MINERAL EQUILIBRIA, GEOTHERMOMETERS AND GEOBAROMETERS IN SOME ICELANDIC HYALOCLASTITES

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MÄKIPÄÄ, HEIKKI 1978: Mineral equilibria, geothermometers and geobarometers in some Icelandic hyaloclastites. *Bull. Geol. Soc. Finland* 50: 113—134.

Distribution coefficients between crystal and magma can be used to establish various properties of magmas. A number of natural hyaloclastites have been used to evaluate some of the established geothermometers and geobarometers. Comparison with experimental data on the same rocks shows that the olivine geothermometer gives the most reasonable results and in some cases plagioclase geothermometer can also be useful.
However before mineral-liquid combinations can be used to evaluate magma properties equilibrium between the various phases must be established. This is not always simple and more experimental data is needed.

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Introduction

The purpose of this paper is to describe the mineral liquid relationships in some common natural Icelandic hyaloclastites. The rocks used here are described by Mäkipää (1978).

The rocks are basalts quenched in water (mainly glacial melt water) upon eruption. Phenocrysts (olivine, plagioclase and clinopyroxene) are therefore unaffected by reactions occurring upon cooling and crystallization of subaerial lavas. All samples are quartz- or olivine normative tholeiites not far from the normative quartz saturation plane.

The quickly cooled glasses offer the possibility to study the state of equilibrium between crystals and melt. The pressure and temperature conditions of the magma during the crystallization of phenocryst phases prior to eruption can be inferred from existing geothermometers and geobarometers.

The geothermometers and geobarometers used are derived from experimental works where the distribution of elements between the coexisting phases have been derived as a function of temperature, total pressure and the fugacities of important volatile components such as water and oxygen. The experiments of Roeder and Emslie (1970), Kudo and

Table 1. Microprobe analyses of some selected representative experimental products.

Sample No.	KRA-731					NAL-13[1]			
Run No.	# 7313	# 7312	# 7314	# 7315	# 7311	[2]	# 3	# 5	# 6
Temperature (°C)	1197	1192	1186	1180	1161		1258	1202	1182
Liquid									
SiO_2	49.93	49.67	50.19	48.83	49.47	47.60	47.77	48.47	49.12
TiO_2	1.70	1.65	1.68	1.73	1.84	1.09	1.21	1.69	1.82
Al_2O_3	13.83	13.20	13.37	13.99	13.44	16.66	15.90	13.82	13.59
FeO^t	12.27	12.07	11.93	12.00	12.69	9.56	9.51	10.76	11.20
MnO	0.22	0.23	0.25	0.24	0.24	0.13	0.17	0.24	0.19
MgO	7.23	7.07	6.93	6.88	6.58	9.56	10.22	8.75	7.59
CaO	11.63	11.39	11.71	10.93	11.15	12.76	12.92	13.32	12.22
Na_2O	2.20	2.22	2.25	2.02	2.00	2.14	1.81	2.03	2.00
K_2O	0.26	0.25	0.24	0.27	0.26	0.11	0.13	0.16	0.14
P_2O_5	0.11	0.16	0.17	0.18	0.20	0.09	0.09	0.19	0.17
Olivine									
SiO_2		39.08	38.56	38.55	38.47		39.43	40.29	38.75
FeO^t		19.62	20.33	20.41	22.51		16.13	15.28	17.11
MnO		0.38	0.35	0.42	0.36		0.30	0.24	0.26
MgO		39.43	39.26	39.41	38.90		47.60	43.47	45.17
CaO		0.26	0.29	0.33	0.48		0.47	0.37	0.41
Plagioclase									
SiO_2				50.45	50.50		46.93	48.85	47.81
Al_2O_3				30.80	30.27		32.06	31.60	31.37
FeO^t				0.71	0.85		0.63	0.70	0.69
MgO				—	—		0.27	0.25	0.25
CaO				15.14	14.86		18.39	16.91	15.47
Na_2O				2.54	2.66		1.56	2.29	2.47
K_2O				0.06	0.12		0.02	0.09	—
Other phases present					CPX				CPX

[1] Experiments by Dr. S. Steinthorsson (unpubl. data)
[2] Analysis by Sigvaldason (1974)

Weill (1970) and Drake (1972) are of particular relevance to the present study.

Some of the samples have also been used for experiments and the results are used for comparison with other experimental results.

The question of equilibrium is also relevant and before the temperature and pressure conditions can be derived the existence of equilibrium needs to be established. In the following account no attempt is made to establish various properties of the hyaloclastites at the time of eruption. The results sofar indicate that useful approximations can be obtained.

Melting experiments

Melting experiments were performed in order to evaluate the possible compositional effect on the distribution coefficients. Some of the experimental results are given in Table 1.

The experiments were carried out in a Pt wound vertical tube quench furnace. The run temperatures were measured using Pt/Pt 10 % Rh thermocouple before and after each run. The temperature fluctuation during each run was within 1°C. The total pressure in the runs was the atmospheric pressure and the furnace atmosphere was a mixture of carbon dioxide and hydrogen (close to the QMF-buffer) which was passed upwards through the furnace at a constant rate. In some runs the oxygen fugacity was controlled following the QMF-buffer and in some runs the oxygen fugacity was kept constant (constant gas mixture and flow rate).

The glasses which were melted at 1315°C were suspended directly into the furnace at the desired temperature. After approximately 24 hours the platinum wire was melted with an electric current so that the sample fell down into the water where it quenched within seconds. The run duration of 24 hours appears to be sufficient for the attaintment of equilibrium (*e.g.* Kennedy 1948, Yoder and Tilley 1962, Seward 1971, Sun *et al.* 1974, Duke 1976). However, Drake and Weill (1975) and Watson (1977) used much longer time to equilibrate their samples. Experiments conducted at the same temperature using longer run times gave identical results and in the present study some 3 and 5 day runs were made without a noticeable change. Equilibrium is also indicated by the homogenity of the produced phases in the present study.

Olivine — liquid combination

General

Bowen and Schairer (1935) demonstrated that there is a complete solid solution between forsterite and fayalite in the system MgO—FeO—SiO_2.

This system provides a simple model to determine the composition of the equilibrium olivine crystals. Compositions (listed in Table 2) were read directly from the phase diagram Mg_2SiO_4—Fe_2SiO_4.

Equilibrium distribution coefficient

According to Roeder and Emslie (1970) the distribution of magnesium and ferrous iron between olivine and liquid can be expressed by the following equation:

$$\mathrm{Mg(olivine)} + \mathrm{Fe(liquid)} = \mathrm{Mg(liquid)} + \mathrm{Fe(olivine)}$$

The replacement of the smaller Mg by the larger Fe ion results in a lowering of the melting temperature. An equilibrium constant (K) for this reaction can be written in terms of the activities (a) of the various chemical species, *i.e.* (Mg, MgO, $MgSi_{0.5}O_2$) in the liquid and solid solutions or in terms of the mole fraction (X) and activity coefficients (γ) of the various species:

$$K = \frac{(a^{ol}_{FeO})\,(a^{l}_{MgO})}{(a^{l}_{FeO})\,(a^{ol}_{MgO})} = \frac{(X^{ol}_{FeO})\,(X^{l}_{MgO})}{(X^{l}_{FeO})\,(X^{ol}_{MgO})} \times \frac{(\gamma^{ol}_{FeO})\,(\gamma^{l}_{MgO})}{(\gamma^{l}_{FeO})\,(\gamma^{ol}_{MgO})}$$

The ratio of the mole fractions were defined in Roeder and Emslie (1970) as the distribution coefficient. This coefficient was previously studied thermodynamically by Bowen and Schairer (1935). Bradley (1962) revised the equations presented by Bowen and Schairer using different specific heat terms and found that the agreement with Bowen and Schairer's work still was very good.

Several authors (*e.g.* Roeder and Emslie 1970, Duke 1976) found that this distribution coefficient

$$K_D = \frac{(X^{ol}_{FeO})\,(X^{l}_{MgO})}{(X^{l}_{FeO})\,(X^{ol}_{MgO})}$$

is equal to 0.30 at equilibrium conditions. Other variables such as pressure, oxygen fugacity and temperature have no significant effect. This value is discussed in detail by Roeder and Emslie (1970).

However, the lunar basalt experiments (Longhi *et al.* 1975, Walker *et al.* 1976) show a somewhat higher average on K_D (0.33).

Table 2. The Fo-content in olivine (mole-%) and K_D values. Columns: 1. Fo content read directly from $Mg_2SiO_4 — Fe_2SiO_4$ diagram. 2. Fo content read from $FeO^l — MgO^l$ diagram (Fig. 4). 3. Analyzed olivine composition (Mäkipää 1978). 4. $K_D = \frac{(FeO^{ol})\ (MgO^l)}{(FeO^l)\ (MgO^{ol})}$
ma — macrophenocryst, mi — microphenocryst. Sample location is shown on the map and given in Appendix 1 (Mäkipää 1978).

Sample No.		1	2	3	4
1		78.5	77.1	78.49	0.282
3		74.5	71.7	75.29	0.256
4	ma			83.06	0.284
	mi	82.4	82.2	83.14	0.282
5	ma			82.11	0.250
	mi	79.8	78.9	77.62	0.328
7		75.2	72.9	75.63	0.266
10		81.0	80.4	79.04	0.329
11	ma			88.77	0.211
	mi	85.1	84.7	84.99	0.294
16		81.0	80.6	80.91	0.297
17		81.8	81.3	80.49	0.320
19	ma			83.77	0.271
	mi	82.7	82.3	84.01	0.267
20	ma			84.91	0.260
	mi	83.4	83.0	81.17	0.340
22		73.4	72.7	69.40	0.361
24		72.8	71.0	64.99	0.405
30	ma			85.73	0.271
	mi	84.7	84.5	85.58	0.275
32	ma			86.01	0.277
	mi	85.3	85.1	85.91	0.279
35		84.7	84.7	85.23	0.286
38		77.9	77.7	76.84	0.320
96		84.5	83.2	85.23	0.264
99	ma			80.36	0.275
	mi	80.7	79.2	80.94	0.286
101A		84.6	83.3	81.06	0.360
101B		78.3	76.6	81.75	0.236
104	ma			85.44	0.321
	mi	87.4	86.5	85.38	0.319

In Roeder and Emslie's (1970) experiments the K_D values are within 0.06 units ($K_D = 0.30$, $SD = 0.03$) and the K_D values in the present study (Table 2) between 0.26 and 0.34 are assumed to represent equilibria.

To get better illustration of this equilibria the elemental distribution (Fe/Mg in olivine versus Fe/Mg in liquid) is plotted in Fig. 1. The area between the lines presents equilibria in this study and most of the samples fall between those limits.

Olivine geothermometers

Roeder and Emslie (1970) graphically presented the dependence of olivine composition on the composition of the liquid by plotting the mole per cent FeO in liquid against the mole per cent MgO in liquid (Fig. 2). Roeder and Emslie discussed in detail the usefulness and limitations of this diagram. Because the composition of the basalts used here are equal to their experimental materials and there is more than enough SiO_2 in liquid to combine with MgO and FeO to form olivine, this diagram offers the possibility to estimate the composition of the equilibrium olivine as well as the equilib-

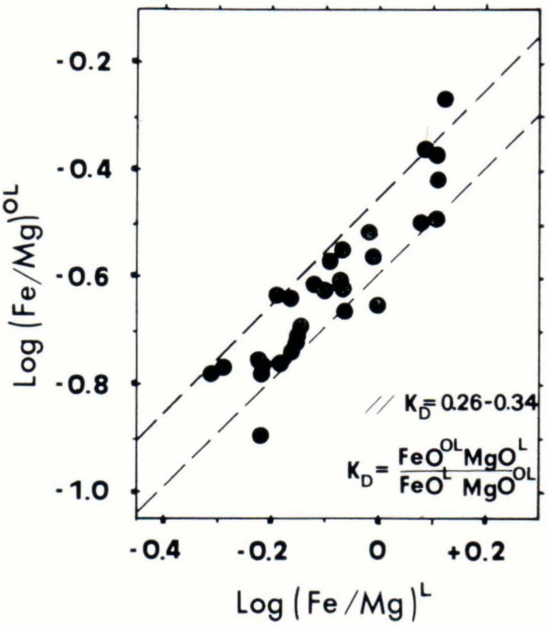

Fig. 1. Log (Fe/Mg) in olivine plotted against log (Fe/Mg) in liquid. The area between the lines indicates equilibrium conditions ($K_D = 0.26—0.34$) assumed in this study.

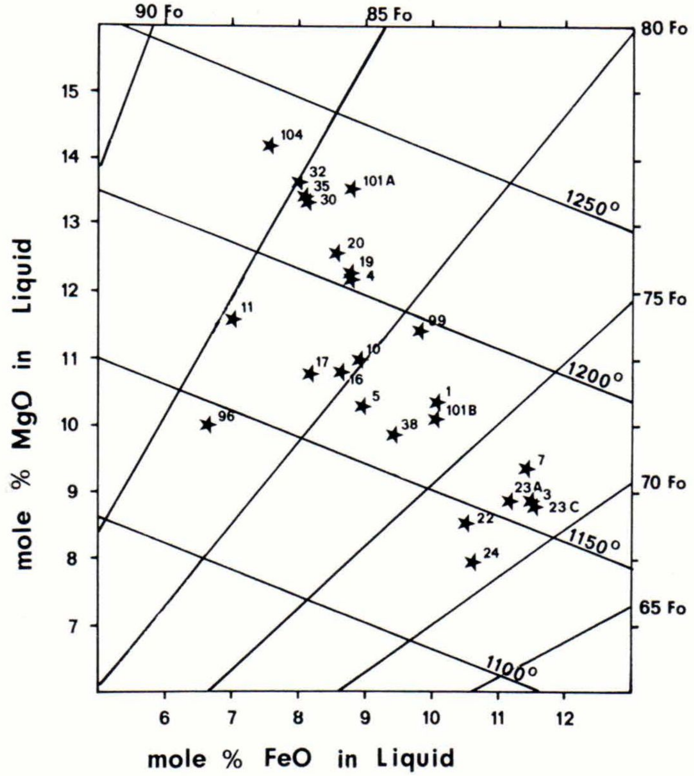

Fig. 2. FeO (mole-%) in liquid plotted against MgO (mole-%) in liquid to estimate the equilibrium temperatures and the compositions of the equilibrium olivines (Roeder & Emslie 1970). Numbers refer to the samples (Mäkipää 1978).

rium temperature. These equilibrium compositions are listed in Table 2.

The equilibrium olivine composition shows no significant dependence upon temperature but there is a good correlation between the elemental distribution and temperature. Roeder and Emslie (1970) produced the following equations for calculating the equilibrium temperature using MgO and FeO distributions:

$$\log \frac{X^{ol}_{MgO}}{X^{l}_{MgO}} = \frac{3740}{T} - 1.87$$

$$\log \frac{X^{ol}_{FeO}}{X^{l}_{FeO}} = \frac{3911}{T} - 2.50$$

where X is the mole fraction of the element and T temperature in K°.

Roeder (1974) modified these equations using data on the solubility of ferrous iron in basic liquids giving the following equations:

$$\log \frac{X^{ol}_{MgO}}{X^{l}_{MgO}} = \frac{3480}{T} - 1.70$$

$$\log \frac{X^{ol}_{FeO}}{X^{l}_{FeO}} = \frac{3740}{T} - 2.38$$

$$\log \frac{X^{ol}_{MnO}}{X^{l}_{MnO}} = \frac{3850}{T} - 2.59$$

The equilibrium temperatures calculated using these equations are given in Table 3. The temperature calculated from the MgO distribution should be the most accurate. The FeO temperature is dependent on the FeO content of the magma which can not be measured directly and for MnO temperature estimates more accurate determinations are needed.

Table 3. Calculated olivine and plagioclase temperatures. OL — olivine (Roeder 1974, Fe/Mg refer to FeO^1/MgO^1 diagram in Roeder and Emslie 1970, Fig. 7). PL — plagioclase (Kudo and Weill 1970, Mathez 1973). ma — macrophenocryst, mi — microphenocryst. Sample location is shown on the map and given in Appendix 1 (Mäkipää 1978).

Sample No.		calculated temperatures (°C)												
		Roeder 1974 (OL)				Kudo & Weill (PL, P_{H_2O})				Mathez (PL, P_{H_2O})				USED
		Mg	Fe	Mn	Fe/Mg	0	0.5	1.0	5.0	0	0.5	1.0	5.0	
RE-1	mi	1178	1206	1202	1177	1212	1164	1129	872	1177	1212	1162	872	1190
	ma					1264	1213	1178	921	1223	1274	1220	921	
TH-3	mi	1150	1203	1182	1158	1197	1150	1114	851	1164	1194	1145	851	1158
	ma					1197	1150	1114	851	1164	1194	1145	851	
TH-4	mi	1200	1228	1226	1203	1289	1238	1204	951	1245	1304	1249	951	1218
	ma	1204	1229	1222		1291	1240	1206	953	1247	1306	1251	953	
RE-5	mi	1165	1223	1172	1168	1209	1162	1127	867	1175	1210	1160	867	1168
	ma	1179	1170	1138		1262	1211	1176	916	1221	1272	1218	916	
TH-7	mi	1160	1203	1169	1168	1215	1167	1132	870	1180	1216	1166	870	1166
TH-10	mi	1194	1182	1149	1184	1210	1163	1129	874	1176	1210	1161	874	1188
	ma					1273	1222	1188	932	1231	1285	1231	932	
RE-11	mi	1182	1199	1308	1180	1246	1198	1164	915	1208	1253	1202	915	1190
	ma	1171	1276	1310		1247	1199	1165	916	1209	1254	1203	916	
RE-16	mi	1181	1196	1211	1177	1221	1174	1139	889	1186	1224	1174	884	1196
	ma					1260	1210	1176	916	1220	1270	1217	919	
RE-17	mi	1176	1173	1191	1173	1208	1161	1126	865	1174	1208	1158	865	1180
	ma					1204	1156	1121	861	1170	1203	1153	861	
RE-19	mi	1204	1246	1189	1206	1239	1191	1158	909	1202	1245	1194	909	1210
	ma	1205	1242	1269		1234	1187	1153	905	1198	1239	1189	905	
RE-20	mi	1215	1193	1158	1209	1244	1196	1163	916	1207	1250	1200	916	1206
	ma	1202	1250	1186										
GR-22	mi	1163	1133	1155	1144	1203	1155	1118	849	1169	1202	1151	849	1154
	ma					1242	1191	1155	886	1203	1248	1194	886	
GR-23A	mi	1161	1167	1091	1155	1212	1163	1127	858	1177	1213	1161	858	1161
GR-23C	mi	1168	1157	1168	1157	1197	1150	1115	851	1165	1196	1145	851	1163
	ma					1189	1142	1107	842	1158	1185	1136	842	
KE-24	mi	1165	1108	1098	1130	1221	1172	1136	871	1185	1224	1171	871	1130
	ma					1206	1158	1122	856	1172	1205	1154	856	
HE-30	mi	1221	1255	1245	1220	1249	1201	1167	920	1211	1256	1205	920	1235
	ma	1220	1257	1220		1238	1190	1157	910	1201	1243	1193	910	
HE-32	mi	1228	1257	1240	1225	1256	1208	1175	931	1217	1264	1214	931	1238
	ma	1226	1257	1242										
HE-35	mi	1223	1246	1250	1222	1256	1208	1175	931	1217	1264	1214	931	1236
LA-38	mi	1171	1169	1133	1163	1217	1169	1134	873	1182	1218	1169	873	1168
TJ-96	mi	1158	1203	1166	1144	1213	1166	1131	873	1179	1214	1164	873	1156
	ma					1165	1121	1086	827	1137	1157	1110	827	
TJ-99	mi	1201	1225	1213	1195	1253	1205	1171	922	1214	1261	1210	922	1207
	ma	1198	1154	1200		1156	1114	1080	833	1131	1147	1103	833	
TJ-101B	mi	1160	1248	1302	1177	1200	1156	1123	884	1168	1198	1152	884	1169
TJ-101A	mi	1242	1203	1282	1228	1256	1207	1172	921	1216	1264	1212	921	1224
TJ-104	mi	1238	1228	1230	1230	1301	1250	1217	973	1257	1317	1263	973	1231
	ma					1289	1239	1206	963	1247	1303	1252	963	

Leeman and Scheidegger (1977) also studied the use of the olivine-liquid distribution as a geothermometer. They concluded that the apparent olivine distribution coefficients found for their samples were reasonable approximations to the true equilibrium values. They also emphasized that factors such as liquid temperature and composition might have significant influence on the partition coefficients in nature.

However, values derived using their geothermometer equation for Mg

$$\ln D_{Mg} = \frac{8916}{T} - 4.29$$

can be compared with the temperatures derived using Roeder and Emslie's (1970) equation.

As seen from the Fig. 3 all temperatures calculated using Leeman and Scheidegger's geothermometer are systematically about 5 °C higher than those calculated from Roeder and Emslie. The disequilibrium samples stand out very clear.

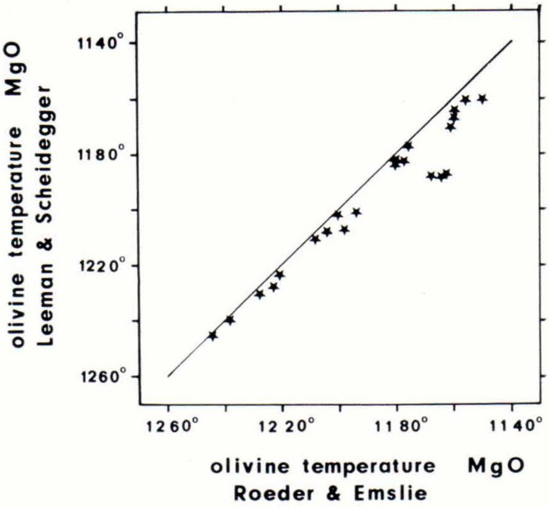

Fig. 3. Calculated olivine MgO-temperatures (after Roeder and Emslie 1970) plotted against calculated olivine Mg-temperatures (after Leeman and Scheidegger 1977).

Plagioclase-liquid combination

General

In his classic investigation of melting in the plagioclase system Bowen (1913) demonstrated that albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$) form a continuous solid solution series at high temperatures. The experimental relationship found between the compositions of liquid and coexisting solid solution and temperature was satisfactorily accounted for by Bowen by assuming that both the liquid and solid solutions were ideal, i.e., that the activities of the Ab and An components were equal to their mole fraction.

Some attempts have been made (*e.g.* Larsen and Irving 1938, Carmichael 1960) to compare Bowen's results in the system directly to magmatic systems. The activities of An and Ab are replaced with their normative concentrations calculated from the liquid compositions. These attempts have not been very successful; the reasons for which are discussed by Botting et al. (1966).

Bowen's (1915) work on the 'haplobasaltic-haplodioritic' system provides a simple model to determine the composition of equilibrium plagioclase crystals. Lack of knowledge of variables such as total pressure and fucacities of important volatile components such as water and oxygen has limited the use of these results. However, several authors (*e.g.* Kudo and Weill 1970) pointed out the suitability of this haplobasaltic system to estimate approximate equilibria. Therefore the compositions in the present study were also read directly from the phase diagrams An-Ab-Di and An-Ab. The purpose of this is

Table 4. The An-content in plagioclase (mole-%). Columns: 1. An content read directly from Ab-An-Di and Ab-An diagrams. 2. Analyzed plagioclase composition (Mäkipää 1978). ma — macrophenocryst, mi — microphenocryst. Sample location is shown on the map and given in Appendix 1 (Mäkipää 1978).

Sample No.		1	2
1	ma		90.07
	mi	84.8	81.64
3	ma		76.96
	mi	85.2	75.75
4	ma		92.28
	mi	87.2	92.14
5	ma		89.58
	mi	82.8	80.38
7		83.5	76.64
10	ma		90.67
	mi	85.4	80.15
11	ma		86.39
	mi	86.0	86.32
16	ma		89.71
	mi	84.9	83.71
17	ma		80.70
	mi	83.3	82.61
19	ma		82.66
	mi	86.6	84.63
20		86.3	83.00
22	ma		88.07
	mi	80.4	78.30
24	ma		66.77
	mi	80.0	71.37
30	ma		86.01
	mi	88.0	87.74
32		88.3	87.34
35		88.6	87.85
38		82.3	77.30
96	ma		59.81
	mi	86.5	83.52
99	ma		50.99
	mi	86.1	86.05
101A		91.0	82.92
101B		85.0	85.51
104	ma		91.11
	mi	89.1	92.10

only to get some idea how far from or close to the equilibria the analyzed plagioclase crystals are.

The measured values (Table 4) compared with the analyzed ones clearly show that all the microphenocrysts are in approximate equilibrium. Almost all the macrophenocrysts appear to be far from the equilibria.

Formulation of a plagioclase geothermometer

The first successful attempt at formulating a plagioclase geothermometer is that of Kudo and Weill (1970), who considered the exchange reaction:

$$\underset{\text{plagioclase}}{(NaSiO_{2.5})\,AlSi_2O_{5.5}} + \underset{\text{liquid}}{(CaAlO_{2.5})\,AlSiO_2O_{5.5}}$$

$$= \underset{\text{plagioclase}}{(NaSiO_{2.5})\,AlSi_2O_{5.5}} + \underset{\text{liquid}}{(CaAlO_{2.5})\,AlSi_2O_{5.5}}$$

The resultant equilibrium condition, assuming the solid solution to be ideal, is

$$-\frac{\mu^\circ}{RT} = \ln \lambda/\delta + \ln \gamma_{Na}\gamma_{Si}/\gamma_{Ca}\gamma_{Al}$$

where $\mu^\circ = \mu^\circ{}_{An} - \mu^\circ{}_{Ab} + \mu^\circ{}_{Na} + \mu^\circ{}_{Si} - \mu^\circ{}_{Ca} - \mu^\circ{}_{Al}$, $\mu^\circ =$ chemical potential of the specific element, T is temperature in Kelvin, $\delta = X_{Ab}/X_{An}$, $\lambda = X_{Na}X_{Si}/X_{Ca}X_{Al}$ and γ = activity coefficient, and suscripts denote the atomic fraction (X) of an element in the melt or mole fractions of Ab and An in plagioclase.

Because the values of the activity coefficients were unknown, Kudo and Weill (1970) assumed that the activity coefficients take a form similar to that found for regular solutions:

$$\ln \gamma = C\emptyset/T,$$

where C is a constant empirically evaluated at $1.29 \times 10^4 T^{-1}$ and Ø is the atomic fraction of the elements in the melt.

Kudo and Weill (1970) derived the following set of linear regression curves for different conditions of crystallization:

$$\ln \lambda/\delta + 1.29\times10^{4}\varnothing/T = 10.34\times10^{-3}T - 17.24 \text{ (dry)}$$
$$\ln \lambda/\delta + 1.29\times10^{4}\varnothing/T = 11.05\times10^{-3}T - 17.86 \ (P_{H_2O}=0.5 \text{ kb})$$
$$\ln \lambda/\delta + 1.29\times10^{4}\varnothing/T = 11.14\times10^{-3}T - 17.67 \ (P_{H_2O}=1.0 \text{ kb})$$
$$\ln \lambda/\delta + 1.29\times10^{4}\varnothing/T = 12.18\times10^{-3}T - 16.63 \ (P_{H_2O}=5.0 \text{ kb})$$

Mathez (1973) modified the Kudo and Weill geothermometer by using Ab and An activity ratios in the calculations. Mathez pointed out that the Kudo and Weill 'dry' equation gives generally higher temperatures than the experimental values. This divergence may result because the 'dry' equation is generated from plagioclase-liquid equilibrium data for granites in the system An-Ab. Therefore Mathez calculated a new 'dry' equation using available basalt data:

$$\ln\lambda/\delta + 1.29\times10^{4}\varnothing/T = 11.05\times10^{-3}T - 17.98$$

The calculated temperatures according to the above equation are in closer agreement with the experimental data than those calculated from Kudo and Weill's 'dry' equation.

By substituting $(X_{Ab}\gamma_{Ab})/(X_{An}\gamma_{An})$ for δ in the equation γ_{Ab}/γ_{An} can be calculated from the experimental results. Fig. 4 compares values of γ_{Ab}/γ_{An} calculated using this equation for the experimental data with similar values calculated from the data of Orville (1972).

This Mathez's modification gives the following 'new' equations for different conditions of crystallization:

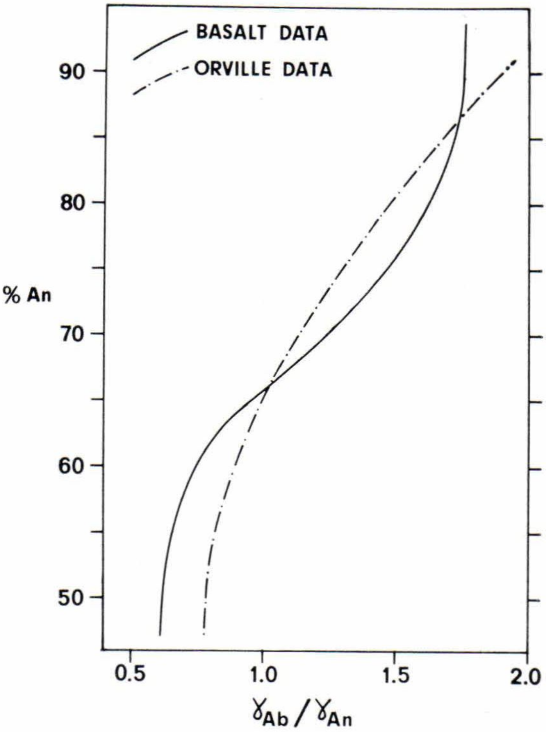

Fig. 4. Comparison of values of γ_{Ab}/γ_{An} as a function of plagioclase composition (Mathez 1973, Fig. 3).

$$\ln \lambda/\delta + 1.29\times10^{4}\varnothing/T = 11.76\times10^{-3}T - 19.01 \text{ (dry)}$$
$$\ln \lambda/\delta + 1.29\times10^{4}\varnothing/T = 8.97\times10^{-3}T - 15.21 \ (P_{H_2O}=0.5 \text{ kb})$$
$$\ln \lambda/\delta + 1.29\times10^{4}\varnothing/T = 9.60\times10^{-3}T - 15.76 \ (P_{H_2O}=1.0 \text{ kb})$$
$$\ln \lambda/\delta + 1.29\times10^{4}\varnothing/T = 12.18\times10^{-3}T - 16.63 \ (P_{H_2O}=5.0 \text{ kb})$$

The required input data are $\lambda = X_{Na}X_{Si}/X_{Ca}X_{Al}$ and $\varnothing = X_{Ca} + X_{Al} - X_{Si} - X_{Na}$, where X=atomic fraction of the element in the melt and $\delta = X_{Ab}\gamma_{Ab}/X_{An}\gamma_{An}$, where X_{Ab}/X_{An} is the plagioclase composition and γ_{Ab}/γ_{An} the corresponding activity coefficients.

Equilibrium distribution coefficient

The elemental partition coefficient. Drake (1975) suggested the use of the major element distribution versus temperature to estimate equilibria. Elemental partition coefficients

D_{Ca}, D_{Na}, D_{Al} and D_{Si} where D_{Ca}=(weight of Ca in plagioclase)/(weight of Ca in liquid), etc. are given in Table 5 together with equilibrium constants (K) for the reactions discussed later. The different partition coefficients are plotted in Fig. 5 against the calculated olivine temperature. The difference between the micro- and macrophenocrysts is very apparent. All the regression lines in Drake's experiments are very different from those found here.

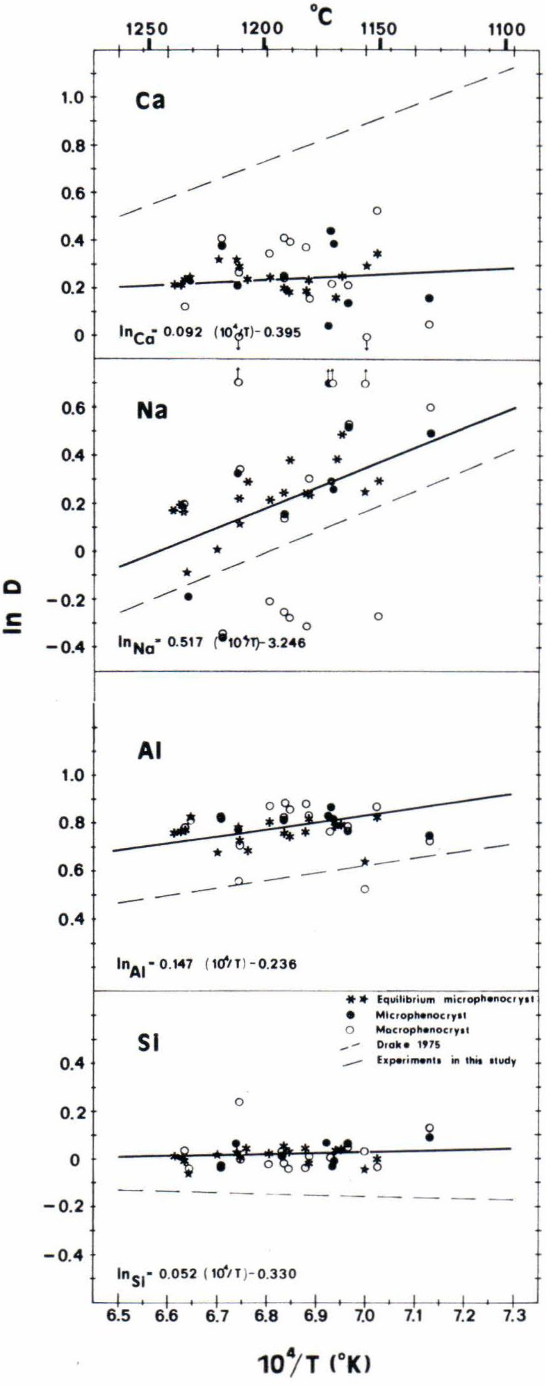

Fig. 5. Regression curves for ln D_{Ca}, ln D_{Na}, ln D_{Al}, ln D_{Si} versus 1/T (°K). D_{Ca}=(weight of Ca in plagioclase)/(weight of Ca in liquid), etc. ★✱=plagioclase assumed equilibrium ○=plagioclase macrophenocryst ●=plagioclase microphenocryst. Dashed lines indicate equilibria in Drake's (1975) experiments. Equations and solid lines are fitted by method of least squares to present experimental data only.

Drake (1975) in his discussion made the following remarks: D_{Ca} is greater than unity and is strongly dependent upon temperature, D_{Na} is less than unity above 1200 °C and is strongly dependent upon temperature, D_{Al} is always greater than unity and is relatively insensitive to temperature and D_{Si} is always less than unity and is invariant with temperature.

The present experimental data shows very strong positive correlation between D_{Na} and temperature. The difference between Drake's (1975) experiments and the present data is caused of different bulk compositions, which in Drake's experiments were unlike those used in the present study. The regression lines derived from the present experimental data correlate well with the hyaloclastites studied.

The equilibrium constants. The distribution of major elements in plagioclase have been calculated in terms of six reactions (defined as K-values in Drake 1976):

$$K_5 = CaO(l) + 2AlO_{1.5}(l) + 2SiO_2(l)$$
$$\rightleftharpoons CaAl_2Si_2O_8(p)$$
$$K_6 = NaO_{0.5}(l) + AlO_{1.5}(l) + 3SiO_2$$
$$\rightleftharpoons NaAlSi_3O_8(p)$$

$$K_7 = CaAl_2O_4(l) + 2SiO_2(l) \rightleftharpoons CaAl_2Si_2O_8(p)$$

$$K_8 = NaAlO_2(l) + 3SiO_2(l) \rightleftharpoons NaAlSi_3O_8(p)$$

$$K_9 = CaO(l) + AlO_{1.5}(l) + NaAlSi_3O_8(p) \rightleftharpoons NaO_{0.5}(l) + SiO_2(l) + CaAl_2Si_2O_8(p)$$

$$K_{10} = CaAl_2O_4(l) + NaAlSi_30_8(p) \rightleftharpoons NaAlO_2(l) + SiO_2(l) + CaAl_2Si_2O_8(p),$$

where (l) refers to liquid and (p) to plagioclase.

The equilibrium constant for reaction (K_8) involving the equilibrium of albite with the melt component $NaAlO_2$ correlates strongly with reciprocal temperature. However the K-values (Table 5) show similar difference compared with Drake's experiments as the partition coefficients do (Figs. 6 and 7). However the equilibrium plagioclases distinguish the disequilibrium ones.

Clinopyroxene-liquid combination

Several authors (e.g. Mysen and Boettcher 1975) pointed out that geochemical parameters such as Fe/Mg in pyroxene are not suitable as indicators of temperature and pressure because the value increases isothermally with decreasing pressure and is dependent on the liquid composition. Because the compositions of basalts studied can be taken to be constant the distribution of iron and magnesium between olivine and clinopyroxene (Duke 1976) might provide a sensitive test for clinopyroxene equilibrium (Fig. 8).

Since $K^{ol/liq}_{D(Fe/Mg)}$ is independent on temperature and Fe/Mg in clinopyroxene depends on pressure and liquid composition, the

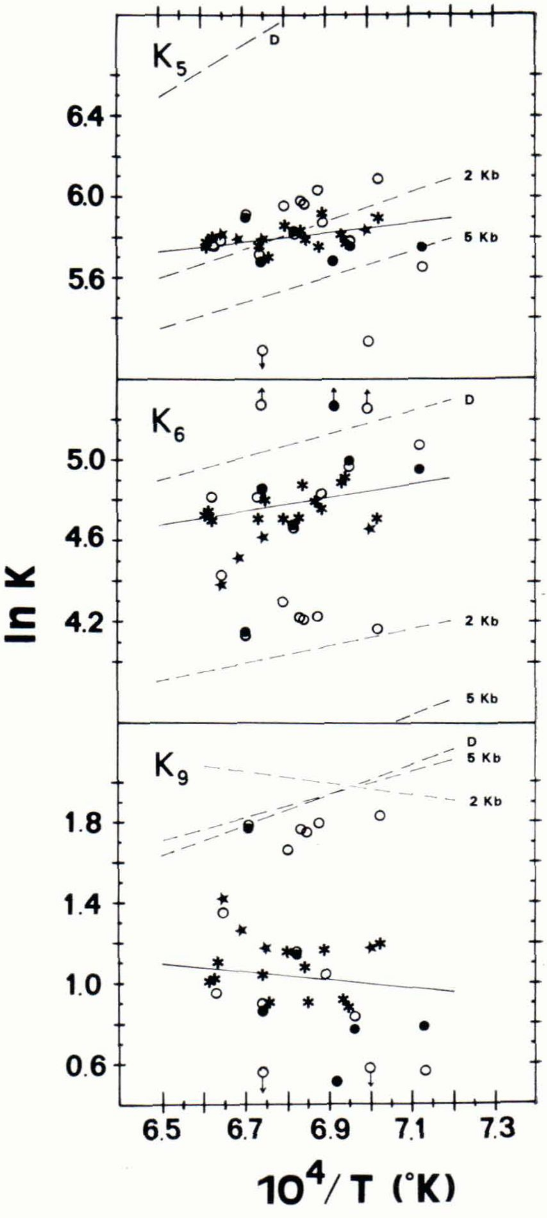

Fig. 6. Effect of pressure on equilibrium constants K_5, K_6 and K_9 (see text). Symbols are the same as in Fig. 5. Dashed lines: D=equilibrium line at 1 atm drawn from Drake (1975), 2kb= calculated from experiments of Piwinskii (1968) at P_{H_2O}=2 kb, 5kb=calculated from synthetic system at P_{H_2O}=5 kb (Yoder et al. 1957). Solid lines are the best fittings by method of least squares to hyaloclastite data only.

Table 5. The elemental partition coefficients and equilibrium constants for the plagioclase-liquid pair. D_{Ca}, etc. and K_5, etc. see text. ma — macrophenocryst, mi — microphenocryst. Sample location is shown on the map and given in Appendix 1 (Mäkipää 1978).

Sample No.		natural logarithm									
		D_{Ca}	D_{Na}	D_{Al}	D_{Si}	K_5	K_6	K_7	K_8	K_9	K_{10}
1	ma	0.41	−0.25	0.88	−0.02	5.82	4.67	2.70	2.17	1.15	0.53
	mi	0.20	0.25	0.75	0.06	5.82	4.67	2.70	2.17	1.15	0.53
3	ma	0.21	0.53	0.79	0.05	5.97	4.21	2.79	1.71	1.76	1.08
	mi	0.14	0.52	0.77	0.07	5.78	4.88	2.60	2.38	0.90	0.22
4	ma	0.41	−0.35	0.83	−0.03	5.78	4.91	2.56	2.41	0.87	0.15
	mi	0.39	−0.36	0.82	−0.03	6.03	4.23	2.89	1.73	1.80	1.16
5	ma	0.37	−0.31	0.88	−0.04	5.86	4.80	2.71	2.29	1.06	0.42
	mi	0.18	0.24	0.76	0.04	5.92	4.13	2.68	1.62	1.79	1.06
7		0.25	0.49	0.79	0.04	5.91	4.14	2.68	1.64	1.77	1.04
10	ma	0.39	−0.28	0.85	−0.04	5.79	4.96	2.51	2.45	0.83	0.06
	mi	0.17	0.38	0.74	0.03	5.76	5.00	2.49	2.50	0.77	−0.01
11	ma	0.25	0.14	0.82	0.03	5.99	4.22	2.80	1.72	1.77	1.08
	mi	0.25	0.15	0.81	0.02	5.84	4.76	2.65	2.26	1.08	0.39
16	ma	0.35	−0.20	0.87	−0.02	5.97	4.30	2.82	1.80	1.67	1.02
	mi	0.25	0.22	0.80	0.02	5.86	4.71	2.71	2.21	1.15	0.50
17	ma	0.16	0.30	0.83	0.02	5.88	4.86	2.75	2.33	1.05	0.42
	mi	0.23	0.24	0.83	−0.03	5.92	4.75	2.78	2.24	1.17	0.54
19	ma	0.27	0.35	0.71	0.01	5.71	4.81	2.50	2.31	0.90	0.20
	mi	0.29	0.22	0.72	0.00	5.75	4.71	2.54	2.20	1.04	0.34
20		0.24	0.29	0.69	0.04	5.70	4.80	2.52	2.29	0.90	0.23
22	ma	0.53	−0.27	0.87	−0.03	6.10	4.17	2.86	1.67	1.93	1.19
	mi	0.37	0.29	0.82	−0.00	5.91	4.71	2.67	2.21	1.20	0.46
24	ma	0.05	0.60	0.73	0.13	5.65	5.08	2.47	2.58	0.57	−0.11
	mi	0.16	0.49	0.74	0.09	5.75	4.96	2.56	2.46	0.79	0.11
30	ma	0.12	0.20	0.78	0.04	5.77	4.82	2.65	2.32	0.95	0.33
	mi	0.24	0.17	0.77	−0.00	5.80	4.70	2.68	2.20	1.10	0.48
32		0.21	0.17	0.75	0.02	5.75	4.73	2.63	2.22	1.02	0.41
35		0.21	0.20	0.77	0.00	5.77	4.75	2.67	2.24	1.02	0.43
38		0.17	0.39	0.79	0.04	5.81	4.90	2.66	2.40	0.91	0.27
96	ma	−0.19	0.95	0.53	0.07	5.32	5.43	2.00	2.93	−0.12	−0.93
	mi	0.30	0.21	0.63	−0.06	5.83	4.67	2.51	2.16	1.17	0.35
99	ma	−0.44	1.13	0.56	0.23	5.02	5.64	1.87	3.14	−0.62	−1.27
	mi	0.32	0.11	0.78	0.02	5.79	4.61	2.63	2.10	1.81	0.53
101A		0.04	0.93	0.84	0.06	5.68	5.47	2.62	2.97	0.21	−0.35
101B		0.31	0.01	0.67	0.02	5.81	4.53	2.63	2.02	1.28	0.61
104	ma	0.23	−0.09	0.81	−0.04	5.80	4.55	2.71	2.05	1.24	0.66
	mi	0.24	−0.21	0.80	−0.06	5.82	4.38	2.73	1.88	1.44	0.86

regression line should be equal to $K_D=1.0$ at equilibrium conditions

If these suggestions are correct, then it follows that $K^{cpx/liq}_{D(Fe/Mg)}$ (Fig. 9) also is independent of temperature but varies as a function of composition. The plotting on the olivine temperature- log (Fe/Mg) in clinopyroxene diagram (Fig. 10) shows linear cor-

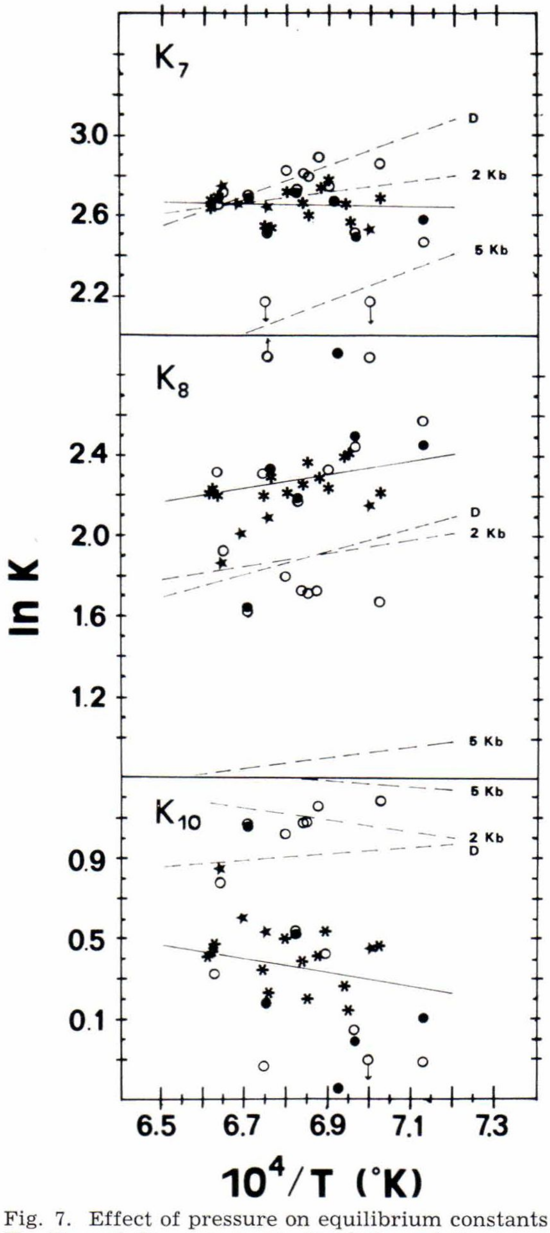

Fig. 7. Effect of pressure on equilibrium constants K_7, K_8 and K_{10} (see text). Symbols and lines are the same as in Fig. 6.

relation between these parameters. However because the Fe/Mg in liquid correlates well with the derived temperatures (Fig. 11) this might cause the correlation between the Fe/Mg in clinopyroxene and temperature.

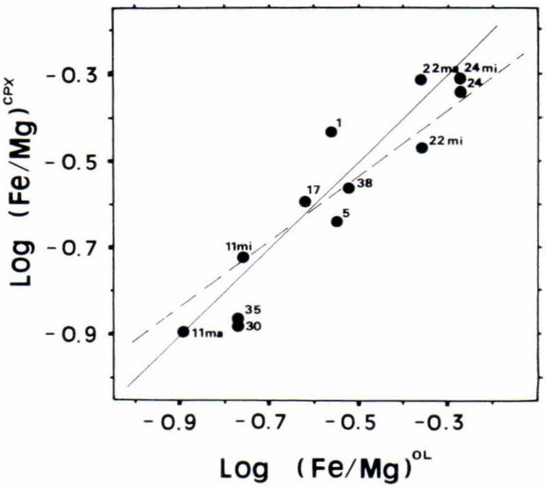

Fig. 8. Log (Fe/Mg) in olivine plotted against log (Fe/Mg) in clinopyroxene. Dashed line indicates equilibrium in Duke's (1976) experiments; solid line ($K_D = 1.0$) in this study. Numbers refer to the samples (Mäkipää 1978).

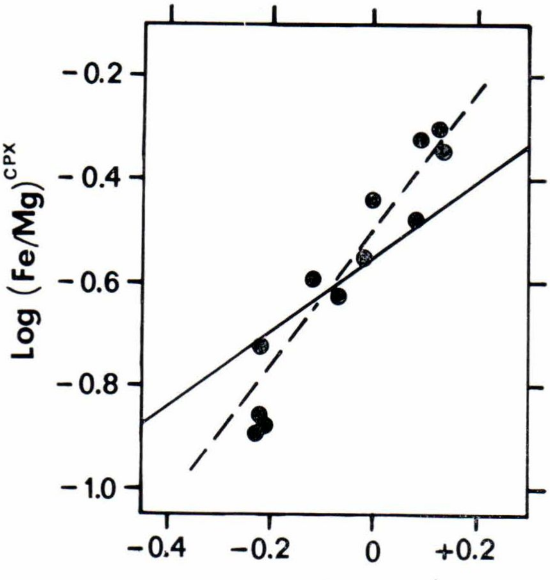

Fig. 9. Log (Fe/Mg) in clinopyroxene plotted against log (Fe/Mg) in liquid. Solid line indicates equilibrium in Duke's (1976) experiments, dashed line in this study.

Powell and Powell (1974) formulated a geothermometer based on a calculated temperature dependence on the distribution of

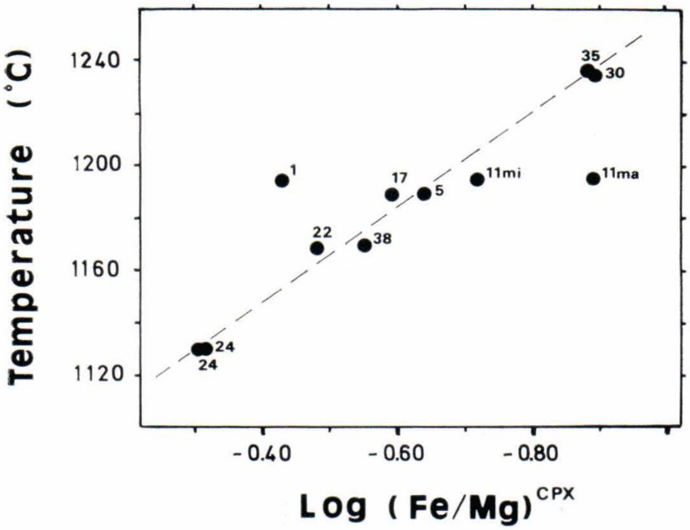

Fig. 10. Log (Fe/Mg) in clinopyroxene plotted against calculated equilibrium temperature (Table 3). Numbers refer to the samples (Mäkipää 1978).

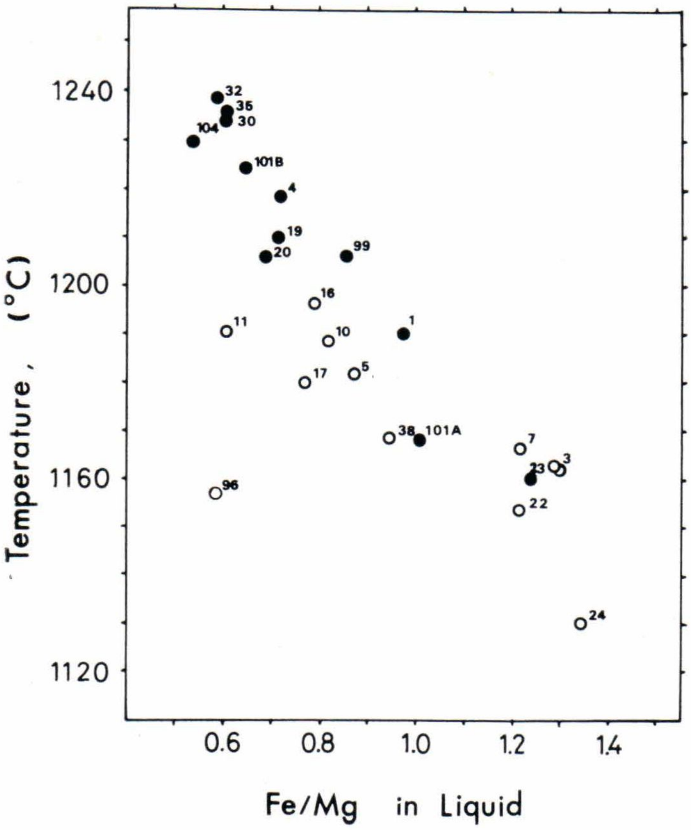

Fig. 11. The Fe/Mg in liquid plotted against calculated equilibrium temperature (Table 3). ● = olivine normative tholeiite ○ = quartz normative tholeiite. Numbers refer to the samples (Mäkipää 1978).

iron and magnesium between olivine and calcic pyroxene. Their model requires that the pressure is known which sets a limit to its use in this study. Wood (1976) concluded that the Powell and Powell geothermometer is not applicable in its present form, because it is independent of olivine and clinopyroxene compositions but depends in fact only on the aluminium content in clinopyroxene.

All other clinopyroxene geothermometers are inapplicable in the present study because they require garnet or a spinel phase to be present and olivine and plagioclase absent.

Discussion

Mineral equilibrium

In the original hyaloclastites the glass phase as well as the phenocrysts were found to be homogenous both in major and trace elements (Mäkipää 1978). Using various equilibrium tests all microphenocrysts are in equilibrium, but some macrophenocrysts are clearly out of equilibrium.

The most successful test for olivine equilibrium is the distribution of Mg and Fe between crystal and liquid. The role of ferric iron in liquid must be evaluated before attempting the distribution coefficient K_D to natural rocks. The average K_D (0.299) agrees well with the Roeder and Emslie value of $K_D=0.30$.

Drake (1972, 1975) suggested the use of major element distribution between plagioclase and liquid versus temperature for an equilibrium test. Using the present experimental results for Icelandic tholeiites the sodium distribution is the most successful test for equilibrium.

The clinopyroxene equilibrium test also is complicated because it depends on major element composition, pressure and temperature. However, the most successful test for clinopyroxene equilibrium is the distribution of Fe and Mg between equilibrium olivines and clinopyroxene.

Geothermometers

The crystallization temperature or the temperature of the magma on eruption can be calculated from the mineral-liquid analyses of the hyaloclastites. The calculated temperatures here using the various methods range from 1130 to 1238°C which are within the crystallization range of basalt measured in experiments of several authors.

The most successful of these geothermometers is the olivine-liquid combination (Roeder and Emslie 1970). Roeder (1974) modified his earlier results and the temperature can be calculated from MgO, FeO and MnO distributions.

The MgO distribution is, however, most useful, because the temperature derived from the FeO distribution is dependent on the oxidation state of the magma which is uncertain and to derive temperature from the MnO distribution special determinations are needed.

The plagioclase temperature estimates are more complicated because the elemental distribution is affected by water pressure. Kudo and Weill (1970) formulated a geothermometer which Mathez (1973) modified. The use of the Mathez modification gives results which are in close agreement with experimental data and calculated olivine temperatures. It is noticeable that using Mathez modification the calculated temperatures have a maximum at $P_{H_2O}=0.5$ kb and then decrease again. Fig. 12 shows schematically the rising water pressure influence on the calculated temperatures.

The odd part about this diagram is the maximum temperature. This might be due to the incorrect assumption by Mathez (1973)

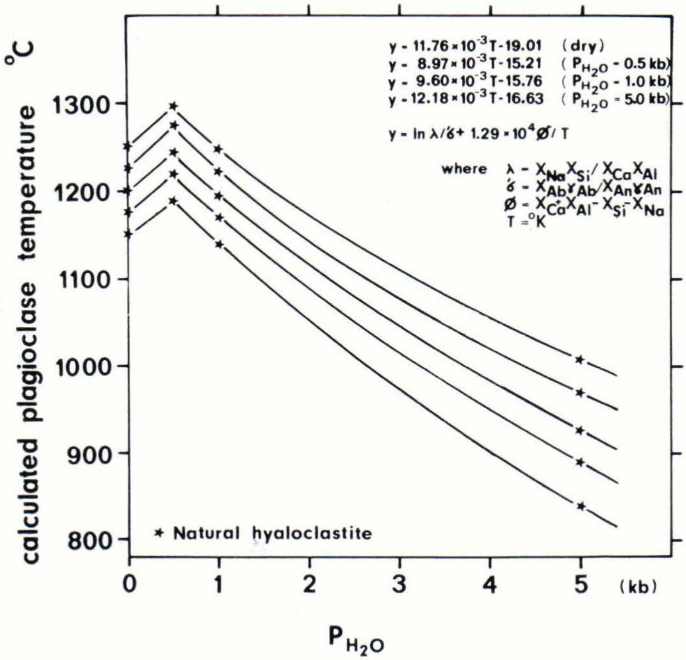

Fig. 12. Effect of water pressure on the calculated plagioclase temperatures. Equations: (dry) — Mathez 1973 (Eq. 7a), (0.5kb) — Mathez 1973 (Eq. 7b), (1.0kb) — Mathez 1973 (Eq. 7c), (5.0kb) — Kudo and Weill 1970.

that neither the temperature nor water pressure significantly affect γ_{Ab}/γ_{An} or else that the effects of these variables oppose each other.

The role of the first crystallization phase

The geothermometers available give equilibrium temperatures which can be substantially lower than the liquidus temperatures. However, in view of the very slight crystallization (usually about 5 %) of the samples the calculated temperatures must be very near the liquidus temperatures. Accepting this there is a complication in these calculations because they depend on the first crystallization phase.

The amount of the crystals present needs not indicate the first phase and the best indicator is the relation of the various crystal phases to each other. Careful observations of the intercrystal relationships showed that either plagioclase or olivine could be the first phase to crystallize. In some cases one phase was closely followed by the other or they may have coprecipitated.

If olivine is the first phase to crystallize from a liquid then the calculated olivine temperatures are liquidus temperatures. This, however, leads to Ca, Na and Al increase in the liquid and the plagioclase temperatures derived are too high. If plagioclase crystallizes first then both Mg and Fe in the liquid will increase. This increase depends on the liquid composition and how much plagioclase crystallizes *i.e.* how far the composition is from the contecticum. Therefore the early crystallization of plagioclase will increase the apparent temperature of the crystallization and it will not affect the composition of the crystallizing phases.

However this increase is not very marked in the present study, because of the slight crystallization. With solidification of 20 % the temperature difference using the FeO^1 — MgO^1 temperatures (Fig. 2) is about 60°C and

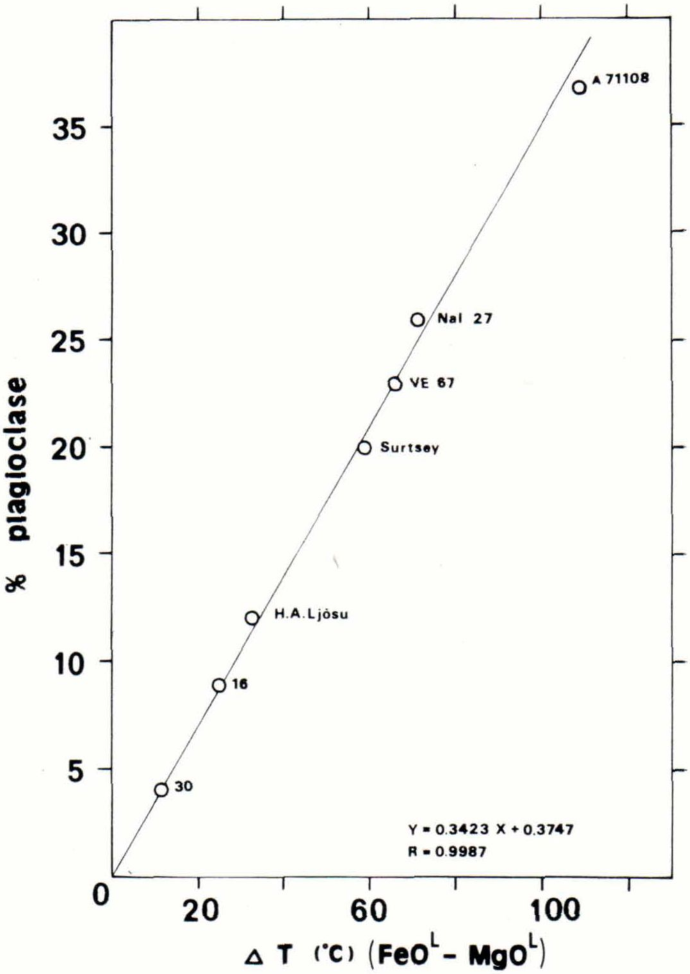

Fig. 13. The change of the measured FeO^l—MgO^l temperature (Table 3) if plagioclase is the first crystallization phase (% by volume). A 71108 — Lava from Drekagil, Dyngjufjöll. Nal 27 — Pillow lava from Leirhafnarfjall, Melrakksletta. VE 67 — Lava from Helgafell, Westman Islands. Surtsey — The first lava in the Surtsey eruption (1963—1967). H. A. Ljosu — Lava near Ljosaskrida, Snæfellsnes. 16 — Vifilsfell (RE-16; Mäkipää 1978). 30 — Hestfjall (HE-30; Mäkipää 1978). Solid line is the best fitting by method of least squares. R = correlation coefficient.

increases regularly with increasing solidification (Fig. 13). In some samples used it is estimated that less than 5 % of plagioclase crystallized before olivine started to crystallize. This means that the maximum temperature difference for these samples would be about 10—20°C.

The Ol-Di-Pl diagram (Fig. 14) shows the possible first crystallization phase in the individual samples. Shibata (1976) divided the Ol-Di-Pl diagram to two major areas, olivine and plagioclase fields. Shibata's division line goes very near that dashed line which makes the difference between plagioclase and plagioclase + olivine fields in the present study. The division between olivine and plagioclase + olivine fields is shown.

Model of the fractional crystallization

As mentioned earlier the calculated temperatures must be very near the liquidus temperatures of these magmas. Therefore it is of particular interest to compare these 'liquidus' temperatures with the simple fractional crystallization curve measured in Hawaiian basalts (Yoder and Tilley 1962). On the A'F'M diagram (Fig. 15) the present data

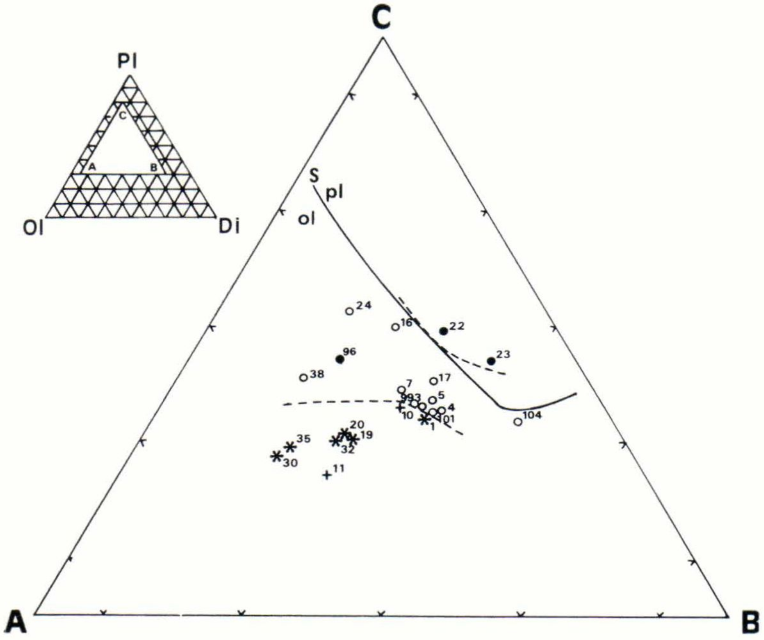

Fig. 14. Plot of the analyses (Mäkipää 1978. Table 1) on the Di-Ol-Pl diagram in molecular proportions. Di = Ca(Mg, Fe)Si_2O_6; Ol = $(Mg, Fe)_2SiO_4$; Pl = $CaAl_2Si_2O_8 + NaAlSi_3O_8$. The first phase to crystallize from the basaltic melt is: ✱+ — olivine ○ — plagioclase+ olivine ● — plagioclase. Solid line (S) separates the plagioclase field (pl) and olivine field (ol) in Shibata's (1976) investigation. Dashed lines separate the phase fields in this study. Numbers refer to the samples (Mäkipää 1978).

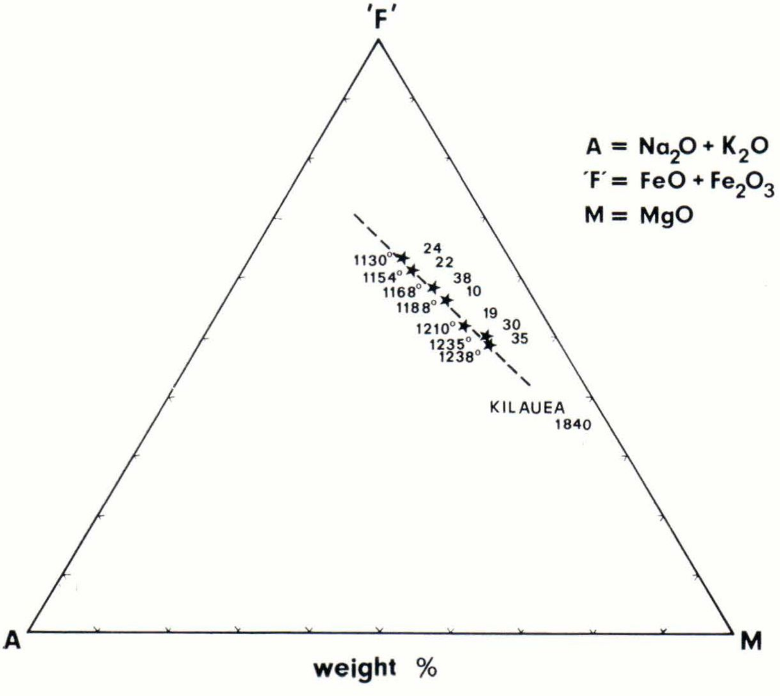

Fig. 15. A'F'M plot of some hyaloclastites with their »silicate liquidus temperatures». Dashed line is the trend of the 1840 flow of Kilauea (Yoder and Tilley 1962, Fig. 8). Numbers refer to the samples (Mäkipää 1978).

shows a trend which is identical with the line formed by the simple fractional crystallization in Hawaiian basalts. On the basis of this diagram the calculated temperatures are in excellent agreement with the experimental data of Yoder and Tilley (1962).

The temperature — $FeO^t/(FeO^t+MgO)$ relation has been shown to be linear for Hawaiian basalts (Tilley *et al.* 1964). As seen in Fig. 16 all the calculated temperatures are higher than those measured experimentally by Tilley *et al.* (1964). This difference (average 18°C) is most likely due to different composition and oxidation state in Icelandic basalts as well as the difference in experimental procedures. Therefore it is interesting to note that those Icelandic basalts (Eldgjá lava) used in Tilley's experiments fall exactly on the line presented here for Icelandic hyaloclastites.

If we compare the present experimentally determined liquidus temperatures (symbol + in Fig. 16) and calculated hyaloclastite temperatures the agreement is excellent.

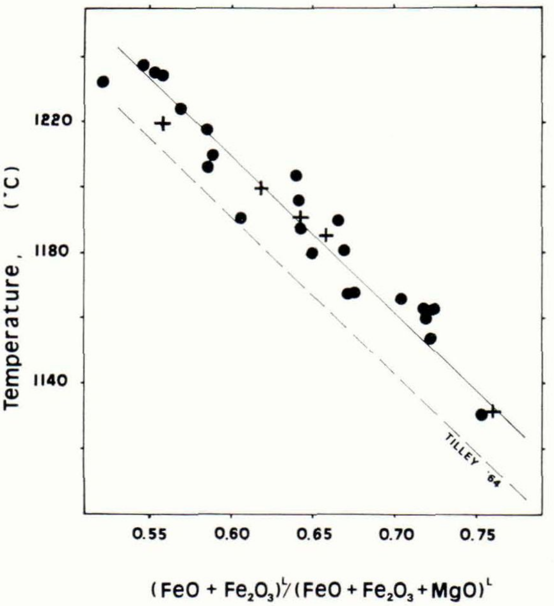

Fig. 16. Plot correlating »liquidus temperatures» with iron enrichment in hyaloclastites. Dashed line drawn after Tilley et al. (1964). ● = hyaloclastite, + = present experiment data. Solid line is the best fitting by method of least squares to hyaloclastite data only.

Geobarometers

The derived plagioclase temperatures are found to vary with water pressures. This offers a possibility to estimate the prevailing water pressure during the crystallization.

Before such estimates can be derived some adjustments must be done. From the Fig. 5 and Table 4 it emerges that samples TH-3, TH-4, RE-11, KE-24 and TJ-104 are slightly out of equilibrium. If the water pressure is derived then it must be done on the basis of equilibrium crystals. To reach the equilibrium the composition of these plagioclases must be changed. This means that the calculated temperature in the sample TH-3 rises about 30—40°C The corresponding value for KE-24 is about 20—30°C. Contrary to the above the temperatures are lower by 10—20°C, 40—50°C and 20—30°C in RE-11, TH-4 and TJ 104, respectively.

In Fig. 17 the calculated temperatures are compared on the basis of different water pressures using temperatures derived from equilibrium olivines and plagioclases. In an earlier paper (Mäkipää 1978) it was concluded on the basis of CMAS- and Ab-An-Di-Fo systems that individual samples represent different water pressures (about 0, 1 and 2 kb). The agreement with the present data is good.

The temperatures calculated for the present 1 atm pressure experiments agree well with the Mathez (1973) 0 kb temperature.

The experimental results show that the fO_2 affects the coexisting phases. In natural basalts the fO_2 follows the QMF-buffer. This gives a value of log fO_2 at 1200°C of about —8.3. It is well known that the fO_2 affects the

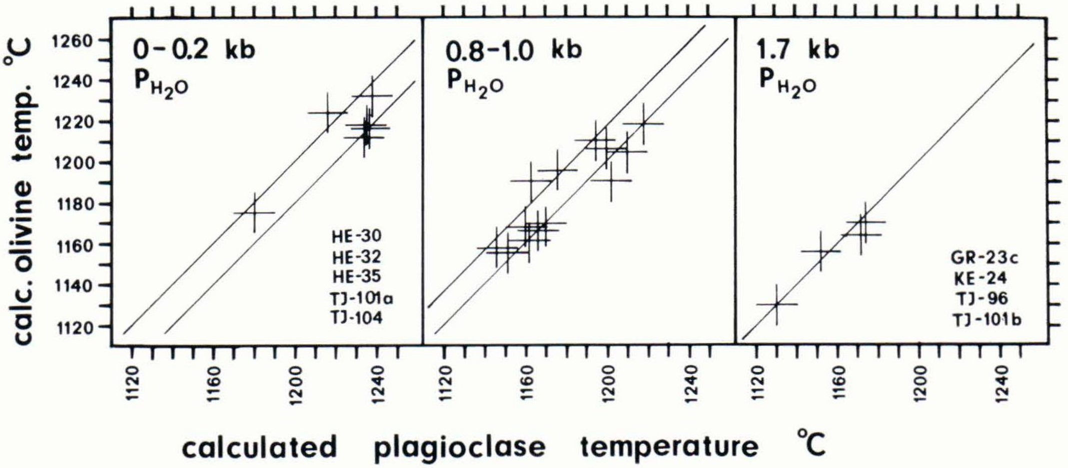

Fig. 17. Comparison of calculated olivine equilibrium temperatures as a function of calculated plagioclase temperatures on the basis of different water pressures. Numbers refer to the samples (Mäkipää 1978).

olivine composition (Roeder and Emslie, 1970). This can easily be seen also in the present experiments where the olivine composition change is only 2 % forsterite although the temperature difference should indicate much greater variation in forsterite content (see Table 1).

Although the fO_2 in some experimental runs (KRA-731) were as low as log $fO_2 =$ —11 this has not seriously affected the calculated plagioclase temperatures. This indicates that water pressure has much greater influence on the calculated equilibrium temperatures than oxygen fugacity. Further experiments will be carried out using direct measurements in furnace to evaluate the effect of the oxygen fugacity. The solubility of water in magmas is known to be dependent on volatile contents of magma and pressure conditions. In a view of the small number of estimates of the water content of the original magma using glass inclusion chemistry (Anderson 1973), it appears that those basalts which have the lowest estimated water pressure also have the lowest original water content.

Accepting the assumption that the calculated temperatures are close to the liquidus temperatures, the use of experimental results by Yoder and Tilley (1962, Fig. 34) in natural olivine tholeiite-water systems, shows that during the crystallization of these hyaloclastites the total pressure was greater than the water pressure.

In conclusion it can be said that a combination of actual melting experiments and the use of published mineral-liquid equilibrium studies can at the present be usefully employed to estimate various properties of the system.

However, there is still some serious discrepancies and the results must be interpreted with great care. However, valid indications about equilibrium, temperature and possibly water pressure can be derived.

Acknowledgements — This study was carried out during the authors fellowship at the Nordic Volcanological Institute, Reykjavik. Drs. Gudmundur E. Sigvaldason, Karl Grönvold and K. Korsman kindly read the manuscript and provided valuable suggestions; this is gratefully acknowledged.

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Manuscript received, May 15, 1978