

clinopyroxenes were based on a series of glasses of variable  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  contents prepared by T. H. GREEN. During analysis of crystals in the high pressure runs, frequent re-analysis of several standards provided a means of monitoring machine drift. The determinations of Fe, Ca and Al (reported as oxides in accordance with normal petrographic practice) are considered accurate to  $\pm 0.2$  weight percent on large homogeneous samples. The limit of detection for Ca and Al with the methods used was 0.1% Ca and 0.2%  $\text{Al}_2\text{O}_3$  respectively. These estimates of accuracy and limits of detection are derived from the reproducibility of results on standards and from the linearity of the calibration curves. Slightly greater uncertainties derive from the nature of the crystals in the high pressure runs — these will be discussed in later sections.

Since the analyses of crystals are only partial analyses, the compositions of pyroxenes, olivines and garnets must be calculated assuming stoichiometry of the crystals and considering the major solid solution end members only i.e. Ca, Mg, Fe silicates or aluminosilicates. Components such as Mn or Ni silicates were neglected. In the clinopyroxenes,  $\text{TiO}_2$  and  $\text{Na}_2\text{O}$  may be present in minor amounts but are not considered in the present study. Olivine was calculated as forsterite, fayalite and larnite solid solution, orthopyroxene and clinopyroxene as enstatite, ferrosilite, wollastonite and  $\text{Al}_2\text{O}_3$  solid solution, and garnet as grossular, almandine and pyrope solid solution. The latter calculation gives a calculated  $\text{Al}_2\text{O}_3$  content which compares quite closely with the measured  $\text{Al}_2\text{O}_3$ , particularly since  $\text{Fe}^{+++}$  is assumed to be zero.

### *e) Changes in Fe Content and Oxidation State*

The use of platinum capsules for the experimental runs means that loss of Fe to solid solution in the platinum and resulting oxidation of remaining FeO, may be of sufficient importance to materially change the chemistry and thus the mineralogy of the basalts. To evaluate this effect, semi-micro chemical analyses for FeO and  $\text{Fe}_2\text{O}_3$  were carried out on 2–8 mg samples from some of the experimental runs. The results of these analyses are given in Table 2. The loss of iron is greater than from the subsolidus runs previously reported (GREEN and RINGWOOD, 1967) and averages about 20–25% of the total iron present. In most cases there is slight reduction of the iron rather than oxidation and this may be attributed to the presence of hydrogen and a reducing environment within the graphite furnace sleeve.

The changes in iron content and oxidation state are not so large as to destroy the basaltic chemistry or even the general character of the normative mineralogy. The normative olivine and hypersthene or nepheline contents of the most altered compositions are calculated in Table 2. The olivine contents in the tholeiitic basalts are considerably decreased and hypersthene is conversely increased. In the alkali olivine basalt compositions both olivine and nepheline decrease but the compositions remain nepheline normative.

The chemical composition of the sample cannot be considered constant for the length of the experimental run and it is uncertain whether observed crystals in glass maintained equilibrium with the changing bulk chemistry throughout the length of the run. Microprobe examination of samples has demonstrated that there may be a range in  $\text{Mg}/\text{Mg} + \text{Fe}$  contents of crystals, controlled by their position in the sample capsule. Crystals which have formed near the edge of the sample are more magnesian than those at the centre — this has been particularly well shown for olivine. In addition some orthopyroxene, olivine and garnet crystals have shown zoning in Fe content — this zoning is the reverse of normal igneous zoning and crystal cores are more iron-rich than crystal edges. This effect is attributed to gradual loss of Fe from the sample with the result that outer zones of crystals either maintain equilibrium with the changing liquid composition while crystal cores do not, or alternatively the outer zones of crystals have grown during the latter part of the experimental runs. Either process would produce the observed zoning of crystals.

A method of evaluating the effect of Fe-loss in relation to the compositions of crystals formed during the experimental runs is to compare the partition coefficients for liquidus crystal-magma equilibria observed in natural basalts with the partition coefficients observed in the experiments. In considering the partition of Mg and Fe between liquidus olivine and liquid, it is convenient to define a partition co-efficient

$$K_{O,L} = \left( \frac{\text{Mg}}{\text{Mg} + \text{Fe}^{++}} \right)_{\text{Olivine}} / \left( \frac{\text{Mg}}{\text{Mg} + \text{Fe}^{++}} \right)_{\text{Liquid}}$$

*Change in oxidation state during experimental runs*

	Conditions			FeO		Fe <sub>2</sub> O <sub>3</sub>	
	Temp. (°C)	Press. (kb)	Time (hrs)	initial	final	initial	final
ite A	1200	9	2	10.07	8.31	1.02	0.21
ite A	1250	9	1	10.07	7.10	1.02	0.94
ite A	1370	9	1	10.07	6.92*	1.02	2.61*
ite A	1375	9	1	10.07	6.42	1.02	1.60
ite A	1440	22.5	1/2	10.07	8.33	1.02	0.88
ite A	1450	22.5	20 min	10.07	8.27	1.02	1.40
ite A	1510	27	20 min	10.07	8.07	1.02	1.11
runs	—	—	—	10.07	7.63+	1.02	1.25+
	1250	18	1	12.42	10.00	1.87	1.14
	1400	18	1	12.42	8.23**	1.87	3.90**
	1440	27	1/2	12.42	7.60	1.87	0.29
(Mix 2)	1310	13.5	1/2	13.06	10.25	0.17	0.70
	1360	18	1	10.64	7.09++	0.42	1.15++
	1300	13.5	50 min	10.64	8.72	0.42	0.82
	1520	18	1/2	8.67	6.48	0.92	0.47

*Compositions after experiments*

7.1% Hypersthene 13.6% Olivine  
 4.6% Hypersthene 16.9% Olivine  
 0.2% Nephelene 19.5% Olivine  
 8.1% Hypersthene 17.5% Olivine

*Initial compositions*

(12.3% Hy, 21.9% Ol)  
 (12.3% Hy, 21.9% Ol)  
 (2.2% Ne, 25.8% Ol)  
 (1.3% Hy, 27.2% Ol)