

Calculation of the temperature of crystallization of silicates from basaltic melts

W. J. FRENCH AND E. P. CAMERON

Department of Geology, Queen Mary College, London E1 4NS

ABSTRACT. This paper discusses the relationship between the chemical composition of basic melts and the temperatures at which olivine, clinopyroxene, and plagioclase begin to crystallize at one atmosphere. Diagrams are given which show the correlation between crystallization temperature and melt composition and which allow some of the temperatures to be estimated. Because the relationship between melt composition and crystallization temperature is virtually linear over short compositional ranges, the data available can be subdivided and examined by linear multivariate statistical techniques. The result is a set of equations which permit the crystallization temperatures to be calculated with an average error of less than 6 °C and a maximum error of 27 °C. These equations have been tested by experimental determination of crystallization temperatures for a range of rocks from the Marquesas Islands.

FOR basalts precipitating the three phases, olivine, clinopyroxene, and plagioclase, in melting experiments carried out at one atmosphere, there are six possible different orders of crystallization of the silicates. In practice this reduces to four because clinopyroxene is rarely, if ever, the first phase to appear. The four common types of basalt therefore crystallize in the orders olivine-clinopyroxene-plagioclase (Class No. 1); olivine-plagioclase-clinopyroxene (Class No. 2); plagioclase-olivine-clinopyroxene (Class No. 3); plagioclase-clinopyroxene-olivine (Class No. 4). Class 1 basalts are typically tholeiites and olivine tholeiites including Hawaiian rocks and continental volcanics such as those of Nuanetsi. Class 2 rocks are alkaline olivine basalts such as those of the oceanic islands, while Class 3 basalts are dominantly associated with calc-alkaline island arc and continental margin associations. Class 4 compositions are rare but also tend to be related to the island arc volcanics. Multivariate discriminant function equations have been given (Cameron and French, 1977) which permit the allocation of basalts to the four classes. It has also been shown that useful discrimination into the classes can be made using simple compositional diagrams such as the Si-Al-Mg triangle.

The purpose of the present paper is to take this work further by examining the relationship between rock composition and the temperature of first appearance of the three silicates from melts cooling at one atmosphere. The data used for this purpose are the same as those listed in Cameron and French (1977) and relate to more than 100 basalts. A separate set of experimental and chemical data was compiled for test purposes. This consisted of eleven samples for which all three temperatures of crystallization are known and seven for which less information is available. These data were obtained from the literature or via personal communication. Experimental work was also carried out using rocks from the Marquesas Islands to test the equations developed.

Oxide abundances, ratios, and crystallization temperatures

The temperatures at which silicate phases crystallize from melts are dependent on the composition of the melts if all other conditions are standardized, and plots of certain oxide or cation proportions of basalts against the precipitation temperatures of particular phases, in some instances, show good correlations. Probably the best such relationship is that found for MgO versus olivine crystallization temperature at one atmosphere (fig. 1, see also Thompson, 1973). Less good correlations are demonstrated by plotting SiO₂, Al₂O₃, CaO, or Na₂O against plagioclase liquidus temperatures. These relationships are all to be expected because the oxide abundances relate directly to the likely mole fractions of the given phases in the basaltic systems. However, estimation of temperatures of crystallization from melts by the use of such relationships is not likely to be much better than intelligent matching of 'unknowns' and rocks for which experimental data are available.

Certain oxide ratios also broadly correlate with crystallization temperatures for particular phases.

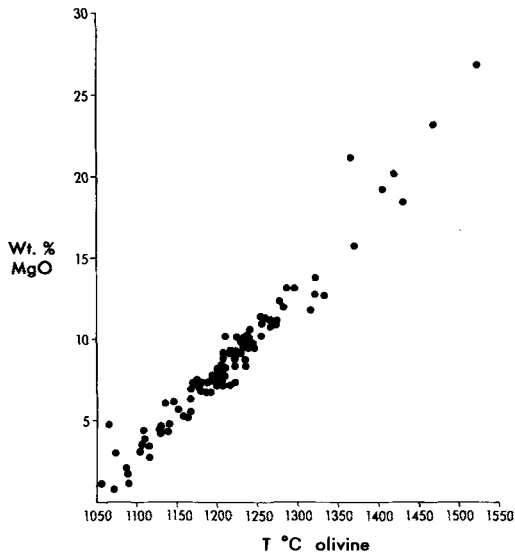


FIG. 1. Plot of MgO *v.* olivine crystallization temperatures for the basalts of Table I of Cameron and French (1977).

Again it is olivine that provides the best correlations as is shown, for example, by the plots of olivine crystallization temperatures against the $(\text{FeO} + \text{Fe}_2\text{O}_3)/(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MgO})$ ratios for basaltic rocks used, for example, by Tilley *et al.* (1964), Tilley *et al.* (1971), Thompson (1972), and Yoder (1976). A very similar relationship is shown by the plot of crystallization temperature against the differentiation index suggested by French (1976) and a comparison of the two diagrams is made in fig. 2. In both diagrams it is only the temperature of the first phase to crystallize, namely olivine, which correlates with the compositional variable.

Improved correlations between melt compositions and crystallization temperatures can sometimes be obtained by considering the influence of two oxides. For example, the TiO_2 contents of rocks relates to the olivine crystallization temperature at given values of MgO: generally higher TiO_2 corresponding with lower olivine temperatures. A plot of MgO against Al_2O_3 can be contoured for both olivine and plagioclase temperatures of crystallization at one atmosphere (fig. 3). Using this figure to find the temperatures of crystallization for the rocks from which the diagram was constructed gives average errors of 22 °C for olivine and 16 °C for plagioclase. The separate test data when used on fig. 3 gave average errors of 22 and 19 °C for olivine and plagioclase respectively. Errors for olivine temperatures of crystallization tend to increase as MgO increases, while errors in plagioclase

crystallization temperatures increase with increasing Al_2O_3 . Fig. 3 also has discriminant qualities in dividing basalts according to their order of crystallization and the temperature contours drawn on the diagram intersect at the boundary which separates those rocks which precipitate olivine first (Classes 1 and 2) from those yielding plagioclase first (Classes 3 and 4).

In fig. 4 the atomic proportions of Mg-Al-Si are plotted, and the discriminant boundaries between

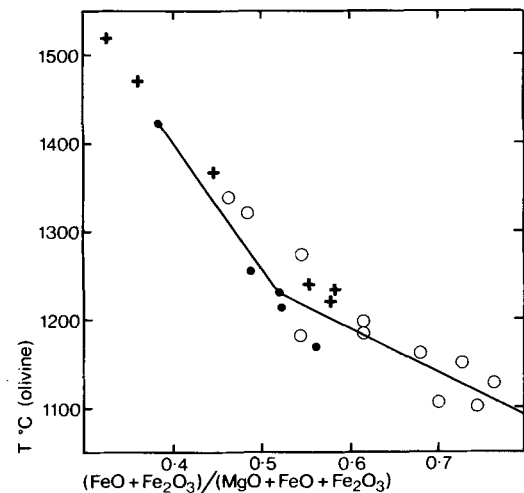
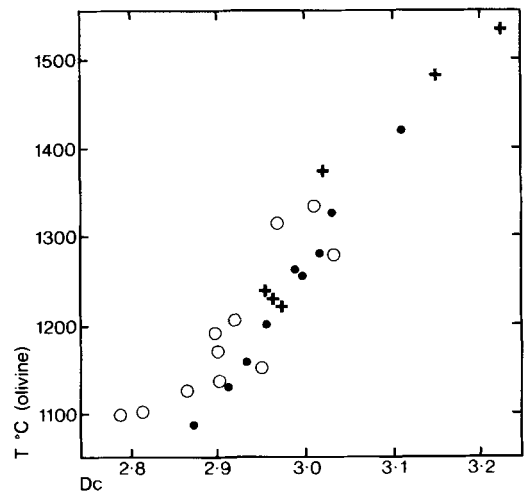


FIG. 2. Phase temperatures for basalts from Reunion (+), Skye (○), and Kilauea (●) against $(\text{FeO} + \text{Fe}_2\text{O}_3)/(\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MgO})$ and D_c where $D_c = 2.6[2N_o/(4N_{\text{Si}} + 3N_{\text{Al}})]^{\frac{1}{2}}$ and N is the number of atoms expressed to a definite number of oxygens; data from Thompson (1972), Tilley *et al.* (1971), Tilley *et al.* (1964).

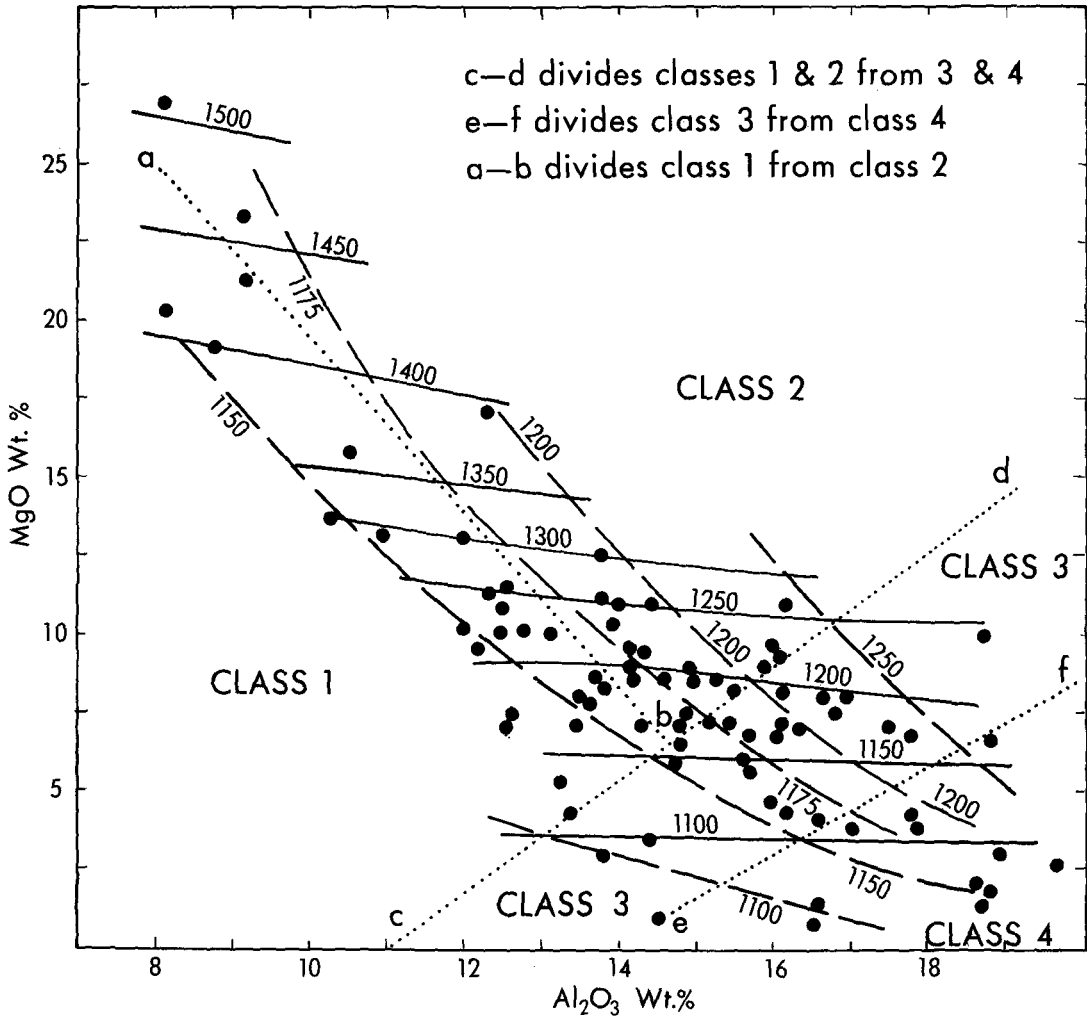


FIG. 3. MgO v. Al_2O_3 for the basalts of Table I of Cameron and French (1977) contoured for olivine (full lines) and plagioclase (broken lines) liquidus temperatures. The dotted lines are discriminant boundaries for the four basalt classes of Cameron and French (1977).

the four classes of basalt are shown. Crystallization temperature contours can be drawn as before but it is the temperature of appearance of the first phase that is most clearly defined. Here the error in liquidus temperature was found to be 11°C using the test data for which the crystallization temperatures of all three phases were known. The high Si part of this diagram, in the field of basaltic compositions, corresponds with those rocks for which the olivine and plagioclase crystallization temperatures are low and close to one another.

Multi-element relationships. The more chemical data used in making the correlations between temperature of crystallization and melt composi-

tion, the better the agreement between calculated and observed values is likely to be. A system was therefore devised in which the experimental data and related analytical data were searched by computer to find the closest match in composition between the standard data and the test rocks. Here the Euclidean distance between the test rock composition and each of the standard rock compositions was calculated in twelve-dimensional compositional space without weighting the elements. The minimum value of this distance between the basalt under investigation and the members of the standard data set was then taken to indicate the best match of compositions. The values of the

temperatures of first appearance of the phases in the matching standard were then assigned to the test rock. Using the set of test data the average errors obtained by this method were 21 °C for olivine, 15 °C for plagioclase, and 16 °C for clinopyroxene. These errors plainly indicate that this system is no better than the simple graphical methods. However, examination of the relationship between the magnitude of the Euclidean distance between standard and test samples, squared, and the sum of the three errors in temperature estimation, shows that the largest errors are associated with the greatest Euclidean distance. In other words the standard data points are not always close enough to allow good estimates of temperature to be obtained by this method, and some form of interpolation between the standard data points is required.

French (1971) showed, using a smaller body of data, that regression analysis could provide equations relating the temperature of first appearance of the three phases to the chemical composition of the rock. The average errors given by these equations were 11.2 °C for olivine, 9.4 °C for plagioclase, and 12.8 °C for clinopyroxene. Applying this simple model to the larger body of data now available gave mean errors of 11.4 °C for olivine, 10.0 °C for plagioclase, and 15.4 °C for clinopyroxene, but the maximum errors were found to be 82.5 °C for olivine, 34.8 °C for plagioclase, and 87.6 °C for clinopyroxene. It is clear that

another method is required if satisfactory calculation of temperatures of appearance of the silicates is to be achieved. It would be beneficial to subdivide the standard data into groups defined by the order of crystallization or some other chemical criterion before seeking a relationship between composition and temperature of appearance of the phases (French, 1971). The standard data were therefore searched by two systems of cluster analysis to see if objectively defined subgroups could be identified. The systems used were those of Ward (1963) and Friedman and Rubin (1967). A fourfold cluster gave the most clearly defined groups and in fact divided the data very nearly into the groups defined by the order of crystallization. This order of classification system was therefore used for the further multivariate analysis of the temperature and composition data, and the discriminant function equations given by Cameron and French (1977) were used as the basis for subdividing the basalts. Multivariate linear regression equations were then calculated for each phase temperature for each basalt class. Application of the regression technique yields equations of the form $T^{\circ}\text{C} = a_1x_1 + a_2x_2 + a_3x_3 + \dots + a_nx_n + K$, where $a_1 \dots a_n$ are coefficients of $x_1 \dots x_n$ (which are the weight percentages of the twelve oxides) and K is a constant. Twelve such equations were therefore generated, one for each phase temperature for each basalt class. The coefficients and constants are given in Table I. In order to calculate the temperatures of appearance of the

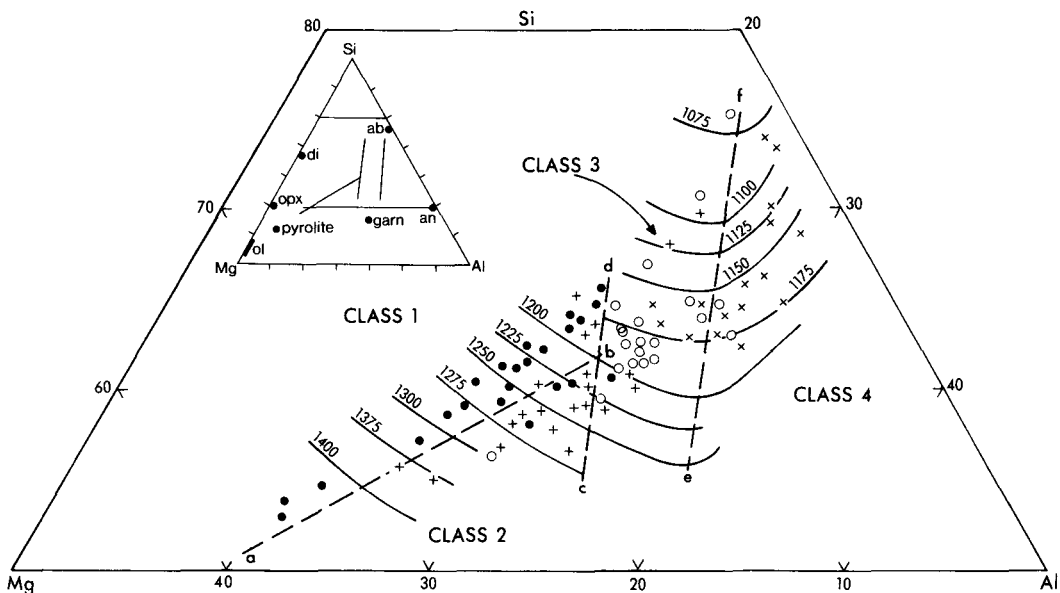


FIG. 4. The Mg-Al-Si atomic proportions triangle for the basalt data of Table I of Cameron and French (1977) contoured for liquidus temperatures. The dotted lines define the four classes.

SILICATES FROM BASALTIC MELTS

Table I

Regression function coefficients and constants for each mineral and for each basalt class.

	Olivine	Plagioclase	Clinopyroxene
Basalt class 1			
SiO ₂	-24.53494	1.36445	-11.10583
TiO ₂	-18.24102	-6.06152	-26.24547
Al ₂ O ₃	-10.09799	-2.19667	-28.06518
Fe ₂ O ₃	-12.80222	4.74574	-8.81572
FeO	-11.43649	4.77375	-10.86060
MnO	432.98562	-25.35302	-94.61387
MgO	1.18591	-0.85861	-16.62302
CaO	-21.16504	1.55552	-15.39506
Na ₂ O	-0.89264	0.80894	-4.46860
K ₂ O	-19.62832	-6.63324	10.08080
H ₂ O+	-31.64329	-2.09858	-35.87872
P ₂ O ₅	-131.94797	-34.89658	7.69271
K	2938.43503	1086.59205	2619.36411
Basalt class 2			
SiO ₂	-1.90311	-0.56570	1.39341
TiO ₂	5.79564	2.52292	5.02014
Al ₂ O ₃	3.16337	10.16436	0.09006
Fe ₂ O ₃	-5.37539	-3.86671	2.59485
FeO	-2.34966	-2.04956	0.93321
MnO	-142.40372	-151.27134	-16.24604
MgO	18.58658	1.19811	5.29665
CaO	-1.40593	-3.72867	10.51798
Na ₂ O	-5.32124	-11.76276	23.87817
K ₂ O	7.42330	-28.22180	1.43194
H ₂ O+	13.72067	4.45657	10.55541
P ₂ O ₅	-29.45336	-13.38883	-52.04727
K	1178.79204	1186.33485	849.21767
Basalt class 3			
SiO ₂	1.31481	-12.14836	-7.67909
TiO ₂	-6.54623	-17.12790	-10.50906
Al ₂ O ₃	2.50421	1.77319	-2.90980
Fe ₂ O ₃	4.28538	-7.14815	-6.71880
FeO	3.16509	-7.74177	-7.47855
MnO	-1.03678	29.77268	-21.51794
MgO	19.10210	-7.51757	-1.12793
CaO	1.04890	1.10313	0.94468
Na ₂ O	14.53954	6.23481	-8.39300
K ₂ O	-15.16595	-23.43879	-18.02507
H ₂ O+	-6.08184	-17.88519	-14.32021
P ₂ O ₅	-15.27937	-41.78081	-27.90833
K	833.20595	1938.08941	1747.21910
Basalt class 4			
SiO ₂	-15.55762	10.33961	-12.32413
TiO ₂	-2.18502	5.59667	1.12834
Al ₂ O ₃	-16.22358	21.59817	7.68922
Fe ₂ O ₃	-25.69279	13.29186	-17.32761
FeO	-21.48517	3.86954	14.01708
MnO	-87.19960	-51.91193	110.66662
MgO	1.33337	7.55158	-17.63945
CaO	-27.65187	14.15711	-8.91155
Na ₂ O	-22.64512	-4.94958	-20.16747
K ₂ O	32.52622	-15.18539	-27.01375
H ₂ O+	7.49756	13.25708	-9.96039
P ₂ O ₅	-40.47851	4.43957	-40.24773
K	2817.18627	113.01671	2338.28242

TABLE II

Errors and correlation coefficients from the application of the regression analysis to the standard basalt data.

Average error in temperature calculation, T°C.				
	Class 1	Class 2	Class 3	Class 4
Olivine	6.9	7.4	3.1	5.4
Plagioclase	3.3	4.1	4.5	3.1
Clinopyroxene	10.5	3.7	5.1	2.8
Maximum error in temperature calculation, T°C.				
	Class 1	Class 2	Class 3	Class 4
Olivine	21.2	24.9	6.4	14.5
Plagioclase	12.7	11.0	12.1	8.9
Clinopyroxene	25.9	10.2	22.1	10.7
Multiple correlation coefficients.				
	Class 1	Class 2	Class 3	Class 4
Olivine	0.992	0.994	0.996	0.970
Plagioclase	0.936	0.980	0.992	0.992
Pyroxene	0.728	0.983	0.998	0.991

TABLE III

Experimental data for the lavas from Ua Pu, Marquesa Islands. Chemical data and rock names for the sample numbers given are from Bishop and Woolley (1973).

Sample	temp. °C	Major silicate phases present
3. Alkali-olivine basalt	1155	glass
	1150	glass + plag
	1140	glass + plag
	1133	glass + plag + cpx
	1130	glass + plag + cpx + ol
6. Alkali-olivine basalt	1167	glass
	1155	glass + ol + plag
	1150	glass + ol + plag + cpx
	1144	glass + ol + plag + cpx
	1130	glass + ol + plag + cpx
11. Alkali-olivine basalt	1178	glass
	1173	glass + plag
	1168	glass + plag
	1155	glass + plag
	1135	glass + plag + ol + cpx
23. Hawaiiite	1150	glass
	1138	glass + plag
	1135	glass + plag
	1120	glass + plag + cpx
	1110	glass + plag + cpx
	1100	glass + plag + cpx
	1090	glass + plag + cpx
1075	glass + plag + cpx + ol	
18. Mugearite	1178	glass
	1168	glass + plag
	1165	glass + plag
	1155	glass + plag
	1135	glass + plag
	1127	glass + plag
1117	glass + plag + cpx + sanidine	
16. Trachyte	1178	glass
	1165	glass + plag
	1140	glass + plag
	1127	glass + plag
	1110	glass + plag
	1100	glass + plag + cpx
1090	glass + plag + cpx	

Sample	Olivine T°C	Plagioclase T°C	Clinopyroxene T°C
3. alk. ol. basalt	obs. 1132	calc. 1136	T +4
	obs. 1152	calc. 1142	T -10
	obs. 1137	calc. 1123-14	T
6. alk. ol. basalt	obs. 1160	calc. 1163	+3
	obs. 1160	calc. 1173	+13
	obs. 1152	calc. 1136-16	T
11. alk. ol. basalt	obs. 1138	calc. 1158	+20
	obs. 1175	calc. 1174	-1
	obs. 1138	calc. 1129 -9	T
23. hawaiiite	obs. 1082	calc. 1080	-2
	obs. 1144	calc. 1145	-1
18. mugearite	obs. 1158	calc. 1170	+12
	obs. 1171	calc. 1122	-45
16. trachyte	obs. 1131	calc. 1172	+41
	obs. 1105	calc. 1109	-4

Table IV

Calculated and observed temperatures of appearance of olivine, clinopyroxene, and plagioclase, from the lavas of Ua Pu, Marquesas Islands, Chemical data from Bishop and Woolley (1973)

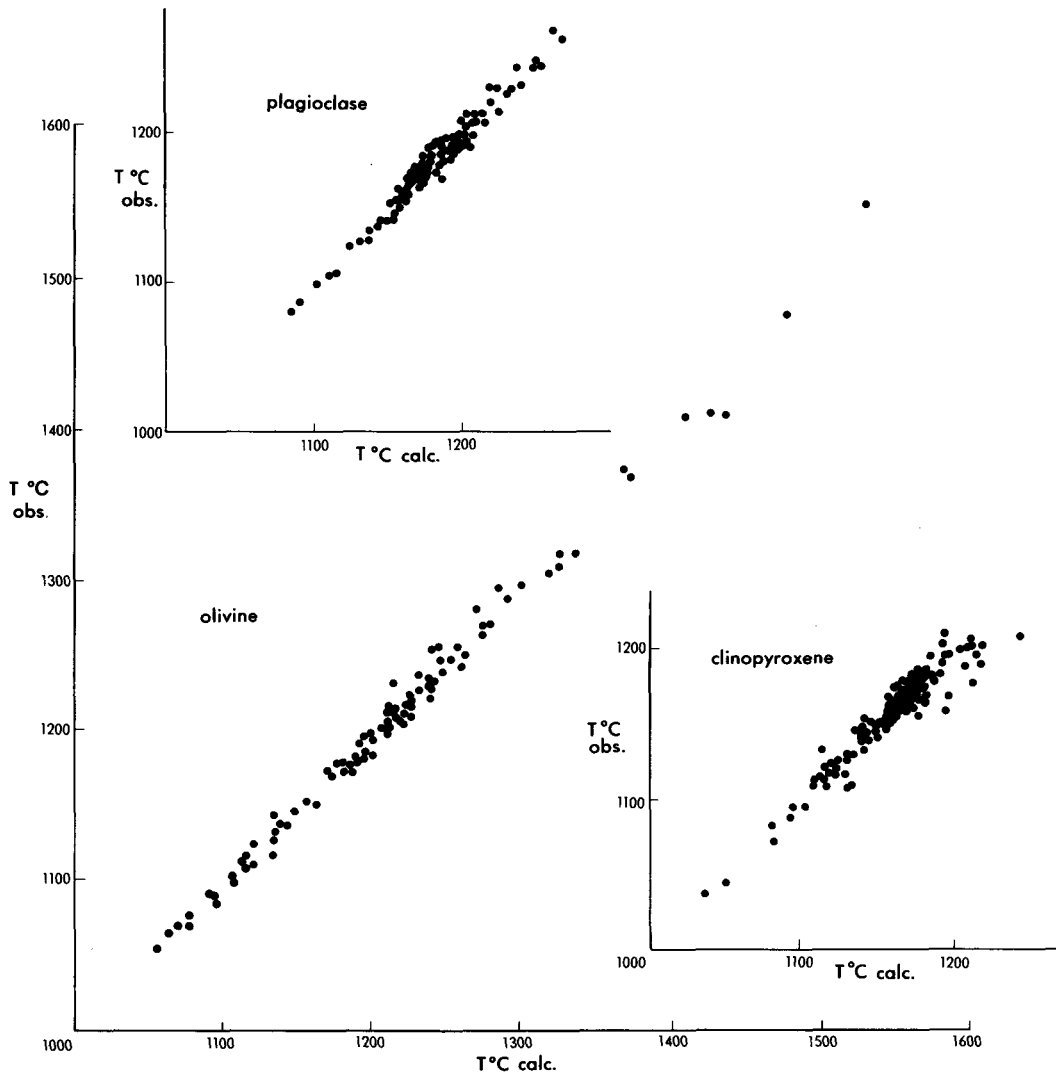


FIG. 5. Calculated *v.* observed temperatures of appearance for olivine, plagioclase, and clinopyroxene for the data of Table I of Cameron and French (1977). The calculated temperatures utilized the discriminant function equations given in Cameron and French (*op. cit.*) and the regression coefficients and constants given in Table I of the present paper.

three silicates for a given rock it is then necessary to calculate the most probable basalt class for the rock and to use the appropriate regression equation to calculate the temperatures.¹ Substituting the standard data into the equations gives the mean errors, maximum errors, and multiple correlation coefficients listed in Table II. All the calculated and observed temperatures are plotted in fig. 5. The

¹ A computer program permitting the calculation of basalt class and temperatures of crystallization is available from the authors (W. J. F.).

over-all mean error in temperature calculation is 5.0 °C and the mean correlation coefficient is 0.963. It is evident that with the possible exception of clinopyroxene in Class 1 basalts (correlation coefficient 0.728) the agreement between calculated and observed temperatures is excellent, especially when the possible experimental errors are considered and where the data derive from different laboratories using different techniques.

Independent tests of the calculations. Application of the system of calculation to the test data gave mean errors of 15.4 °C for olivine, 9.9 °C for

plagioclase, and 15.9 °C for clinopyroxene. Since some of these data were excluded from the standard data because they are incomplete the results must be regarded as reasonably satisfactory. To test the method further, a series of six rocks from the Marquesas Islands (Bishop and Woolley, 1973) were melted and their phase temperatures determined. These rocks spanned the composition range of the basalts and in two cases fell outside the range of the standard data.

The powdered (200 mesh) rock samples were dried at 105 °C and sealed in platinum capsules after crimping and heating to remove air. It was presumed that the experimental environment was buffered for f_{O_2} by the terminal ferric to ferrous ratio of the charge. In a few experiments the capsule burst, implying a gas pressure of a few bars. The experimental runs were of 90 to 120 minutes' duration and were made in a vertical tube furnace heated to a prearranged temperature. The experiments were made at intervals of less than 10 °C and the range of temperatures investigated was limited by calculation of likely temperatures of appearance of the phases. The charges were examined visually and were also analysed by X-ray diffraction by a method known to have a detection limit for plagioclase and clinopyroxene of less than 2% when samples of the size of the charges were analysed and when the matrix was glass. Olivine gave a detection limit of between 2 and 5% under the same conditions. The total range of possible error was expected to be of the order of 18 °C at the 95% confidence level.

The experimental results are given in Table III, and a comparison of calculated and observed temperatures is given in Table IV. For samples 16 and 18 (Table III) the technique predicted, incorrectly, the crystallization of olivine and gave large errors in other crystallization temperatures. However, these were the most siliceous rocks examined and they did not fall within the basalt field as defined by the standard data. If these two rocks are excluded the remaining four basalts give mean errors in calculated temperatures of 7.2 °C for olivine, 6.75 °C for plagioclase, and 13.0 °C for clinopyroxene.

Effect of increased pressure on crystallization temperatures. There are insufficient data pertaining to the changes in crystallization temperatures of three silicate phases with pressure for a detailed analysis to be possible. The rate of change of temperature with pressure reflects the possibility that solid-solution compositions may change with pressure (Ito and Kennedy, 1968). However, a common sequence for the liquidus phase, in going from low to high pressure under dry conditions, is olivine-orthopyroxene-clinopyroxene-garnet, and

the pressure at which olivine is the liquidus phase increases as the normative forsterite content of the rock increases, while the pressure at which garnet is on the liquidus decreases as Al_2O_3 increases. This is shown in fig. 6 where the approximate limits of pressure at which a given phase can be the primary liquidus phase are plotted against the ratio MgO/Al_2O_3 .

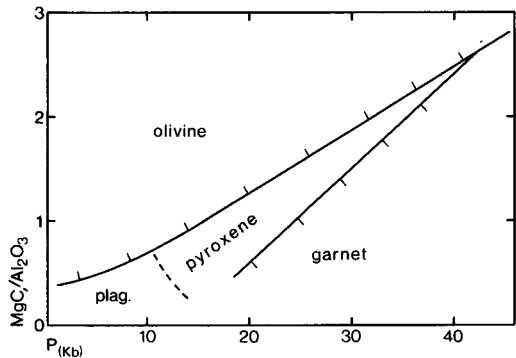


FIG. 6. Approximate limits for the composition-pressure fields for which olivine and garnet are the first phases to crystallize from basic melts. Silicate phases that appear first in the intervening region are also indicated. The diagram is based on data from Ringwood (1975), Thompson (1974), Green and Ringwood (1967), Ito and Kennedy (1967, 1968, and 1971), Cohen *et al.* (1967), Bultitude and Green (1971), Chipman and Hays (1972), O'Hara (1963).

It becomes less likely that early crystallization of garnet will influence the differentiation path of melts as the MgO/Al_2O_3 ratio of the melt increases. Conversely, differentiation of more aluminous basalts beginning to crystallize at pressure above 20 kilobars may be more profoundly influenced by garnet crystallization. This is particularly significant in view of the position of garnet and olivine compositions on fig. 4, and their relationship to the boundary between basalt classes 1 and 2 and classes 3 and 4, and hence to the boundary between the calc-alkaline associations and other basic volcanic suites.

Conclusions

Linear multiple-regression analysis coupled with discriminant function analysis of the data allow the temperatures of crystallization of silicates from basaltic melts to be related to the chemistry of the rocks. Tests on data not included in the original set and experiments on the rocks from the Marquesas Islands suggest that the errors in calculation are not too dissimilar from the experimental

errors. The routine should be of value in establishing likely crystallization temperatures before experiments are made and should allow the most useful rock compositions to be selected for experiments. It seems that the temperature for the first phase to crystallize can be calculated with the least difficulty, but that clinopyroxene tends to be the second or third phase and to give larger errors in calculated temperature. This may partly reflect the fact that clinopyroxene temperatures are more sensitive to f_{O_2} variations than are those for the other two phases (Fudali, 1965). The calculations allow normative factors to be defined even in the absence of experiments and permit the construction of variation diagrams such as figs. 3 and 4 which make useful comparators for igneous provinces. It should be possible to extend the model to elevated pressure conditions once sufficient data become available. Given a wider range of elemental determinations and more precise control of experimental conditions and of analytical techniques, it may prove possible for the generalizations given here to be considerably simplified.

REFERENCES

- Bishop, A. C. and Woolley, A. R. (1973). *Contrib. Mineral. Petrol.* **39**, 309-26.
- Bultitude, R. J. and Green, D. H. (1971). *J. Petrol.* **12**, 121-47.
- Cameron, E. P. and French, W. J. (1977). *Mineral. Mag.* **41**, 239-51.
- Chipman, D. W. and Hays, J. F. (1972). *Trans. Am. Geophys. Union*, **53**, 552.
- Cohen, L. H., Ito, K., and Kennedy, G. C. (1967). *Am. J. Sci.* **265**, 475-518.
- French, W. J. (1971). *Contrib. Mineral. Petrol.* **31**, 154-8.
- (1976). *Geol. Mag.* **4**, 371-6.
- Friedman, H. P. and Rubin, S., (1967). *J. Am. Stat. Ass.* **62**, 1159-78.
- Fudali, R. F. (1965). *Geochim. Cosmochim. Acta*, **29**, 1063-75.
- Green, D. H. and Ringwood, A. E. (1967). *Contrib. Mineral. Petrol.* **15**, 103-90.
- Ito, K. and Kennedy, G. C. (1967). *Am. J. Sci.* **265**, 519-38.
- (1968). *Contrib. Mineral. Petrol.* **19**, 177-211.
- (1971). *Am. Geophys. Union, Monograph*, **14**.
- O'Hara, M. J. (1963). *Carnegie Inst. Washington Yearb.* **62**, 71-6.
- Ringwood, A. E. (1975). *Composition and Petrology of the Earth's Mantle*, McGraw-Hill.
- Thompson, R. N. (1972). *Am. J. Sci.* **272**, 901-32.
- (1973). *Contrib. Mineral. Petrol.* **41**, 197-204.
- (1974). *Ibid.* **45**, 317-41.
- Tilley, C. E., Yoder, H. S., and Schairer, J. F. (1964). *Carnegie Inst. Washington Yearb.* **63**, 93-6.
- Thompson, R. N., Wadsworth, W. J., and Upton, B. J. (1971). *Mineral. Mag.* **38**, 344-52.
- Yoder, H. S. (1976). *Generation of Basaltic Magma*. National Acad. Sci., Washington.
- Ward, J. H. (1963). *J. Am. Stat. Ass.* **58**, 236-44.

[Manuscript received 29 January 1980;
revised 21 July 1980]