981) have documented the development over time of a similar high-silica zoned magma at the Twin Peaks rhyolite field in west-central Utah. The chemical gradients in both the Twin Peaks and the Bishop tuff magmas are remarkably similar to those in the Mineral Mountains and are illustrated by the enrichment factors shown in Figure 1. Enrichment factors are ratios of concentrations in the most evolved rhyolite divided by concentrations in the least evolved rhyolite. Elements which plot upward are enriched upward in zoned magmas. These gradients are characterized by upward increases in volatiles, silicon, all alkalis other than potassium, heavy rare earths, and highly charged cations; and decreases in all alkaline earths

Figure 1. Enrichment factors (concentrations in most evolved rock divided by those in least evolved rock). Elements with values greater than 1.0 are concentrated upwards in silicic magma chambers. See text for discussion.

heavier than beryllium, iron, titanium, aluminum, and light rare earths. Other characteristic changes upward are decreases in temperature, oxygen fugacity, phenocryst content and density. The net density gradient, due primarily to the upward increase in water, is strongly stabilizing with respect to large-scale convection (Hildreth, 1979; Crecraft et al., 1981).

The origin of these compositional gradients has been problematical. In some areas such as the Paintbrush tuff in southern Nevada (Lipman and et al., 1966) and Crater Lakes, Oregon (Williams, 1942; Ritchie, 1979), chemical data appear consistent with crystal fractionation. However, the high viscosity and correspondingly slow settling velocities, and the lack of physical evidence for crystal settling, severely constrain crystal settling as a mechanism for fractionation in high-silica systems. In other areas, such as the Jemez Mountains, New Mexico (Smith, 1979), the Bishop tuff (Hildreth, 1979), Sierra La Primavera, Mexico (Mahood, 1981), and at Twin Peaks, (Crecraft et al., 1979, 1980, 1981), crystal fractionation apparently fails to account for the antithetic behavior of the light and heavy rare earth elements and for the extreme variations of many trace elements. Largely because of the apparent failure of crystal fractionation to account for the observed mineralogical and chemical gradients in the Jemez Mountains and in the Bishop tuff, Shaw et al. (1976) proposed a new mechanism of differentiation to generate these magmas which they referred to as "thermogravitational diffusion", or simply "liquid-state differentiation". This model is based on the supposition that compositional gradients result from an approach to steady-state conditions. A combination of various influences, which could include the thermal gradient, gravitational field, and changes in liquid structure, induces diffusive potentials on components which drive mass flux and promote formation of gradients. More recently, investigations into phenomena associated with

double-diffusive convection have suggested that such mechanisms may be important in developing compositional stratification in magmas (Chen and Turner, 1980; McBirney and Noyes, 1979). This report is concerned primarily with analyzing the chemical and physical processes associated with the development of a stratified high-silica roof zone in the Mineral Mountains magma system, and with evaluating the evidence for liquid-state differentiation and double diffusive convection in this and similar systems.

Summary of Silicic Volcanism

The Mineral Mountains constitute a large horst approximately 50 km in length and about 10 km at its maximum width. It is made up mostly of a large composite Tertiary silicic pluton through which Quaternary rhyolite was erupted for 15 km along the crest and western flank of the mountain range. The earliest eruptions at 0.8 m.y. ago produced two extremely fluid rhyolite flows, whereas subsequent eruptions from 0.6 to 0.5 m.y. ago produced at least 10 rhyolite domes which were preceded by the eruption of air-fall and ash-flow tuffs. Contemporaneous basaltic volcanism occurred along the northeastern flank of the Mineral Mountains (0.9 m.y.) and the Cove Fort volcanic field (0.5 m.y.; Best et al., 1980). A general geologic summary is given by Ward et al. (1978), a description of the volcanic rocks is provided by Lipman et al. (1978), and a detailed study of the petrology and mineralogy is given by Evans and Nash (1978).

Chemical analyses for major elements are given in Table 2 and for trace elements in Table 3. Chemical variations among the eruptive units are subtle in terms of major elements, as all samples are high in silica with limited chemical variability. Trace element concentrations, on the other hand, show significant differences which are similar to those exhibited in other silicic

Table 1. Key to Analyses

<u>Sample No.</u>	<u>Locality</u>	<u>Lithology</u>
74-2	Bailey Ridge flow	obsidian
74-3	Bailey Ridge flow	obsidian
74-4	Bailey Ridge flow	pumice
74-7	Big Cedar Cove dome	felsite
74-8	Wild Horse Canyon flow	obsidian
74-13	Bailey Ridge flow	perlite
74-16	Bearskin Mountain dome	obsidian
75-14	Little Bearskin Mtn. dome	obsidian
75-20	North Twin Flat Mtn. dome	obsidian
76-22	Bailey Ridge flow	glass separate
76-23	Wild Horse Canyon flow	glass separate
76-24	North Twin Flat Mtn. dome	glass separate
76-25	Little Bearskin Mtn. dome	glass separate
77-3	Small dome between North and South Twin Flat Mtns.	felsite
77-5	South Twin Flat dome	obsidian

Table 2. Chemical Analyses of Volcanic Rocks and Residual Glasses (G) from the Mineral Mountains, Utah. For Key to Samples, see Table 1.

	74-3	74-3G	74-4	74-4G	74-8	74-8G	74-7	74-16	74-16G	75-14	75-14G	75-20	75-20G
SiO ₂	76.52	76.6	74.51	74.1	76.51	77.1	76.82	76.00	76.0	76.42	76.5	76.45	76.5
TiO ₂	0.12	0.12	0.12	0.12	0.12	0.12	0.10	0.06	0.06	0.08	0.07	0.08	0.07
Al ₂ O ₃	12.29	12.4	11.98	12.0	12.29	12.4	12.64	12.58	13.0	12.79	12.6	12.79	12.8
Fe ₂ O ₃	0.31	-	0.33	-	0.23	-	0.61	0.24	-	0.20	-	0.30	-
FeO	0.46	0.73	0.43	0.65	0.51	0.74	0.15	0.39	0.56	0.38	0.53	0.29	0.58
MnO	0.05	0.06	0.04	0.05	0.05	0.06	0.05	0.07	0.09	0.09	0.11	0.10	0.11
MgO	0.08	0.09	0.10	0.06	0.10	0.09	0.10	0.37	0.05	0.11	0.04	0.12	0.04
CaO	0.64	0.55	0.62	0.56	0.65	0.55	0.50	0.45	0.42	0.44	0.38	0.40	0.40
Na ₂ O	3.80	3.68	3.56	3.29	3.77	3.58	4.03	4.27	4.14	4.42	4.23	4.39	4.29
K ₂ O	5.24	5.10	5.10	4.78	5.28	4.95	5.00	4.64	4.26	4.72	4.58	4.73	4.53
P ₂ O ₅	0.02	-	0.01	-	0.01	-	0.01	0.01	-	tr	-	0.06	-
H ₂ O+	0.12	-	2.27	-	0.06	-	0.02	0.26	-	0.13	-	0.10	-
H ₂ O-	0.06	-	0.23	-	0.06	-	0.04	0.06	-	0.01	-	-	-
F	0.16	0.16	0.13	0.08	0.14	0.15	0.12	0.38	0.25	0.42	0.34	0.44	0.33
Sum	99.87	99.5	99.43	95.7	99.76	98.7	100.14	99.62	98.7	100.21	99.4	100.25	99.7
LessO=F	0.07	0.1	0.05	0.03	0.06	0.1	0.05	0.16	0.1	0.18	0.1	0.19	0.1
Total	99.80	99.4	99.38	95.7	99.70	99.6	100.14	99.62	98.7	100.03	99.3	100.06	99.6

Table 3. Trace Element Analyses of Mineral Mountains rhyolites and glass separates.

(values in ppm unless otherwise indicated)

	74-2	74-3	74-4	74-13	76-22	74-8	76-23	74-7	74-16	75-20	76-24	76-25	75-14	77-3	77-5
Li ¹	53	48	42	56	-	59	-	43	87	109	-	-	-	-	-
Be ¹	5.1	-	5.2	5.2	-	5.2	-	6.6	10	12	-	-	-	-	-
Cl ²	-	495	-	-	-	475	-	155	735	605	-	-	565	-	-
Sc	2.52	2.55	2.50	2.57	2.55	2.54	2.51	2.82	3.35	3.86	3.87	3.71	3.79	3.24	3.25
Mn	350	350	340	355	350	350	350	420	575	720	735	705	715	585	580
Fe ²	0.56	0.56	0.54	0.56	0.54	0.57	0.55	0.56	0.43	0.44	0.45	0.40	0.44	0.42	0.43
Cu ¹	4.1	-	4.8	4.9	-	5.0	-	4.2	-	-	-	-	-	-	-
Zn	32	36	29	33	34	30	-	39	39	47	43	-	-	-	-
Rb	206	195	209	215	215	213	217	232	352	388	376	380	380	240	255
Sr ²	-	35	-	-	-	35	-	30	n.d.	n.d.	-	-	-	-	-
Y ²	-	15	-	-	-	15	-	15	20	20	-	-	-	-	-
Zr ²	-	100	-	-	-	100	-	80	85	90	-	-	-	-	-
Nb ²	-	25	-	-	-	25	-	30	40	35	-	-	-	-	-
Mo	6	7	4	6	8	5	7	4	9	12	8	10	7	6	7
Cd ¹	0.14	-	0.18	0.29	-	0.27	-	0.20	-	-	-	-	-	-	-
Sb	0.22	0.12	0.13	0.10	0.13	0.14	0.16	0.11	0.22	0.34	0.38	0.26	0.34	0.22	0.22
Cs	3.6	3.6	3.4	3.5	3.5	3.6	3.51	3.3	6.2	7.3	7.4	7.2	7.2	6.5	6.7
Ba	170	173	166	168	164	170	162	127	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
La	43	45	44	45	44	44	46	42	24	33	34	33	36	23	20
Ce	86	87	85	86	86	85	87	85	46	57	57	57	58	43	40
Nd	25	25	25	25	26	25	25	18	10	12	11	10	10	10	9
Sm	3.3	3.3	3.3	3.3	3.5	3.4	3.3	2.2	1.1	1.4	1.3	1.1	1.1	1.14	1.09
Eu	0.38	0.37	0.38	0.37	0.382	0.37	0.37	0.21	0.032	0.038	0.032	0.043	0.038	0.025	0.030
Tb	0.42	0.43	0.41	0.40	0.41	0.43	0.38	0.30	0.21	0.21	0.21	0.21	0.17	0.20	0.14
Dy	2.6	2.6	2.7	3.0	2.7	2.7	2.6	2.0	1.2	1.6	1.7	1.5	1.8	2.0	1.8
Yb	2.82	2.84	2.74	2.77	2.87	2.80	2.80	2.83	3.35	3.74	3.93	3.83	3.88	4.11	4.07
Lu	0.38	0.41	0.39	0.40	0.40	0.42	0.44	0.43	0.53	0.61	0.62	0.67	0.67	0.68	0.69
Hf	4.4	4.6	4.7	4.5	4.6	4.5	4.4	4.7	5.2	5.9	5.8	6.0	6.2	5.9	5.6
Ta	-	-	-	-	1.67	-	1.67	-	-	-	2.91	2.76	-	-	-
W	-	-	-	-	2	-	5	-	-	-	3	n.d.	-	-	-
Pb ²	-	35	-	-	-	35	-	40	45	35	-	-	-	-	-
Th	22.7	23.0	22.4	23.1	23.2	23.1	22.9	26.2	38.1	42.0	41.8	42.1	41.7	39.4	39.3
U	5.1	5.1	4.8	4.9	5.2	5.1	5.3	5.5	8.3	9.7	9.6	9.8	10.5	9.3	9.6

- = not determined

n.d. = not detected

1. Atomic absorption; analyst W. P. Nash

2. X-ray fluorescence; analyst S. H. Evans, Jr.: all other analyses by instrumental neutron activation; analysts F. Asaro and H. Michaels.

Table 4. Fluid Parameters

Symbol Name	Units	Na ₂ CO ₃ -H ₂ O (aqueous solution)	H ₂ O-magma (hydrous magma)
ρ density	g/cm ³	1.2	2.2
ν kinematic viscosity	cm ² /sec	0.03	10 ⁸
c heat capacity	cal/g °C	1	.3
K thermal conductivity	cal/cm ² sec	.0014	.005
$ \alpha $ thermal diffusivity	cm ² /sec	.0013	.007
α thermal expansivity	°C ⁻¹	.00021	5x10 ⁻⁵
D solutal diffusion coefficient	cm ² /sec	.7x10 ⁻⁵	10 ⁻⁸
β solutal expansivity	1	0.97	2
S ₁ solute concentration (average)	g/cm ³	0.2	0.04
S ₂ solvent concentration (average)	g/cm ³	1.0	2.2
W ₁ molar mass-solute	g/mole	107	18
W ₂ molar mass-solvent	g/mole	18	60
T temperature (average)	°K	290	1100

centers in the late Cenozoic in the western United States. For example, rare earth element (REE) abundances are illustrated in Figure 2 for the Mineral Mountains, Twin Peaks, Utah, and the Bishop tuff, California. The REE patterns are not only similar in gross aspect but also in detail. In all cases the least evolved rocks in each evolutionary sequence contain the highest light rare earth (LREE) contents and the lowest heavy rare earth contents (HREE). As evolution proceeds LREE contents decline while HREE contents increase. This pervasive characteristic of high-silica systems cannot be accounted for by traditional models of magmatic evolution and has led to the development of alternative models such as liquid-state differentiation to account for the chemical behavior of granitic magmas in the upper crust.

Evidence Concerning Liquid-State Differentiation

Implicit in the concept of liquid-state differentiation is that chemical gradients and stratified magmas develop in response to an approach to a steady-state distribution of magmatic components. This idea presumes the existence of diffusive potentials which cause an initially homogeneous magma to develop the compositional gradients observed in zoned magmas. The actual mechanism of transport need not be by diffusion alone, however; Shaw et al. (1976) recognized the severe rate-limiting constraints of diffusion and proposed a mechanism of "convective-aided" thermogravitational diffusion. The diffusive potentials are envisioned to result from the gravitational field and a thermal gradient. Changes in liquid structure and composition are considered important for trace elements (Hildreth, 1979; Mahood, 1981), but this requires preexisting gradients in some structure-controlling components such as SiO_2 or water.

Figure 2. Rare earth element concentrations for suites of high-silica rhyolites. Values are normalized to an average chondrite (Evensen et al., 1978).

The overall chemical variations during evolution of the Mineral Mountain sequence are represented in Figure 1. In this figure enrichment factors are the ratios of concentrations in the latest domal rhyolites divided by concentrations in the first eruptive sequence of obsidian lava flows. Hence, bars plot upward for elements enriched over time. There is a depletion of LREE, a progressive shift towards enrichment of HREE, and a pronounced depletion of europium. There is an increase in volatiles (fluorine, water, chlorine), lithium, beryllium, rubidium, highly charged cations (uranium, thorium, tantalum, antimony); and decreases in europium, barium, strontium, phosphorus, titanium, and zirconium. These changes are similar to those observed at other silicic centers in the western United States such as at Twin Peaks (Crecraft et al., 1981) and the Bishop tuff (Hildreth, 1979).

Trace element data, noticeably REE, suggest that liquid-state differentiation is important in developing stratified magmas. However, compositional changes in major elements and in many of the trace elements are chemically consistent with crystal fractionation (Evans and Nash, 1978). On the other hand the initial rhyolites erupted in the Mineral Mountains are aphyric, containing virtually no phenocrysts, and Hildreth (1977, 1979) has argued convincingly that crystal settling is not appropriate for the Bishop tuff. A mechanism whereby crystal fractionation can generate compositional gradients with no apparent crystal settling is not clear. However, some other mechanism of crystal fractionation, other than crystal settling, is apparently required to account for both the chemical and physical characteristics of stratified roof zones.

The model developed for the Twin Peaks magma system (Crecraft et al., 1981; Nash and Crecraft, 1981) appears appropriate for silicic systems in

general. In the model, crystallization of an initially homogeneous magma takes place along the sides and roof of the magma chamber where heat losses are greatest. Crystallization produces a residual liquid along the crystallization front which is enriched in H_2O because the crystallizing phases are dominantly anhydrous. The increased water content reduces the magma density locally, and the buoyant boundary layer flows toward the top of the magma chamber. Crystallization at the top of the chamber produces a water-rich, less dense magma as well. The decrease in density is sufficient to stabilize the upper magma region with respect to thermal convection; thus a stagnant, chemically and thermally stratified volume may persist in the upper portion of the magma chamber.

In order to test this model, we conducted several laboratory experiments involving crystallization of an initially homogeneous solution. These experiments are described in the following section.

Experimental Studies

Introduction: Models of magma chambers, using aqueous solutions in the laboratory, have provided a great deal of information on the effect of crystallization in these systems. Chen and Turner (1980) produced continuous temperature and compositional gradients in a stagnant "roof zone" by crystallization at the top of an initially homogeneous solution. Crystals extended through this zone, and crystal liquid equilibrium was approximated throughout by upward decreases in both temperature and concentration. Their experiment suggests the possibility of a similar mechanism for generating a stratified roof zone in a magma chamber.

In both silicic magma and aqueous solution, crystallization produces a

less dense fluid at the interface. Hence, when crystallization proceeds downward, a buoyant layer forms, across which components must diffuse and gradients develop. $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ crystals in the above experiment grew in such a zone and were large and loosely packed, indicative of slow growth rates from a quiescent liquid. Where crystallization proceeded from the sides, vigorous, upward streaming of the buoyant, water-rich fluid was observed (Chen and Turner, 1980). Crystallization from the side resulted in small, closely packed crystals, indicating rapid convection near the crystal interface. In both cases, the composition of liquid at the crystal interface was different from the composition of the bulk fluid, as expected for finite rates of incongruent crystallization (Rosenberger, 1979). This provides a means by which a homogeneous fluid can become stratified and stable in composition. Once a stable compositional gradient is established, it is then of interest to determine the effect of a superimposed thermal gradient which is destabilizing. Under certain circumstances, diffusive regime convection can result, even when the net density gradient is stabilizing, (Turner, 1979; Chen and Turner, 1980; Rice, 1981; Huppert and Linden, 1979). In such a situation the initially continuous gradients break up into nearly homogeneous horizontal convection cells. Convection of each cell is driven by the flux of heat into the base of each cell as in ordinary convection; the upward diffusion of the heavy solute tends to inhibit convection but is orders of magnitude slower than the flux of heat and is too slow to prevent convection.

In order to observe the effects of crystallization in developing compositionally zoned fluids and the conditions under which diffusive regime convection can develop in such fluids, we ran several experiments involving crystallization of $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ from initially homogeneous solutions. Experiments were performed in a system of our own design and fabrication

consisting of a 32 x 40 x 10 cm tank constructed of 1/4 in plexiglas within which four sides could be individually heated or cooled. Fluid parameters for the solution used and for a hydrous magma system are given Table 4. Physical scaling factors between the magma system and the aqueous solution are determined by ratios of kinematic viscosities ($\nu_r = 10^8/10^{-2}$) and of gravity ($g_r = 1$) where r refers to the ratio of the magma system to the aqueous system. Thus $l_r^2/t_r = 10^{10}$ and $l_r/t_r^2 = 1$ (where l_r and t_r are the length and time ratios) yield $l_r = 40 \text{ km} : 1 \text{ cm}$, and $t_r = 35 \text{ min} : 1 \text{ sec}$. Model convection rates, heat flux, and crystal growth rates are all correspondingly high. The scaling factors do not permit quantitative extrapolation, but they do provide insight into and understanding of convective and diffusive transport mechanisms, and of the effects of crystallization.

Experiment results: For the first experiment only the right side of the chamber was cooled with the other three sides maintained at ambient temperature (23°C). The initial solution had a composition of 20.4 weight % Na_2CO_3 with a saturation temperature of 22.0°C. Coolant at 6.7°C was circulated along the right side of the tank where a copper screen had been placed to hold crystals. Convection of fluid downward behind the right side screen was quickly initiated in response to the side coolant. Within 25 minutes, small crystals began growing in the lower right corner where the solution was coldest. Fingers of less dense fluid, depleted in sodium carbonate by crystallization, were clearly visible streaming upward from them. Within three hours, a well-defined turbulent flow of cool but buoyant fluid had formed. It streamed upward from the corner crystals and extended the length of the right wall. Five hours into the experiment, this upward flux of buoyant fluid produced a stagnant layer at the top of the tank 3 cm thick on the right and 1.5 cm thick on the left. Following the formation of

the first layer, horizontal convection cells rapidly formed downward from the uppermost layer. Shadowgraphs of these cells are shown in Figure 3 at 9:05, 19:00, 21:10 and 24:08 hours.

Dye, visible in the photographs at 9:05 and 24:08, indicates the direction of convective flow in the cells. The uppermost layer shows no convective flow. Convection in the other layers was driven by a narrow layer less than 2 mm thick which flowed down and away from the crystallizing margin along the base of each cell. The direction of convection is opposed to the upward flux of water-rich fluid along the crystallizing margin which was still clearly visible at 9:00. Buoyant rise of this fluid, however, was apparently blocked by the cell interfaces and was confined to individual cells. No rise of fluid was observed at 9:00. The photographs in Figure 3 also indicate that the convection cells themselves were moving downward. Between 19:10 and 24:08 cell interfaces descended from 0.4 to 0.7 cm/hr. These rates decreased significantly from rates up to 3.6 cm/hr which were recorded during the first five hours after cells had formed.

Temperature profiles through each side of the tank were taken at 24:00 (Figure 4). Temperature was determined by a calibrated thermocouple and precision was $\pm 0.1^{\circ}\text{C}$. There was little overall vertical change in temperature through the lower half of the tank, although the left side was about 0.7°C warmer than the right side. In the upper portion, the temperature decreased from 20.5°C to 18.4°C above 8 cm along the crystallized side, but increased from 20.8°C to 23.3°C above 12 cm on the opposite side. The cold spikes in the right-hand profile correlate closely to the positions of cell interfaces of 24:00 (Figure 3) and indicate the positions of the cool thermal boundary layers.

Figure 3. Shadowgraph of crystallization of an initially homogeneous solution of 20.4 wt % NaCO_3 with right side wall cooled, all others at ambient temperature. The tank is 30 cm high by 40 cm wide. Time is shown in hours and minutes. In (a) and (d) dye injected along the crystallizing right wall indicates patterns of flow in horizontal convection cells.

Figure 4. Temperature profiles for the first experiment taken at 24:00. Open circles = right-hand (cooled) side of tank, closed circles = left-hand (ambient) side of tank. Squares are the temperatures calculated for saturation for the measured concentrations. This demonstrates that most of the solution is saturated, or super saturated, with the exception of the warm upper left-hand portion of the tank.

Concentration profiles (Fig. 4) were determined by withdrawing fluid and analyzing for sodium by flame photometry; precision is estimated to be ± 0.2 weight % Na_2CO_3 . No difference in the concentration between the ends of each cell was detected. Concentration increased from 17.0 weight % Na_2CO_3 at the top to 19.3% at the base. Below the stagnant layer, concentration increased an average of 0.16% per cell, corresponding to a density increase downward of 0.02 g/cm^3 per cell. The solution along the crystallizing margin was supersaturated over the entire vertical length, as is required for finite crystallization rates. The degree of supersaturation, however, decreased upward. Because of the increase in temperature in the upper left portion of the tank, this region was significantly undersaturated.

Before proceeding to the second experiment, it is useful to summarize the pertinent results of the first experiment. In this experiment, cooling from the side of an initially homogeneous solution resulted in formation of horizontal convection cells which underlay a narrow stagnant layer at the top. Each cell increased in concentration in density downward. Convection of the cells was downward along the crystallizing margin and was driven by side cooling. This direction of convection was opposite in sense to the upward flux of buoyant Na_2CO_3 - depleted fluid along the crystallizing margin which was clearly visible during the early stages of the experiment.

In the second experiment, the top and two sides were cooled, and the bottom was simultaneously heated by circulation of fluids of 6°C and 30°C , respectively. The same initial homogeneous solution was used as in the previous experiment. During the first several hours, this experiment was similar to the first. Crystals started growing by 1:30 at the bottom corners, where, despite the bottom heating, the solution was coldest because of thermal

convection. As before, fingers of buoyant Na_2CO_3 - depleted fluid rose above these crystals. By 3:00 crystals were also growing along the top and sides (Fig. 5). Throughout the experiment, crystals along the sides were small and close-packed, characteristic of growth from a convecting fluid. At the top, crystals were large and loosely packed, indicative of growth from a quiescent fluid. A distinct water-rich layer 1 to 2 cm thick developed at the top of the tank after four hours, as in the first experiment. A series of convecting layers then formed rapidly after formation of the first layer but cells were much narrower, and the upper stagnant layer expanded much more rapidly than previously. By 9:40, five hours after formation of the initial layer, the upper stagnant layer had thickened to 9 cm and 11 additional layers had formed between 9 and 22.3 cm. A very distinct interface occurred at the base of the region at 22.3 cm. This interface persisted throughout the remainder of the experiment and separated the upper "roof zone" just described from a basal zone consisting of a single large convection cell. These two regions are clearly discernable in Figure 5.

The basal layer remained relatively constant throughout the experiment. Crystallization was very restricted in this region due to bottom heating. The marginal crystal layers never exceeded 1 cm in width, in contrast to a maximum thickness of 4 cm which was reached after 51 hours in the upper zone. A diffuse and highly arched interface occurred near the bottom of the basal zone. The solution in the narrow region below this interface was warm and very concentrated and is thought to have formed by the dissolution of small crystals which settled during the experiment. Except for this, the basal zone remained homogeneous and convected throughout the experiment.

Figure 5. Shadowgraphs of crystallization of an initially homogeneous solution with left, right and top walls cooled, and bottom heated. Tank dimensions are the same as in Figure 3. See text for discussion.

Each convection layer in the upper zone contained two convection cells due to symmetrical cooling from the sides, and each cell had a flow pattern similar to cells from the first experiment. The position of the cells at 24:00 is indicated in Figure 5. In contrast to the previous experiment, a distinct thickening of the layers downward is evident. The stagnant zone in the upper region continued to expand downward at the expense of the narrow convection layers after 9:40, and by 14:20 it had extended downward to 21 cm. It was separated from the convecting basal zone only by a 2 cm layer which was also stagnant and which persisted until after 23:30. The upper roof zone then consisted of a single, broad, stagnant zone.

Narrow horizontal convection cells reappeared within the upper zone at 35 hours. Interfaces were much more diffuse than previously, but were most distinct along the margins, and convection was down along the sides driven by side cooling. During the remainder of the experiment, these cells generally occurred between 10 and 20 cm depth but were never distinct, and at times they disappeared altogether (Fig. 5, 97:15).

Temperature profiles were taken along the right-hand margin of the tank at various times starting at 9:40. These profiles are indicated by isotherms which are plotted as a function of depth and time in Figure 6. The interface between the upper and basal regions is indicated by the heavy line. The basal zone is nearly isothermal throughout, whereas the upper region is significantly zoned in temperature. Isotherms are somewhat more widely spaced through the regions of layered convection, but thermal gradients are still significant. Temperature profiles were taken along the right-hand margin and through the center at 71 hours. These profiles allow estimation of both vertical and horizontal gradients. The ratio of horizontal to vertical

Figure 6. Vertical temperature (circles) and concentration (triangles) profiles for the second experiment at (a) 22:40, (b) 35:10 hours. Squares are calculated saturation concentrations determined from temperature data. Profiles were taken approximately 11 cm inward from the right margin of the tank. The profiles illustrate the strong thermal and concentration gradients in the stagnant volume which is at or above saturation, whereas the higher temperature convecting volume is undersaturated.

gradients is plotted in Figure 7, and it is seen that the position of layered convection at 71 hours corresponds closely to where the ratio exceeds 0.5.

Concentrations were determined by measuring the index of refraction: precision is ± 0.1 weight % Na_2CO_3 . Profiles taken at 22:40 and 35:10 are given in Figure 6. The concentration increased downward through the roof zone and was constant both vertically and horizontally through the basal zone. Temperature profiles taken at 23:30 and 35:10, interpolated from data taken at 27:20 and 48:10, and the saturation temperature profile determined from the concentration data are also given. All profiles were taken near the right margin of the tank. The solution through the upper stagnant region was generally supersaturated. At the very top, however, the solution appears slightly undersaturated, due largely to a slight increase in the temperature. It is not certain that this increase is real. However, such an increase was noted by Chen and Turner (1980) only when crystallizing was from the side; an increase was never noted when cooling was from the top. The increase can be reasonably explained as a result of side cooling (see discussion below), and it extends deeper than the diameter of the access portal and seems too deep to be due to the port. Undersaturation seems required by the observation that crystallization at the top reached a maximum extent at 9:20 and then started to dissolve. At 46:20, the maximum extent of crystals at the top was only 4.5 cm, and by 70:30 it was 2.5 cm. The lower region was predominantly undersaturated because of the basal heating, and this resulted in a very restricted crystal growth as previously noted.

Discussion of experimental studies: In each experiment, crystallization produced vertical gradients in temperature and concentration from an initially homogeneous solution. These gradients could have formed in response to two

Figure 7. Ratio of horizontal (x) to vertical (z) temperature versus depth in the second experiment at 71:00 hours. The solid vertical line at $\Delta T_x / \Delta T_z = 0.5$ defines the region of diffuse convection cells similar to those shown in Figure 5d.

mechanisms: convective flux upward of H_2O -rich fluid and crystal fractionation. Convection was clearly important early in each experiment when fingers of buoyant fluid were seen streaming upward from growing crystals. In both experiments, crystal fractionation buffered the ratio of the temperature and concentration gradients along the crystallizing margins. The magnitude of these gradients, however, differed considerably in each experiment. In the first experiment, where no vertical temperature gradient was imposed, convection dominated, and gradients were gradual overall; in the second experiment, a strong vertical temperature gradient was imposed, diffusion dominated, and gradients in temperature and concentration were steep. The roles of crystal fractionation and of diffusive and convective transport in developing the features observed in these experiments are discussed below.

In both experiments, crystallization initially occurred along the margin. Bouyant water-rich fluid streamed upward from the growing crystals, resulting in the formation of a buoyant layer along the top. As the crystallizing interface moved into the solution and away from the cooling chamber wall, the temperature and hence the concentration of the interfacial fluid increased. The density of the interfacial fluid therefore also increased with time. As new fluid ascended, it accumulated below more buoyant fluid which had previously fractionated and ascended. This resulted in the development of a stabilizing concentration gradient. Cooling from the side of such a gradient generally produces layered convection cells (Turner, 1979, chapter 8) and, in both experiments, this resulted in the formation of layers downward from the uppermost layer.

Convective flow within the individual cells was downward along the cooled sides and was clearly due to side cooling. This direction of flow opposed the

upward flux of the buoyant boundary layer which was observed within individual cells. This flow resulted from the much greater diffusivity of heat ($1.4 \times 10^{-3} \text{ cm}^2/\text{sec}$) compared to Na_2CO_3 ($.7 \times 10^{-5} \text{ cm}^2/\text{sec}$), buoyancy effects of a temperature gradient extend much further into a convection cell and control the direction of flow. Convection was seen to be driven by a narrow thermal boundary layer $< 2\text{mm}$. This is typical of high Prandtl fluids ($\text{Pr} = 20$ for the solution) and the low diffusivity of heat compared to momentum (Rosenberger, 1979).

Because of the development of a pronounced thermal gradient in the second experiment, the sequence of events following the development of the convection layers differed for the two experiments. In the first experiment, convection cells persisted throughout its duration; whereas in the second, the convection cells, which initially formed, disappeared and were replaced by a stable, continuously stratified "roof zone."

Throughout the first experiment, interfaces between cells remained distinct, indicating that compositional gradients across them were maintained. Interfaces were also observed to descend continuously with time. These observations contrast with purely diffusive regime convection in which interfaces are stationary but become indistinct and disappear as diffusion across them causes homogenization of the layers (Huppert and Linden, 1979). Near the beginning of the first experiment after formation of convection cells, the light, fractionated fluid streamed up along the side of each cell and appeared to stop at the top of the cell. This fluid must have been denser than the fluid in the cell above, but it was probably closer in density to the cell above than the cell it fractionated from. It was therefore incorporated into the cell above, resulting in a net convective transport of water-rich,

fractionated fluid upward into the cell above; this then resulted in a downward shift in the cell boundary. An accumulation of progressively denser fluid into the uppermost layer probably resulted in the formation of the stabilizing concentration gradients in the uppermost stagnant layer.

A correspondence in the rate of descent of the cell interfaces with crystal growth rate and cell width, which provides a larger area of fractionation, is consistent with the mechanism of cell descent described above. Calculating the rate of cell boundary lowering, using the measured crystal growth rate after 19:00 of .5 mm/hr, we find that a typical cell width of 4 cm, and a concentration difference between cells of 0.16%, results in a rate of 0.6 cm/hr which corresponds well to observed rates of 0.4 to 0.7 cm/hr. Convection of water-rich fluid due to continued crystal growth must have persisted after 19:00 to account for the continued cell interfaces and their stability. Such a flux was not observed, however, and must have become laminar. Flux of fluid upward along the crystallizing margin also probably accounts for the decrease in temperature upward along the right side, in contrast to the opposite end of the tank and despite a warmer ambient temperature at the upper surface.

Because the concentration gradient was maintained and perhaps still growing after 19:00, the convective transport of water upward must have been equal to or greater than diffusive transport downward due to the gradients across cell interfaces. One may then write a relation between the diffusive flux of Na_2CO_3 upward through the cell interface and the advective flux due to the descent of the interface. Thus, $SV_z \geq \frac{\Delta S D}{\Delta z}$ where S is the solute concentration. $\Delta = 0.16\%$ is the difference in concentration across an interface, $V_z = 6\text{mm/hr}$ is the velocity of interface descent, and $D = 7 \times 10^{-5}$

cm^2/sec is the diffusivity of Na_2CO_3 . For these values, $\Delta Z \geq 4 \times 10^{-3} \text{ mm}$ and cm^2 this represents a minimum thickness of the diffusive layer between convection cells.

In the second experiment, a pronounced vertical temperature gradient was established and still growing at 9:05. Crystallization along the side resulted in a concentration gradient which was so strongly stabilizing as to prevent diffusive regime convection, and thus resulted in the formation of the zoned stagnant layer. The decrease in temperature upward also resulted in an upward decrease in the horizontal temperature gradient across the margin between the solution and the coolant. The horizontal convection cells were driven by the horizontal temperature gradient, and its decrease upward resulted in a narrowing of the cells upward as previously noted. As the temperature gradient extended downward, crystal-liquid buffering caused expansion of the stagnant layer and the layered convection cells which had developed over the first 9 hours became progressively narrower and more diffuse, and ultimately disappeared.

Measured temperature and concentration gradients demonstrated that the degree of supersaturation decreased upward in each experiment, and in the second that the uppermost solution was undersaturated. It is clear that undersaturation cannot result from crystal fractionation alone and that upward convective transport of a water-rich boundary layer must have occurred as in the first experiment. The thickness of the crystal layer along the margins was uniform. This indicates that the compositional gradients in the solution formed in response to a net upward flux of water, rather than simply from crystal-liquid buffering which would not have resulted in any net vertical mass flux. Continued growth of small, densely packed crystals along the side

throughout most of the experiment also requires continued convection of fluid along the interface.

Water-rich fluid evidently convected upward as a continuous boundary layer along the margins of the stable, stratified solution. Any horizontal density gradient (along a vertical surface) causes instability and convection; there is not a threshold density difference or critical Rayleigh value as in convection between horizontal surfaces (Turner, 1979; Rosenberger, 1979). In this experiment, however, there is a pronounced vertical density gradient which is stabilizing. A horizontal temperature difference can induce a horizontal density gradient, but because of the stable vertical gradient, any element of fluid can only rise or sink a limited amount before it reaches a stable level. This gives rise to narrow horizontal convection cells such as those in the first experiment and in the early stages of the second. A threshold gradient is necessary for this type of convection, however (Turner, 1979). Thus, with an increasing vertical density gradient developing during the first 15 hours of the second experiment, the critical value for convection also increased. The effect of crystallization along the margin of a stable stratified fluid, however, will be quite different. Any finite rate of crystallization causes a chemical boundary layer depleted in the crystallizing component relative to the fluid further from the interface. This causes a density perturbation and rise of fluid. Because of the relatively rapid diffusivity of heat, the fluid is continually being cooled and depleted in Na_2CO_3 by crystallization along the margin as it rises into cooler and less dense levels. Hence, even in a continuously zoned stable density gradient, a finite rate of crystallization can form a continuous boundary layer that at every point is less dense than the fluid further from the interface. As long as this condition holds, there is no threshold gradient required for

convection, just as in the homogeneous fluid. Thus, convective transport of a water-rich boundary layer upward seems to be both required by observations and expected theoretically.

The vertical gradients in temperature and composition resulted in the formation of a large stagnant volume. Although these gradients promoted stability, after 35 hours horizontal convection cells again developed in the upper stagnant zone in response to horizontal temperature gradients. Their position correlated closely to where the ratio of horizontal to vertical temperature gradients exceeded 0.5. This region was also characterized at 22:40 and 35:10 by a smaller ratio of vertical concentration to temperature gradients (0.52 and 0.53 respectively) compared to the upper 10 cm (1.0 and 0.73 respectively). Hence, this region also had a less stabilizing ratio of temperature and concentration gradients. This is in contrast to the effect of equilibrium alone which causes a decrease in the ratio $\Delta S/\Delta T$ with decrease in temperature. This further indicates convective transport of water upward.

The cause of the reappearance of convection and the implied increase in the horizontal temperature gradients can be explained as follows: if an element of solution with a concentration of 18% Na_2CO_3 at the base of the stratified zone flowed toward the crystal interface, and then convected upward in response to crystallization and reached the top with a concentration of 12% Na_2CO_3 , then the rate of crystallization during the first 31 hours of 1.1 mm/hr would have resulted in a descent of the bulk interior fluid of 6.0 mm/hr = 1.7×10^{-4} cm/sec. For a thermal diffusivity of 1.3×10^{-3} cm²/sec this convective flux downward would have reduced the purely diffusive upward heat flux by 13%. Crystallization ceased altogether after 51 hours, and it probably decreased continuously from an initial maximum rate. During the

earlier part of the experiment, the net heat flux could have been more strongly depressed than the average value over the first 31 hours. Decreasing the rate of crystallization and the rate of descent of the stratified zone resulted in an increase in vertical heat flux with time. The effect of this was to increase the temperature of the interior, while near the margins no such increase was noted (Fig. 6). The horizontal gradient therefore increased over time and resulted in the reappearance of the convection cells.

Thermodynamic Analysis of Diffusive Regime Convection

The effect of crystal fractionation in a complex magma system depends strongly upon the mechanisms of mass transport and their relation to crystallizing margins. It is therefore essential to understand these transport mechanisms and their causes before the results of the previous experiments can be applied to magma systems. Turner (1979) and Huppert and Linden (1979) discuss many of the phenomena associated with double diffusive convection from a fluid dynamic approach. In the following discussion, these phenomena are considered more generally in terms of irreversible thermodynamics. Systems not too far from equilibrium approach equilibrium in such a manner that the rate of entropy production is minimized (deGroot and Mazur, 1962). This principle is a fundamental postulate of irreversible thermodynamics and can be viewed as an extension of the Second Law. A thermodynamic approach has a great advantage over mechanistic approaches. General principles permit prediction of which of various possible processes a system will take in approaching equilibrium without necessitating detailed analysis of the system. As with classical thermodynamics such an analysis cannot provide mechanistic details of any process, but it can predict whether a certain process is thermodynamically more favorable than another.

Rate of entropy production: The rate of entropy production is given in general form by (deGroot and Mazur, 1962)

$$\Theta = \frac{1}{V} \frac{dS}{dt} = \sum_i J_i X_i, \quad (1)$$

where J_i is the flux of component i (which is not restricted to matter) and X_i is its driving potential. For flux of heat q and of mass i in an n component system, (1) may be written

$$\Theta = J_q X_q + \sum_i^n J_i X_i = J_q X_q + \sum_i^{n-1} J_i (X_i - X_n). \quad (2)$$

The last expression of (2) follows from the preceding because of the sum of diffusive fluxes must equal zero, and hence there are only $n-1$ independent mass fluxes. For one-dimensional diffusion of matter i and of heat q over a distance ΔZ , these terms are given by (Bird et al., 1960; deGroot and Mazur, 1962)

$$J_q = -K \frac{\Delta T}{\Delta Z} \quad (3a)$$

$$J_i = -D_i \frac{\Delta S_i}{\Delta Z} \quad b$$

$$X_q = -\frac{\Delta T}{T^2} \approx \frac{1}{T^2} \frac{\Delta T}{\Delta Z} \quad c$$

$$X_i = \frac{1}{T} \frac{(\Delta \mu_i)}{\Delta Z} T = \frac{R}{X_i} \frac{\Delta X_i}{\Delta Z} = \frac{R}{S_i} \frac{\Delta S_i}{\Delta Z} \gamma_i. \quad d$$

For the $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and water-magma binary systems, values for K and $D = D_1 = D_2$ are given in Table 4; S_i and X_i are the concentration (g/cm^3) and mole fraction of solute i ; and γ_i is a factor to convert from mole fraction to concentration and is given by:

$$\gamma_i = \frac{S_i - S_i' \frac{M_2 S_1 + M_1 S_2}{M_2 S_1' + M_1 S_2'}}{S_i - S_i'}$$

where M_i is the molar weight of i and $S_i - S_i' = \Delta S_i \cdot \gamma_i$ is weakly dependent on S_i but is nearly independent of ΔS and may be considered constant. By combining the expressions for fluxes and potentials in equation (3) into the general equation for the rate of entropy production (equation (2)), one can derive an expression for the rate of entropy production due to diffusion of heat and mass. Ignoring cross effects (i.e., heat of transfer), substitution of (3) into (2) yields for the rate of entropy production in a two-component system

$$\Theta = \frac{k}{T^2} \left(\frac{\Delta T}{\Delta Z} \right)^2 + D \frac{\Delta S^1}{\Delta Z} \left(\frac{R}{S_1} \frac{\Delta S^1}{\Delta Z} \gamma_1 - \frac{R}{S_2} \frac{\Delta S_2}{\Delta Z} \gamma_2 \right) \quad (4)$$

The contribution to the total entropy production due to diffusion of component 2 (solvent water for the aqueous system; anhydrous magma for the hydrous magma system) is much smaller than and is nearly proportional to the entropy production due to component 1 (solute). It is convenient to consider explicitly only the diffusion of solute and to incorporate the effect of the solvent into a factor, Γ , which also incorporates γ . We may then rewrite (4) as

$$\begin{aligned} \Theta &= \frac{K}{T^2} \left(\frac{\Delta T}{\Delta Z} \right)^2 + \frac{D}{S_1} \left(\frac{\Delta S_1}{\Delta Z} \right)^2 R \gamma_1 \left\{ 1 - \left(\frac{S_1}{S_2} \right) \left(\frac{\Delta S_2}{\Delta S_1} \right) \left(\frac{\gamma_2}{\gamma_1} \right) \right\} \\ &= \frac{K}{T^2} \left(\frac{\Delta T}{\Delta Z} \right)^2 + \frac{D}{S} \left(\frac{\Delta S}{\Delta Z} \right)^2 \Gamma \end{aligned} \quad (5)$$

where the subscript (1) has been dropped. Γ is nearly independent of ΔS and ΔZ and it is assumed constant. For concentrations given in Table 4,

$$\Gamma = \begin{cases} 0.11 & \text{cal/g}^0\text{K for water-magma} \\ 0.018 & \text{cal/g}^0\text{K for Na}_2\text{CO}_3 - \text{H}_2\text{O} \end{cases} \quad (6)$$

Equation (5) expresses the rate of entropy production due to diffusion of mass and heat across a length ΔZ . In diffusive regime convection, diffusion is confined to narrow interfaces which separate convection layers (Fig. 3). In contrast to diffusive transport where heat (matter) is transported irreversibly down a gradient, convective transport is more nearly reversible and approaches a Carnot cycle. As heat (matter) enters the base of a convecting cell, a portion of the energy associated with the transfer is converted reversibly into mechanical work of thermal (solutorial) expansion of a fluid element. In a multicomponent or multiphase system, energy may also be converted reversibly into chemical work by chemical reaction or phase changes within the fluid element. The fluid element rises buoyantly and expands adiabatically as pressure decreases. At the top the fluid releases heat (matter) gained at the base, sinks adiabatically to the base of the cell, and returns to its initial state, thus completing the cycle. Some entropy is produced due to viscous dissipation, but in free convection this is generally negligible. Entropy may also be produced due to diffusion at the top and base of the convection cell because gradients are required for finite convection rates, but this is insignificant compared to diffusion in the diffusive layer. The entropy produced by diffusion and viscous dissipation in the convective layer is therefore negligible or at least small compared to the entropy production of the diffusive layer and will not be considered further. All of the entropy production due to diffusive regime convection will therefore be ascribed to the diffusive layer and is given by equation (5).

Application of minimum entropy production to diffusive regime convection: In our analysis of diffusive convection, we wish to consider the rate of entropy production in a unit consisting of a single diffusion layer and an

overlying convection layer with a fixed total thickness ΔZ , temperature difference ΔT , and concentration difference ΔS (Fig. 8). We need to determine under what conditions expansion or contraction of the diffusion layer causes a reduction in the rate of entropy production. In the following discussion, the superscripts c and d refer to convective and diffusive portions of the unit system. Instead of entropy production per unit volume, we will consider the rate of entropy production per unit area of the diffusive-convection cell, due to diffusion only, averaged over the thickness ΔZ . We therefore will use:

$$\theta^* = \Delta Z \theta = \frac{K}{T^2} \frac{\Delta T_d^2}{\Delta Z^d} + \frac{D}{S} \frac{\Delta S_d^2}{\Delta Z^d} \equiv \theta_t^* + \theta_s^* \quad (7)$$

θ is inversely proportion to ΔZ^d and proportional to $(\Delta T^d)^2$ or $(\Delta S^d)^2$, whichever term dominates. In the analysis below we need to determine the conditions under which θ is minimized either by a decrease in the diffusive layer thickness ΔZ^d (resulting in diffusive regime convection) or by an increase in ΔZ (resulting in the development of stable, continuously zoned fluids).

The effective Rayleigh number is defined as $Ra_{eff} \equiv Ra_t - Pr Ra_s / (1 + Pr)$ (Turner, 1979) where $Ra_t = \frac{\alpha g \Delta T^c d^3}{\nu K}$, $Ra_s = \frac{\beta g \Delta S^c d^3}{\nu K}$, g is the gravitational acceleration, d is the height of the convection cell, and definitions and values of other terms are in Table 4. Ra_{eff} must exceed a certain critical value in order for convection to occur. For diffusive regime convection, both Ra_t and Ra_s are positive; the thermal gradient thus promotes convection and the compositional gradient inhibits it. Assuming $Pr \gg 1$ (appropriate for both the aqueous-solution and hydrous magma) and setting $Ra_t = Ra_s$, it is evident that $\Delta S^c / \Delta T^c = \alpha / \beta$ when the two terms are comparable, and for convection to occur, $\Delta S^c / \Delta T^c < \alpha / \beta$. Values given in Table 4 indicate that

Figure 8. Schematic diagram of convective and diffusive layers of diffusive regime convection. See text for discussion.

$$\Delta S^C / \Delta T^C < \begin{cases} 10^{-4} \text{ g/cm}^3 \text{ } ^\circ\text{C} \text{ for aqueous solution;} \\ 10^{-5} \text{ g/cm}^3 \text{ } ^\circ\text{C} \text{ for hydrous magma} \end{cases} \quad (8)$$

Total gradients in the two systems are buffered by crystal-liquid equilibrium to approximately

$$\frac{\Delta S}{\Delta T} \approx \begin{cases} 10^{-2} \text{ g/cm}^3 \text{ } ^\circ\text{C} \text{ aqueous solution} \\ 3 \times 10^{-4} \text{ g/cm}^3 \text{ } ^\circ\text{C} \text{ hydrous magma} \end{cases} \quad (9)$$

From equations (8) and (9), it is seen that $\Delta S^C \ll \Delta S$ and that ΔS^d can be assumed to be nearly one and independent of ΔZ^d . Thus, the solutal term θ_s^* in (7) is inversely proportional to ΔZ^d , and the derivative of θ_s^* with respect to ΔZ^d can be given by

$$\frac{d\theta_s^*}{d\Delta Z^d} = -r \frac{D}{S} \left(\frac{\Delta S^d}{\Delta Z^d} \right)^2 < 0 \quad (10)$$

The negative value for $d\theta_s^*/d\Delta Z^d$ indicates that θ_s^* is minimized by expansion of the diffusive layer and the concentration gradient therefore promotes stable stratification.

It is shown below that the thermal term promotes diffusive regime convection; that is, the rate of entropy production due to thermal flux, θ_t^* , is minimized by decreasing diffusive layer thickness. Differentiating θ_t^* , (equation (7)) with respect to ΔZ^d yields

$$\frac{d\theta_t^*}{d\Delta Z^d} = \frac{K}{T^2} \frac{(\Delta T^d)^2}{d\Delta Z^d} = \frac{K}{T^2} \frac{\Delta T^d}{\Delta Z^d} \frac{d\Delta T^d}{d\Delta Z^d} + \Delta T \frac{d(\frac{\Delta T^d}{\Delta Z^d})}{d\Delta Z^d} \quad (11)$$

For $\Delta Z^d \ll \Delta Z$, the convective flux and hence diffusive flux are nearly independent of small changes in the diffusive layer thickness ΔZ^d . It follows that

$$\frac{d\Delta g}{d\Delta Z^d} = - \frac{d \frac{\Delta T^d}{\Delta Z^d}}{d \Delta Z^d} \approx 0 \quad (12)$$

and from (12)

$$\frac{d\Delta T^d}{d\Delta Z^d} \approx \frac{\Delta T^d}{\Delta Z^d} . \quad (13)$$

Substituting (12) and 13) into (11) yields

$$\frac{d\theta_t^*}{d\Delta Z^d} \approx \frac{K}{T^2} \left(\frac{\Delta T^d}{\Delta Z^d} \right) > 0 \quad (14)$$

for $\Delta Z^d \ll \Delta Z$.

In the limit $\Delta Z^d = 0$, we have $\theta_t^* = 0$, and θ_t^* is positive for any non-zero diffusive layer thickness. It follows from this and (14) that θ_t^* is minimized for $\Delta Z^d \rightarrow 0$, and that the thermal component therefore promotes a continuous decrease in the diffusive layer thickness.

It has been shown that the solutal and thermal terms of the entropy production equation (7) have opposing effects. When θ_t^* dominates, the diffusive layer contracts, but when θ_s^* dominates, the diffusive layer expands. The rate of entropy production will be minimized when

$$\frac{d\theta^*}{d\Delta Z^d} = \frac{d\theta_t^*}{d\Delta Z^d} + \frac{d\theta_s^*}{d\Delta Z^d} = 0 . \quad (15)$$

Substituting equation (10) and equation (14) into (15) yields

$$\frac{\Delta S^d}{\Delta T^d} = \left(\frac{SK}{RT^2} \right)^{1/2} \quad (16)$$

Using appropriate values from equation (7) and Table 4, equation 16 indicates that the solutal term dominates and the diffusive layer should expand under the following conditions:

$$\Delta S^d / \Delta T^d > \begin{cases} 10^{-2} & \text{aqueous solution} \\ 0.6 & \text{hydrous magma} \end{cases} .$$

When a stably stratified diffusive layer in the $\text{Na}_2\text{CO}_3 - \text{H}_2\text{O}$ system has $\Delta S / \Delta T < 2 \times 10^{-2} \text{ } ^\circ\text{C}^{-1}$, then the formation of a convecting layer and contraction of

the diffusive layer should result.

In the second experiment, and in the experiments of Chen and Turner (1980) where gradients were primarily vertical, zones in which $\Delta S/\Delta T$ were buffered by crystal-liquid equilibrium to about 10^{-2} were observed to produce stably stratified gradients. When $\Delta S/\Delta T < 10^{-2}$, as below the crystal zones in Chen and Turner's experiments, stratified convection cells were observed. The expected critical ratio for solutal and thermal gradients is apparently too high by about a factor of two, but this seems to be a reasonable agreement. The theory predicts that for magma, diffusive regime convection will occur with a ratio of $\Delta S/\Delta T < 0.6$. In the magma, $\Delta S^d/\Delta T^d = 3\%/100^\circ = 3 \times 10^{-4} \text{ } ^\circ\text{C}^{-1} \ll 0.6$. Thus, temperature and compositional gradients typically formed by crystal-liquid buffering in magmas should always break down into diffusive regime convection and, by analogy, we expect the same behavior to have occurred in the Mineral Mountains magma system, i.e., $\Delta S^d/\Delta T^d < 0.6$. The high value of $\Delta S/\Delta T$ permitted for convection in magma is directly related to the extremely low diffusivity of solute (i.e., water) and the small contribution this term will have on the net rate of entropy production in equation 8.

No consideration of horizontal gradients was made in the analysis above. In the first experiment, crystal-liquid equilibrium buffered the gradients to $\Delta S/\Delta T \sim 10^{-2}$ but convection was strongly dominant. Convection also developed in the stably stratified zone in the second experiment. In these cases, convection was driven by a horizontal component of the thermal gradient. A horizontal thermal gradient adds an additional term to equation (1), due to horizontal diffusion; this term is negligible when the fluid convects. This effect provides an additional impetus for convection. In the second experiment convection occurred only where $\Delta T_x/\Delta T_z$ exceeded 0.5. In the

first experiment the horizontal temperature gradient dominated and convection occurred throughout the experiment except in the narrow uppermost volume.

It was further assumed in the analysis above that ΔT and ΔS were fixed for each layer. In that case, criteria were established by which one could estimate whether vertical flux would be by diffusive regime convection or by diffusion alone. In the experimental solution and in magma, $\Delta S/\Delta T$ will be buffered, but the absolute values of ΔS and ΔT across each cell are not fixed. Increasing the number of layers could decrease ΔT^d and ΔS^d across each diffusive layer and increase the sum of the diffusive layer widths. Because $\Theta_t^* \propto \frac{(\Delta T^d)^2}{\Delta Z^d}$ and $\Theta_s^* \propto (\Delta S^d)^2 / \Delta Z^d$, a net decrease in the rate of entropy production would result. Thus, a roof zone made up of horizontal convection cells should continue to extend downward as long as there is room, and the spacing between layers should decrease until Ra_{eff} for each cell assumes a minimum value necessary for convection.

Thermal Evolution

Chemical and physical modeling of cooling magma chambers indicates that magma bodies crystallize primarily inward from their margins. Crystallization along the margin causes a flux of fluid from the interior into the interfacial zone due to advection of fluid through the crystal-liquid interface (i.e., crystallization) and convective flux of buoyant residual fluid upward. Hereafter, "advective flux" will denote both of these effects together. For the Mineral Mountains magma the average velocity of crystallization can be estimated to be between 1×10^{-6} and 7×10^{-7} cm/sec (Evans and Nash, 1980), similar to growth rates determined by Swanson (1977). Chemical modeling (Evans and Nash, 1978) suggests that 70% of the magma in the boundary layer was crystallized, which requires a flux of magma into the interfacial zone of

about 1.3×10^{-6} cm/sec. If this fluid cooled 90°C (Evans and Nash, 1978) and crystallized 70%, as suggested by chemical modeling, the net advective heat flux due to the flux of magma toward the interface would be $J_q^{\text{ad}} = W [F H_f + \Delta T C_p \rho] = 2.7 \times 10^{-4}$ cal/cm² - sec where W is the flux of magma (1.3×10^{-6} cm/sec), F the weight fraction crystallized (0.7), H_f the heat of fusion (100 cal/cm³), $\Delta T = 90^\circ\text{C}$, c_p is the heat capacity (0.3 cal/°C-cm³) and ρ the density (2.4 g/cm³). If the interior is isothermal, conduction or convection would be negligible, and heat flux from the interior to the margin would be due to advective flux alone. It follows that an element of magma would lose no heat until it was advected into the interfacial region; increasing the flux of heat away from the magma chamber would only cause an increase in rate of crystallization and in the advective heat flux.

Thermal modeling by Carrier and Chapman (1981) indicates that substantial heat input into the Twin Peaks magma body was necessary to sustain volcanism for 300,000 yrs; conductive cooling should have solidified the body in 30,000 years. Large thermal deficits appear to be typical for shallow-level silicic magma systems, and it is generally thought that thermal input is due to underplating by basalt (Lachenbruch and Sass, 1978; Hildreth, 1981). Convective heat flux from the base of the magma chamber to the margins could account for increased heat flux from the Mineral Mountains magma. The analysis by Shaw (1974) on convection in magmas indicates that convection can provide 2×10^{-5} to 50×10^{-5} cal/cm²-sec with a thermal boundary layer of 50 to 5 meters in dry to wet granitic magma, respectively. In his analysis, convection was assumed to be driven by a 10°C lateral temperature difference. In our analysis, advection is much greater than conduction, and there is no mechanism to generate a substantial lateral thermal gradient inward from a crystallizing margin. However, vertical gradients, as would

result from underplating of basalt, could drive convection. The convective velocity in dry granite as calculated by Shaw (1974) is two orders of magnitude greater than the advective velocity, and hence, convection would greatly augment the heat flux due to advection alone. The thermal effects of convection are confined to a narrow zone less than 50 meters (Shaw, 1974), and the interior magma should still remain nearly isothermal, as predicted above and deduced for the eruptive period of the Mineral Mountains magma chamber.

Conclusions

By examination of the volcanic products of successive eruptive episodes, it is possible to establish the nature of time-dependent petrological and thermal processes for the Mineral Mountains magma system. The chemical characteristics of the Mineral Mountains volcanic rocks are similar to those of other silicic systems in the western U.S., including large, long-lived systems such as Yellowstone and Long Valley, and more moderate systems such as Coso (Hildreth, 1981); the Mineral Mountains system represents the small volume end of this volcanic spectrum. A second fundamental characteristic is that, regardless of size, these systems are active for periods of time that exceed those predicted from conductive cooling models and are sustained by the injection of mafic magmas into the crust. In the Mineral Mountains, surface manifestations of mafic magmas are seen in contemporary basaltic lava flows to the east and north, as well as quenched basalt inclusions in the Bailey Ridge rhyolite which demonstrate injection of mafic magma directly into silicic magma. The small volume, phenocryst-poor rhyolite magma which persisted for at least 300,000 years in the Mineral Mountains requires the presence of continued thermal input from a mafic magma source. Furthermore, the physical model developed in this report requires thermal input into a crystallizing system which results in double-diffusive behavior.

Because high-silica rhyolites are developed over time in a magma chamber that has heat supplied to it, the occurrence of these silicic lavas signifies that there is a substantial thermal anomaly both in the crust and upper mantle. The production of silicic lavas requires 1) the heating of the lower crust to near the solidus for silicic melts, 2) partial fusion by the additional convective transfer of heat from the mantle by injection of

basaltic magma, and 3) continued input of heat in excess of the conductive and convective heat loss to allow the crustal melt to grow to some critical size so that it can rise buoyantly into the upper crust. Pre-heating of the crust is evident from nearby basaltic episodes of 7, 2.5 and 1 m.y., and by the Twin Peaks silicic system (2.6 - 2.3 m.y.) immediately north of the Mineral Mountains. In the case of the Mineral Mountains, oxygen isotopes (Bowman et al., 1982) preclude shallow crustal melting because whole rock $\delta^{18}O$ values of 6.3 to 6.9 per mil indicate an I-type source; i.e., not recycled sediments which had undergone surficial weathering processes.

In the Basin and Range Province, it would appear that the controlling factor in the delivery of magma to the surface is the thermal input and tectonic environment. In the Mineral Mountains there has been an inadequate prolonged thermal flux to produce caldera-forming eruptions. Moreover, the distributed extension in the Basin and Range allows for the propagation of small volumes of magma upward, probably in dike-like bodies, parallel to the direction of maximum horizontal compressive stress; i.e., generally north-south, parallel to major range-bounding faults. The erupted lavas represent a highly differentiated and presumably small fraction of the total volume of silicic magma which is contained at considerable depth. In this respect the Mineral Mountains system closely resembles the larger Coso system (Bacon et al., 1981) where the magma chamber is thought to be at least 8 km deep.

Although there have been no rhyolites erupted in the last 500,000 years, the future of the Mineral Mountains volcanic system cannot be predicted. It may be declining, although basalt was erupted 300,000 years ago in the eastern margin of the range, indicating thermal input to the system 200,000 years after the last rhyolite eruption. The youngest volcanic activity is now 40-60

km north in the Black Rock Desert, which may indicate a shift in the major lower crust thermal anomaly to the north. It is within this volcanic field, ranging in age from 1.5 m.y. to Holocene, that the youngest rhyolite in Utah (0.4 m.y.) is found.

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