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APPLICATION OF DUHEM'S THEOREM TO THE ESTIMATION OF EXTENSIVE AND INTENSIVE PROPERTIES OF BASALTIC MAGMAS

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ABSTRACT

Duhem's Theorem applied to igneous systems has stimulated petrologists to examine simultaneously the extensive and intensive properties of the system. Simultaneous solution of equations for material balance and thermodynamic equilibrium in a closed magma-system, at known temperature and pressure, yields an invariant description of the equilibrium state of the magma. The technique is illustrated using olivine and plagioclase porphyritic lavas from the Snake River Plain and southeast Oregon. The crystallization history of these lavas is constrained by matching the observed abundances and compositions of phases with the predicted values. The phenocryst assemblages in these lavas have crystallized from liquids with compositions close to the respective whole-rock compositions. The McKinney basalts have a phenocryst assemblage that reflects an initial low-pressure (2–4 kbar) equilibrium crystallization of olivine and plagioclase followed by cotectic fractional crystallization of the same assemblage. The Cow's Lake lava assemblage can be explained by higher-pressure fractional crystallization of the whole-rock composition. The amount and composition of olivine precipitating reflect the cooling history of the magma and change drastically with the addition of plagioclase to the liquidus assemblage. The increase in amount of olivine crystallizing during cotectic precipitation may result in the generation of microphenocrysts of olivine.

Keywords: thermodynamic, modeling, basalt, magma, petrogenesis, Oregon.

SOMMAIRE

L'application du théorème de Duhem aux systèmes ignés a mené à l'examen simultané de propriétés extensives et intensives du système. La solution simultanée des équations pour la conservation des masses et pour l'équilibre thermodynamique dans un système magmatique fermé, à température et pression connues, donne une description invariante de l'état d'équilibre du magma. On illustre la technique avec les laves porphyritiques à olivine et plagioclase de la plaine de Snake River et du Sud-Est de l'Oregon. La séquence de cristallisation de ces laves est contrainte en simulant correctement l'abondance et la composition des phénocristaux. L'assemblage des phénocristaux dans ces laves aurait cristallisé de liquides ayant une composition semblable à celle des roches totales. Les basaltes de McKinney possèdent un assemblage de phénocristaux qui indique une formation initiale d'olivine et de plagioclase équilibrés à basse pression (2–4 kbar), suivie d'une cristallisation cotectique fractionnée du même assemblage. L'assemblage dans la lave du lac Cow indiquerait une cristallisation fractionnée à pression plus élevée d'un magma de composition égale à celle de la roche totale. La quantité et la composition de l'olivine précipitée reflètent les événements pendant le refroidissement du magma et changent radicalement quand le plagioclase devient une phase stable sur le liquidus. L'augmentation de la quantité d'olivine qui cristallise pendant l'évolution cotectique pourrait avoir comme résultat la formation de microphénocristaux d'olivine.

(Traduit par la Rédaction)

Mots-clés: thermodynamique, modèle, basalt, magma, pétrogenèse, Oregon.

INTRODUCTION

Igneous petrology is commonly directed toward an unraveling of the processes that generate the diverse range of lavas erupted at the earth's surface. To this end, petrologists collect volumes of eclectic data on suites of volcanic rocks. Data that are generally considered essential in providing a complete petrological description include the whole-rock composition, compositions of the mineral phases, and a mode. Constraints on the nature of magmas parent to the sampled rocks are commonly imposed by mass-balance equations that use the whole-rock chemistry and thermodynamic calculations that utilize the phase chemistry. Although modal proportions of the coexisting phases reflect equally the equilibrium state of any closed system, they are rarely employed quantitatively in igneous petrology (Bryan 1983).

The value of modal data in metamorphic petrology has been recognized by Thompson *et al.* (1982) and Laird (1980). Their consideration of extensive variables in the metamorphic system is adequately compensated for by the constraints imposed when considering a closed system. From the approach of Thompson *et al.* (1982), metamorphic petrologists are able to make quantitative conclusions about metamorphic systems that have a variance of 2 or greater. Igneous petrologists are more often than not resigned to working with systems with high degrees

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*Present Address: Department of Geological Sciences, University of British Columbia, Vancouver, British Columbia V6T 2B4 of freedom. The Gibbs phase rule generally offers limited new insight to petrologists investigating systems with 10 or more oxide components. Hence igneous petrologists considering the import of Duhem's Theorem simultaneously examine extensive and intensive variables (Verhoogen 1949). Nicholls (1977) has effectively applied the consequences of Duhem's Theorem to the calculation of equilibrium phase-assemblages and chemistry in the upper mantle. It is implicit in the work of Nicholls (1977) that as much information concerning the equilibrium state of the system resides in the mineral modes as in the phase chemistry. With the innovative work of Ghiorso & Carmichael (1980) and Ghiorso *et al.* (1983), it is now possible to apply these conclusions to melt - solid systems (*i.e.*, magma chambers).

The bulk composition of selected volcanic rocks are used to calculate the unique phase assemblage, phase compositions, and proportions at equilibrium for a related magma at a specified pressure and temperature. Successive calculations at subliquidus temperatures can model potential paths of equilibrium crystallization for basalt magmas. Paths of fractional crystallization are determined by removing previously precipitated solid phases from the system before repeating the equilibrium calculation at a slightly lower temperature or pressure. The calculated path of equilibrium crystallization is invariant for a fixed starting temperature, pressure and composition. Whereas the path of perfect fractional crystallization is also invariant for the same fixed starting conditions, the model only approximates this path by reducing the size of the temperature or pressure interval between successive iterations. A comparison of the calculated variables with the observed phase-assemblage, compositions, and proportions illustrates 1) whether the phenocryst assemblage can be precipitated solely from the whole-rock composition, and 2) whether processes of equilibrium or fractional crystallization dominated the early crystallization-history of the related magmas.

DUHEM'S THEOREM

A special case of heterogeneous equilibrium is realized when the system being examined acts as a closed chemical system. The additional mass-balance constraints, implied by the closed aspect of the system, allow the calculation of both extensive and intensive properties pertinent to the equilibrium state. Duhem's Theorem formally states the relation between the variance of a closed system and its equilibrium position. The theorem states that for a closed system of known composition (*i.e.*, known individual masses of N components), only two other independent variables are required to define the equilibrium state of the system (Prigogine & Defay 1954). The description of the equilibrium position includes complete knowledge of the extensive and intensive properties of the system. This is applicable to all closed systems but is most powerful for systems with high variances.

The Gibbs phase rule determines if the two independent variables must be intensive properties of the system or not. Consequently the high variance of a natural silicate melt ensures that it is our privilege to choose extensive or intensive parameters as the independent variables. Therefore, in a magma of known composition, the amounts and compositions of all phases as well as all other extensive and intensive variables are determined by fixing two pertinent independent variables.

CALCULATION OF MAGMA CHARACTERISTICS

In the following calculations, the volcanic rocks are assumed to represent samples of magmas that approximate closed systems. Further, amounts and compositions of phenocrysts observed in the rock samples are assumed to be representative of either equilibrium or fractional crystallization processes from liquids equivalent in composition to the whole-rock chemistry. If these criteria hold, the equilibrium state of the magma in a pre-eruptive condition may be determined with knowledge of phenocryst compositions or independent estimates of temperature and pressure. The solution reflects equilibrium crystallization.

An adequate description of the magmatic system includes variables to describe the bulk composition of the magma, the amounts of each solid phase present, the amount of the residual silicate melt and the composition of the solid and coexisting melt phases. Table 1 lists the variables required to define the system for olivine- and plagioclase-phyric lavas. The inclusion of temperature and pressure as the two additional independent variables defines entirely the equilibrium state of the system. Given the choice, petrologists tend to choose intensive variables such as temperature and pressure as the independent ones, rather than extensive properties because of the difficulty of determining meaningful values for the latter variables.

Both the bulk composition of the magma and the composition of the residual liquid are described by the 12 components used in the regular-solution model for silicate liquids of Ghiorso *et al.* (1983). These components are recalculated from the oxide components using the equations in Table 1. The solid phases olivine and plagioclase are treated as binary solid-solutions each requiring only one independent compositional variable. Including pressure and temperature, there are 31 variables that describe equilibrium in the magmatic system.

Solution of the equilibrium state in this C-component system demands 17 independent equations (31–C–2 = 17). Thirteen equations ensure conservation of material (F1–F13; Table 2). Equation F13 states that the sum of mole fractions of components in the residual liquid is unity.

The four remaining equations come from the expected equilibrium between the crystalline phases and the residual silicate liquid. These equilibria are described by four relationships equating the chemical potentials of components prominent in the solid phases with the stoichiometric chemical potentials of components used to describe the silicate melt-phase. Table 3 lists the four equations derived from these equilibria (F14 - F17). The equilibria between solid (s) and melt (m) are expressed by equations F14 - 17 'a'. Equations 'b' and 'c' are the equivalent thermodynamic (in terms of Gibbs free energy) and mathematical expressions for the appropriate equilibria.

The expressions used to relate the compositions of the solid phases to the required activities are equivalent to those chosen by Ghiorso *et al.* (1983). This is necessary to preserve the integrity of the activities of the liquid components calculated using the regular-solution model of Ghiorso *et al.* (1983). The standard-state thermodynamic data required to formulate $\Delta G^0_{(P,T)}$ are also extracted from the work of Ghiorso *et al.*

Simultaneous solution of these 17 equations is performed by the Newton–Raphson method for non-linear equations (Burden *et al.* 1978), which yields the expected convergence, provided a sufficiently accurate initial guess is entered and the inverse of the Jacobian matrix exists. The entries required on the Jacobian matrix are the first derivatives of the functions F1 - 17, taken with respect to each of the seventeen unknowns. In several of the examples, significant precipitation of olivine occurs prior to the addition of plagioclase to the solid assemblage. For such lavas (or lavas that precipitate plagioclase initially), modified sets of equations are used that do not include variables or equilibria involving the absent phase. The solution vector includes values for the amounts and compositions of olivine, plagioclase and silicate melt in equilibrium at a specified temperature and pressure.

TABLE 1. COMPOSITION VARIABLES REQUIRED TO DESCRIBE THE OLIVINE AND PLAGIOCLASE PORPHYRITIC MAGMAS AT EQUILIBRIUM

BULK COMPOSITION VARIABLES; RELATION TO OXIDE COMPONENTS

W1 $Si_4O_8 = 0.25(SiO_2 - 0.5(FeO + MnO + MgO + CaO) - Na_2O - K_2O$

W2 $Ti_4O_8 = 0.25\ TiO_2$

W3 $Al_{16/3}O_8 = 0.375\ Al_2O_3$

W4 $Fe_{16/3}O_8 = 0.375\ Fe_2O_3$

W5 $Fe_4Si_2O_8 = 0.25\ FeO$

W6 $Mn_4Si_2O_8 = 0.25\ MnO$

W7 $Mg_4Si_2O_8 = 0.25\ MgO$

W8 $Ca_4Si_2O_8 = 0.25\ CaO$

W9 $Na_{16/3}Si_{8/3}O_8 = 0.375\ Na_2O$

W10 $K_{16/3}Si_{8/3}O_8 = 0.375\ K_2O$

W11 $P_{16/5}O_8 = 0.625\ P_2O_5$

W12 $H_2O = H_2O$

SILICATE MELT PHASE	
COMPONENTS	MOLE FRACTION
Si_4O_8	X6
Ti_4O_8	X7
$Al_{16/3}O_8$	X8
$Fe_{16/3}O_8$	X9
$Fe_4Si_2O_8$	X10
$Mn_4Si_2O_8$	X11
$Mg_4Si_2O_8$	X12
$Ca_4Si_2O_8$	X13
$Na_{16/3}Si_{8/3}O_8$	X14
$K_{16/3}Si_{8/3}O_8$	X15
$P_{16/5}O_8$	X16
H_2O	X17

SOLID PHASES		
AMOUNT	COMPOSITION	
X1	OLIVINE	X2 (Mg_2SiO_4)
X2	PLAGIOCLASE	X4 ($CaAlSi_2O_8$)

W1, W2, W3 – moles
X1, X3, X5 – (AMOUNTS) moles
X2, X4, X6,...., X17 – mole fractions

TABLE 2. EQUATIONS USED TO DESCRIBE MASS-BALANCE RELATIONS BETWEEN SOLID AND MELT PHASES AND THE BULK COMPOSITION

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F(1) = X5*X6 + .375*X3*X4 + .625*X3*(1-X4)     - W1 = 0
F(2) = X5*X7                                    - W2 = 0
F(3) = X5*X8 + .375*X3*X4 + .1875*X3*(1-X4)    - W3 = 0
F(4) = X5*X9                                    - W4 = 0
F(5) = X5*X10 + 0.5*X1*(1-X2)                   - W5 = 0
F(6) = X5*X11                                   - W6 = 0
F(7) = X5*X12 + 0.5*X1*X2                       - W7 = 0
F(8) = X5*X13 + .25*X3*X4                       - W8 = 0
F(9) = X5*X14 +.1875*X3*(1-X4)                  - W9 = 0
F(10) = X5*X15                                  -W10 = 0
F(11) = X5*X16                                  -W11 = 0
F(12) = X5*X17                                  -W12 = 0
F(13) = X6 + X7 + X8 + X9 + X10 + X11 + X12 +
        X13 + X14 + X15 + X16 + X17 - 1.0 = 0
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LIMITATIONS OF THE CALCULATIONS

The validity and accuracy of the calculations made with this approach depend upon the validity of the thermodynamic data used in equations, F14 - 17, and the geological assumptions implicit in the model.

The whole-rock composition and an estimate of temperature and pressure are the only variables that need to be determined prior to the calculation. The model assumes that: 1) the rock closely approximates the composition of the magma at some time and within some space, 2) the magma equilibrated at the estimated temperature and pressure, 3) the calculation is for equilibrium crystallization; fractional crystallization is approximated by iterative calculations on residual liquid compositions at incremented changes in temperature or pressure (or both), and 4) the calculated cumulative mode of solid crystalline products does not allow for potential settling or floating of crystals (*i.e.*, the system remains closed).

TABLE 3. EQUATIONS USED TO IMPOSE THERMODYNAMIC EQUILIBRIUM CONSTRAINTS ON THE MAGMA SYSTEM

$$F(14) = \text{a) } Mg_2SiO_4 \text{ (s)} \rightleftharpoons 1/2Mg_4Si_2O_8\text{(m)}$$

$$\text{b) } a_{Fo}^{s} - \exp(\Delta G_{14}^{0}/Rt) * (a_{12}^{m})^{1/2} = 0$$

$$\text{c) } (X_2^{s})^2\{\exp(2000(1-X_2^{s})(1-X_2^{s})^2/RT)\}^2 - \exp(\Delta G_{14}^{0}/RT) * (X_{12}^{m})^{1/2}(\gamma_{12}^{m})^{1/2} = 0$$

$$F(15) = \text{a) } Fe_2SiO_4 \text{ (s)} \rightleftharpoons 1/2Fe_4Si_2O_8 \text{ (m)}$$

$$\text{b) } a_{Fa}^{s} - \exp(\Delta G_{15}^{0}/RT) * (a_{10}^{m})^{1/2} = 0$$

$$\text{c) } (1-X_2^{s})^2\{\exp 1000(3-2X_2^{s})(X_2^{s})^2/RT\}^2 - \exp(\Delta G_{15}^{0}/RT) * (X_{10}^{m})^{1/2}(\gamma_{10}^{m})^{1/2} = 0$$

$$F(16) = \text{a) } CaAl_2Si_2O_8 \text{ (s)} \rightleftharpoons 1/4Ca_4Si_2O_8 \text{ (m)} + 3/8Al_{16/3}O_8 \text{ (m)} + 3/8Si_4O_8 \text{ (m)}$$

$$\text{b)} a_{An}^{s} - \exp\ (\Delta G_{16}^{0}/RT) * (a_6^{m})^{3/8} * (a_8^{m})^{3/8} * (a_{13}^{m})^{1/4} = 0$$

$$\text{c)} X_4^{s} - \exp(\Delta G_{16}^{0}/RT) * (X_6^{m})^{3/8} * (X_8^{m})^{3/8} * (X_{13}^{m})^{1/4} * (\gamma_6^{m})^{3/8} * (\gamma_8^{m})^{3/8} * (\gamma_{13}^{m})^{1/4} = 0$$

$$F(17) = \text{a) } NaAlSi_3O_8 \text{ (s)} \rightleftharpoons 3/16Na_{16/3}Si_{8/3}O_8 \text{ (m)} + 3/16Al_{16/3}O_8 \text{ (m)} + 5/8Si_4O_8 = 0$$

$$\text{b) } a_{Ab}^{s} - \exp(\Delta G_{17}^{0}/RT) * (a_6^{m})^{5/8} * (a_8^{m})^{3/16} * (a_{14}^{m})^{3/16} = 0$$

$$\text{c) } (1-X_4^{s}) - \exp(\Delta G_{17}^{0}/RT) * (X_6^{m})^{5/8} * (X_8^{m})^{3/16} * (X_{14}^{m})^{3/16} * (\gamma_6^{m})^{5/8} * (\gamma_8^{m})^{3/16} * (\gamma_{14}^{m})^{3/16} = 0$$

Where;

$$\gamma_i = \exp\{(\textstyle\sum_{j=6}^{17} W_{ij}X_j - \sum_{m=6}^{16} \sum_{n=m+1}^{17} W_{mn}\, X_m X_n)/RT\} * X_{17}$$

$$W_{ii} = 0$$

Equations F(14) and F(15) pertain to olivine - melt equilibrium and F(16) and F(17) describe plagioclase equilibrium.

If these assumptions approach reality, then the observed assemblage of minerals and their compositions will match the calculated values. Even if the model closely approximates the crystallization path of the magma, we can expect slight discrepancies to arise from sampling problems. Modal amounts and proportions of phenocryst phases are variable throughout individual flows, and electron-microprobe analyses of phenocryst cores may not always record the extreme compositions due to phenocryst orientation within the probe mount (Pearce 1984). Each calculation will produce an expected composition of olivine, plagioclase and residual silicate liquid. Fractional crystallization is approximated by reducing the temperature by some increment and using the last residual liquid to make an identical calculation at the new temperature and the same pressure. This approach explains the observed phase-chemistry in the examples used here, and models isobaric fractional crystallization. Discrepancies beyond that attributable to sampling error require that one of the assumptions not be true. The thermodynamic model accurately predicts compositions and modes in experimentally determined systems; with natural melts we must infer that discordance between observed and calculated properties indicates an incorrect geological assumption.

Another potential source of error arises in the data required for the thermodynamic equilibria described by equations F14 - 17. The regular-solution model of Ghiorso *et al.* (1983) adequately predicts saturation temperatures and compositions of olivine and plagioclase in silicate melts. Whereas the low-pressure experimental data of Grove & Bryan (1983) were reproduced by the regular-solution model, the capability of the model at higher pressures is not guaranteed (M.S. Ghiorso, pers. comm.). The inability of the thermodynamic model to predict appearances and compositions of phases accurately at higher pressures simply reflects the paucity of high-pressure experimental data used in the calibration of the regular-solution model. However, the success of the calculations in this work suggests that at least for plagioclase and olivine, the thermodynamic data have smaller uncertainties than those due to the geological constraints. Certainly the regular-solution model can be expected to remain valid throughout the early crystallization-history of these olivine–plagioclase-phyric lavas. The compositional change of the residual liquid will not be sufficiently extreme to create a melt composition outside the compositional range of the original data-base (Ghiorso *et al.* 1983).

Whereas the initial approximation to the solution is critical for a final solution using the Newton–Raphson method, choosing values that are close to the observed modes and compositions of olivine, plagioclase and silicate liquid generally leads to a successful refinement. Successive iterations of 'new' rock compositions use the updated guesses from the last calculated values. Solutions are generally obtained with less than 15 iterations on the Cyber 170 at the University of Calgary. The calculation is terminated and the final solution vector returned when the successive components of the vector differ by less than 0.00001.

APPLICATIONS

Solutions to the proposed system of equations return equilibrium compositions and modes for a specified pressure and temperature. Hence the pressure-temperature path taken by a magma may be constrained by matching the chemistry of the observed phenocrysts. Two examples illustrate these calculations.

The McKinney basalt

Estimates of the composition of the McKinney basalt from the Snake River Plain are available in the literature (Thompson 1972, Leeman & Vitaliano 1976, Stout & Nicholls 1977). Data for these Recent lava flows include mineral compositions, modes, and chemical compositions of the whole rocks (Table 4), as well as high-pressure experimental data. The basalts are olivine-plagioclase-phyric, and exhibit a small range in bulk composition. The whole-rock chemistry and phenocryst compositions are used to restrict the early crystallization-history of the relevant magma. Calculated paths of crystallization for three samples analyzed and described by Leeman & Vitaliano (1976) are described below. The calculations compare favorably with the observed modes and chemistry, and do not contradict the experimental phase-relations documented by Thompson (1972).

Samples 59P13, 62P68 and 70-15 are glassy, porphyritic pillowed flows of the McKinney basalt unit. The glassy texture of these basalts ensures a more precise modal analysis, and establishes that this eruptive phase had a uniform distribution of phenocrysts; volume % estimates are: olivine 7.4–8.1, plagioclase 17.3–18.5 (Leeman & Vitaliano 1976).

The modeled fractional crystallization of these melt compositions derived from rock compositions generates the sequence of mineral compositions and modes illustrated in Figures 1a and 1c. The liquidus temperatures for each sample are calculated at a pressure that will generate, upon cooling, an initial composition of plagioclase equivalent to the observed phenocryst-core composition (Table 4). The size of the temperature increment used in modeling fractional crystallization has little effect upon the composition or mode of any of the phases. The step size

TABLE 4. COMPOSITIONS OF MCKINNEY AND COWS LAKE BASALT

SAMPLE:	70-15 *	62P68 *	59P13 *	59P13T **	59P13TG **	CL-81-2 ***
SiO_2(Wt.%)	47.10	47.85	47.66	47.76	47.99	47.72
TiO_2	3.03	2.83	3.13	3.03	3.99	1.59
Al_2O_3	15.20	14.95	14.76	14.93	13.24	16.89
Fe_2O_3	0.65	1.29	1.44	1.36	1.61	0.97
FeO	12.85	12.15	12.45	12.37	13.60	8.19
MnO	0.21	0.20	0.20	0.20	0.23	0.16
MgO	7.58	7.39	6.88	6.70	5.32	9.41
CaO	9.50	9.39	9.49	9.41	9.56	10.05
Na_2O	2.59	2.58	2.64	2.62	2.64	2.94
K_2O	0.74	0.73	0.75	0.75	0.91	0.80
P_2O_5	0.50	0.47	0.51	0.53	0.69	0.37
			OBSERVED PHENOCRYST COMPOSITIONS			
X(FO)	72-66	75-70	73-69	72.9	nd	PH 86-85 MP 84-83
X(An)	70-60	67-47	65-59	65.3	nd	70-68
			OBSERVED MODES (VOL %)			
OLIV	7.8	8.1	7.4	nd	nd	6.9
PLAG	17.8	17.3	18.5	nd	nd	10.6
			CALCULATED LIQUIDUS TEMPERATURE AND PRESSURE			
T (°C)	1235	1230	1220	1215	nd	1255
P (kbar)	5.0	6.0	6.5	7.0	nd	10-15
			CALCULATED EQUILIBRIUM TEMPERATURE AND PRESSURE			
T (°C)	1160	1175	1165	1160	nd	nd
P (kbar)	2.0	3.5	4.0	3.0	nd	nd

nd not determined

Sources of data include: {*Leeman and Vitaliano (1976); **Thompson (1972) and ***Russell (1984)}

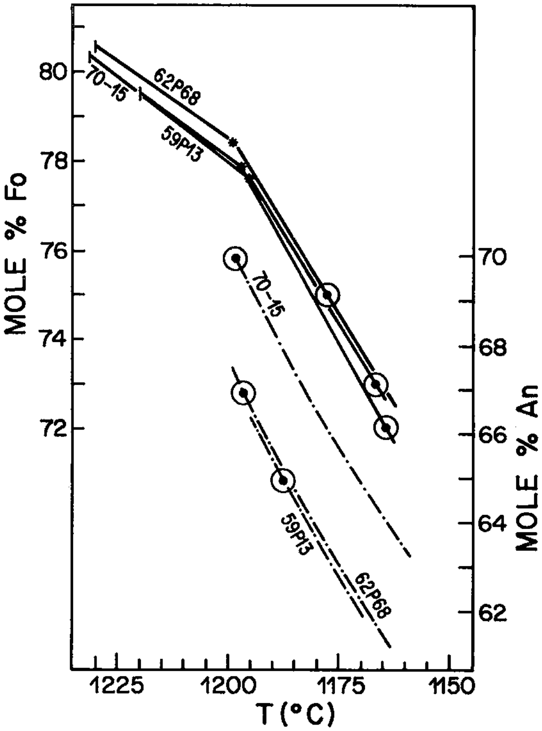

FIG. 1a. Compositions of solid phases predicted as a function of temperature during fractional crystallization of McKinney basalt lavas from liquidus temperatures. Solid lines are for olivine compositions and dotted lines are for plagioclase. The observed core-compositions of phenocrysts are marked by dotted open circles.

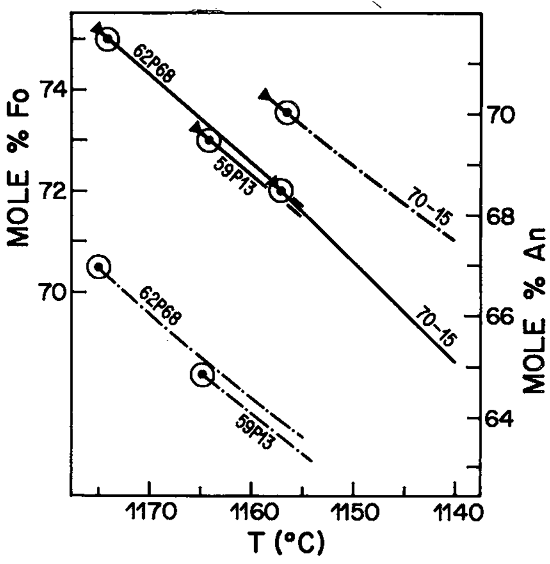

FIG. 1b. Compositions of solid phases predicted as a function of temperature during fractional crystallization of the McKinney basalt from subliquidus temperatures. The initial equilibrium crystallization matches the observed phenocryst compositions. Fractional crystallization produces the subsequent shifts in olivine and plagioclase compositions. Observed core-compositions of phenocrysts are illustrated also.

may, however, control the saturation temperature of plagioclase slightly and the initial composition of the feldspar. Fractional crystallization of these basaltic melts from liquidus temperatures begins with a 20 - 30°C interval of olivine precipitation followed by cotectic precipitation of olivine and plagioclase. Figure 1a illustrates the calculated chemistry of the solid phases during the early crystallization-history of these magmas. Olivine changes composition continuously and constantly from $Fo_{79.5-80.6}$ to Fo_{78-79}, at which point plagioclase begins crystallization. Once cotectic precipitation begins, both solid phases change composition constantly with decreasing temperature. The observed compositions of phenocrysts are plotted in Figure 1a. The calculated initial composition of olivine is significantly more forsteritic than the observed phenocryst-core compositions (by 5-8 mole %). The calculated modes, however, are within 1 vol. % of the observed modal assemblages (Fig. 1c).

Equilibrium crystallization of phenocryst-core compositions followed by fractional crystallization of the residual liquid generates the composition–temperature relationships expressed in Figure 1b. The calculated temperature and pressure for equilibrium coprecipitation of olivine and plagioclase are included in Table 4. The three samples describe different ranges in mineral chemistry but appear to have equilibrated under similar conditions (1160–1175°C and 2–4 kbar). This path of crystallization predicts more accurately the proportion and composition of the solid phases, and the lower pressure is compatible with the phase relations established experimentally by Thompson (1972).

The experimental data suggest that at low pressures (less than 4 kbar), olivine precipitates alone at close to 1180°C. At slightly lower temperatures, plagioclase joins the liquidus assemblage. At higher pressures (greater than 5 kbar), plagioclase is the initial solid phase to precipitate at close to 1190°C, with

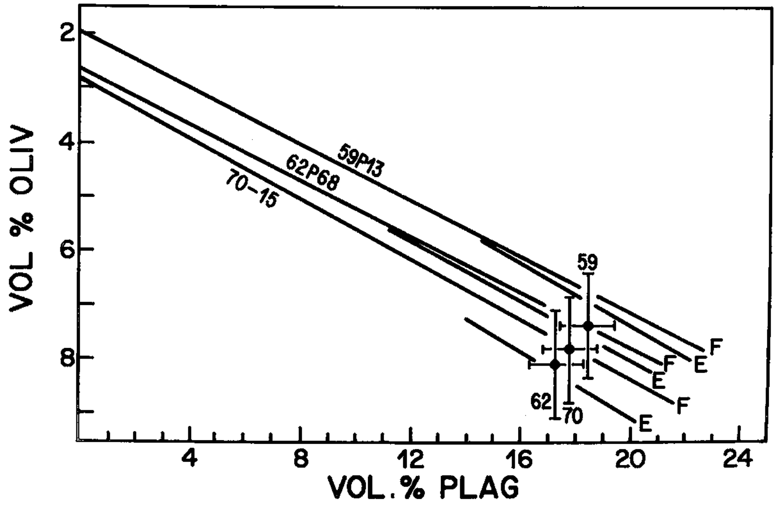

FIG. 1c. Predicted modal mineralogy of McKinney basalts during fractional crystallization (F) and equilibrium crystallization (E). Observed modes of the samples are also plotted with 1 volume % uncertainty bars.

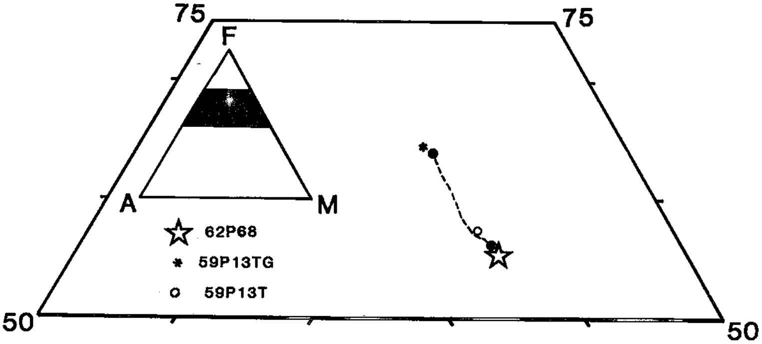

FIG. 2. AFM plot of Thompson's (1972) whole-rock composition (59P13T) and residual glass composition (59P13TG), with calculated path of fractional crystallization for sample 62P68.

olivine crystallizing at slightly lower temperatures. From the reconnaissance-type experiments of Thompson (1972), there is a suggestion of a very small range in pressure where olivine and plagioclase coprecipitation is the initial form of crystallization. These experimental data perhaps cannot be used quantitatively; however, the compatibility of the illustrated phase-relations (Thompson 1972) with the model calculations is encouraging.

An alternate explanation is that olivine precipitated at higher temperatures and continued to equilibrate with the magma until a lower temperature or pressure initiated plagioclase precipitation. The re-equilibration of olivine phenocrysts in crystallizing magma is documented in the Makaopuhi lava lake down to 800°C (Moore & Evans 1967). The diffusion process between melt and olivine can be rapid at elevated temperatures (Misener 1974), but decreases rapidly with falling temperature. The application of Misener's data to olivine - melt re-equilibration by Gerlach & Grove (1982) illustrated that a change in temperature from 1100 to 1000°C increased the required time for erasing patterns of zoning in olivine phenocrysts by an order of magnitude.

The compositions of the residual liquid calculated throughout fractional crystallization can rarely be tested with natural data. Thompson (1972) does, however, have a single composition for the intersertal glass found in the sample 59P13T. Figure 2 is an AFM plot showing the composition of the whole rock (59P13T) and that of the intersertal glass (59P13TG) for the McKinney basalt determined by Thompson (1972). Also illustrated is the path of the residual liquids for sample 62P68 that were calculated for fractional crystallization. The calculated path for the liquid falls close to the two observed compositions of Thompson (1972).

Cow's Lake lava

The Jordan Craters lava field is located in southeasthern Oregon, approximately 50 kilometres from the Idaho border. Sample CL-81-2 is from the youngest flow (Cow's Lake lava flow) and has been analyzed by Russell (1984). The rock is an olivine-plagioclase-phyric alkali olivine basalt. The rock and mineral compositions are listed in Table 4, with the pertinent modal data. Calculations with this sample clearly illustrate the variation of extensive variables throughout the magma's early crystallization-history. The lava flow has phenocrysts and microphenocrysts of olivine that have different compositional ranges. The core of olivine phenocrysts is homogeneous in composition, whereas the rim exhibits strong zoning. Plagioclase phenocrysts occur as radiating laths, clustered onto knots of olivine phenocrysts. Modeling of fractional crystallization of the rock composition at high pressure from 1255°C reproduces the observed phenocryst assemblage and compositions. Higher pressures (10–15 kbar) are compatible with the estimated crustal thickness for southeastern Oregon of 40 - 45 km (Thiruvathukal *et al.* 1970, Leaver *et al.* 1984).

The crystallization history of the Jordan Craters basalt is similar in many respects to that of the McKinney basalt. A calculated path of fractional crystallization for the whole-rock composition from 1255°C and 15 kbar generates the parameters illustrated in Figure 3. Changes in olivine composition with decreasing temperature are constant until plagioclase precipitates at 1220°C. At the onset of cotectic precipitation the change in olivine composition with reduced temperature becomes more pronounced. The amount of olivine (grams, moles, *etc.*) crystallized with cooling also increases dramatically when the residual liquid reaches the cotectic

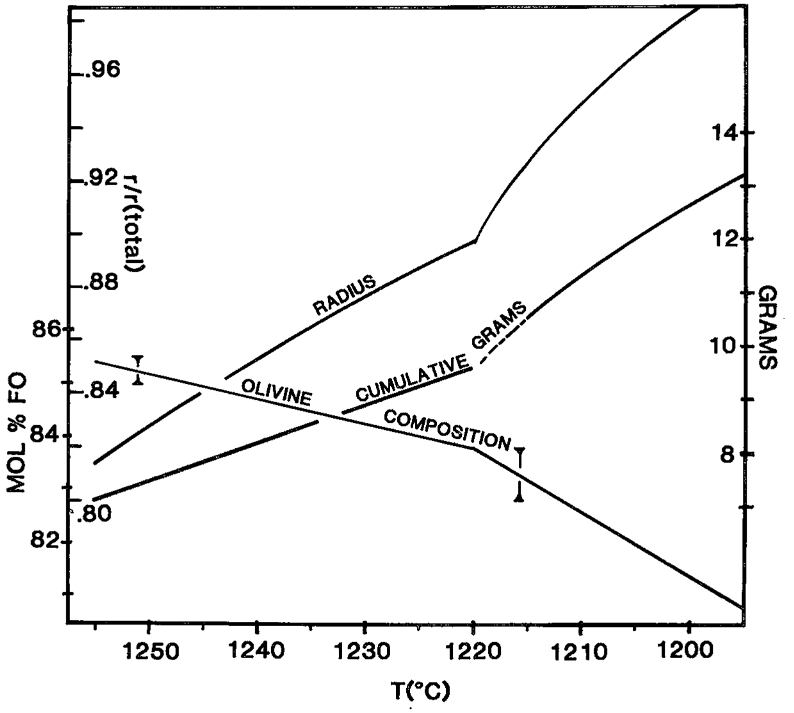

FIG. 3. Predicted compositions and amounts of olivine crystallized during high-pressure fractional crystallization of sample CL-81-2. The radius of a hypothetical phenocryst of olivine is plotted as a function of temperature (crystallization). The observed range of compositions for olivine phenocrysts and microphenocrysts is also illustrated, although it is fixed arbitrarily with respect to temperature.

field (Fig. 3). These are phenomena that should manifest themselves in the zoning patterns of olivine phenocrysts.

Figure 3 illustrates the equilibrium composition and mass of olivine calculated as a function of temperature for fractional crystallization of the Jordan Craters basalt. The observed ranges in phenocryst and microphenocryst composition are also plotted in Figure 3. It is possible that the microphenocrysts reflect the onset of cotectic precipitation in the magma and are a direct response to the doubled rate of olivine precipitation.

The precipitation of olivine in the early crystallization history of the Jordan Craters basalt may be examined by calculating a zoning profile for a hypothetical phenocryst. The olivine crystal is approximated by a sphere, and the radius of the crystal at any temperature R_{i+1} is related to the mass of the olivine precipitated M_{i+1} and the existing radius R_i by:

$$R_{i+1} = (0.75\ M_{i+1}/\rho\pi + R_i^3)^{1/3} - R_i$$

where ρ is the density of the olivine solid-solution. Figure 3 illustrates the variation of the ratio of the radius at an interval of temperature to the total radius of expected throughout the whole interval of crystallization (R_i/R_{total}). Cotectic precipitation marks a break in this slope as well, implying that with plagioclase precipitating, olivine (micro-)phenocrysts expand more rapidly with constant rate of cooling. The amount of olivine precipitated more than compensates for the expanding volume of the crystal. The hypothetical phenocryst of olivine is illustrated in Figure 4. The phenocryst is contoured in 5°C temperature increments to illustrate the calculated amounts of growth with falling temperature. These calculations predict that 80% of the phenocryst is precipitated at 1255°C. The remaining 20% of the phenocryst is precipitated over a 60°C interval of temperature. The last 10% of the crystal, which grew after plagioclase began to crystallize, is marked by an increase in calculated spacings between isotherms. Whereas it might be expected that this would translate into a similar expression of contours using isopleths of mole-fraction forsterite, this does not happen. The increase in radius is balanced by the change in olivine composition such that the composi-

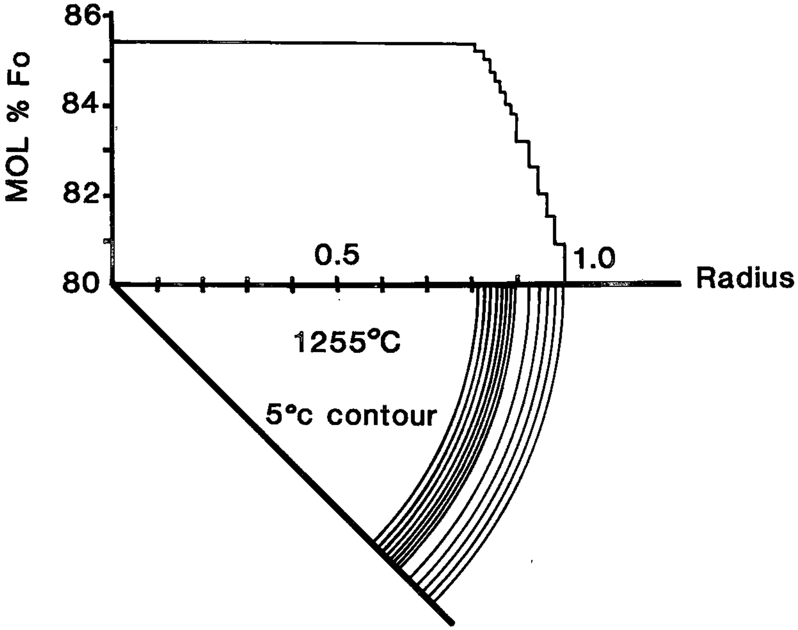

FIG. 4. Growth increments expected in the hypothetical phenocryst of olivine during crystallization of sample CL–81–2. The lower diagram represents the increase in radius of the phenocryst with 5°C drops in temperature. The uncontoured portion of the crystal represents the olivine precipitated initially at 1255°C. The upper diagram illustrates the expected variation in composition as a function of the same interval in temperature.

tional gradient (*versus* radius) remains smooth. For this basaltic melt, the only effect that might be discernable is the initial increase in crystallized olivine when plagioclase first saturates the liquidus.

DISCUSSION

The proposed model and calculations can only accomodate processes accompanying equilibrium crystallization. Even paths of fractional crystallization are approximated by iterative equilibrium calculations. Most importantly, the well-documented effects of undercooling on phase assemblage, phase compositions and textures cannot be predicted with this model (Lofgren 1980, Schiffman & Lofgren 1982). However, there are general observations that can be made on these calculations that have important implications for processes of equilibrium crystallization in magmas. Again these observations are only relevant where the kinetic effects on crystallization are small.

The cooling and crystallization histories of these magmas have little effect upon the position of subsequent equilibrium. In order words, dramatic changes or drops in temperature do not cause the magma to deviate greatly from the prescribed line of liquid descent. The differences between the end products of fractional crystallization and equilibrium crystallization in the McKinney and Jordan Craters basalts are observed only in the range of compositions of solid phases. The predicted differences in modes and liquid composition for these lavas undergoing fractional or equilibrium crystallization are small. This is especially true when the liquid has reached the cotectic field, as the relative proportions of plagioclase and olivine that crystallize at any temperature are nearly constant. The success of these calculations in matching the observed mineral modes and compositions in the McKinney basalt and the Cow's Lake lava is evidence that these rock compositions are equivalent to those of the melts that precipitated the phenocryst assemblage. Calculations such as these will have an increasing role in the recognition of the composition of primary magmas.

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