

*The chemistry and mineralogy of the olivine nodules  
of Calton Hill, Derbyshire.*

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[Read 7 June 1962.]

*Summary.* Chemical analyses, optical data, and cell parameters are given for olivine ( $\text{Fo}_{90.3}$  and  $\text{Fo}_{91.4}$ ), orthopyroxene ( $\text{Ca}_{1.5}\text{Mg}_{89.0}\text{Fe}_{9.5}$  and  $\text{Ca}_{0.6}\text{Mg}_{88.6}\text{Fe}_{10.8}$ ), clinopyroxene ( $\text{Ca}_{39.6}\text{Mg}_{55.6}\text{Fe}_{4.6}$ ), and chromian spinel from olivine nodules from the Carboniferous basalt of Calton Hill, Derbyshire. Chemical and modal analyses of the nodules and of their host rock are also presented. The distribution of Mg and Fe in the coexisting pyroxenes is fairly similar to that observed by Ross, Foster, and Myers (1954) but differs slightly in that the extension of the pyroxene tie-line intersects the Ca-Mg side of the Ca-Mg-Fe triangle. The clinopyroxene is a normal augite rather than the hydrous augite previously reported (Tomkeieff, 1928). The high chromium content of the spinel and clinopyroxene contrasts with the low value for this element in the host rock, suggesting that these minerals are not differentiated from the basaltic magma: the nodules are considered to represent fragments from a deep-seated peridotite.

THE working quarry in the volcanic complex of Calton Hill, Derbyshire, provides exposures of fresh basaltic rocks containing relatively abundant olivine nodules. These nodules were described by Arnold-Bemrose (1910) who concluded that they are segregations from the magma rather than enclosures of older rocks. Later Tomkeieff (1928) studied the volcanic complex as a whole and dealt briefly with the mineralogy of the nodules. He separated and analysed their olivine and so-called hydrous augite, the latter having a specific gravity (2.937) and refractive indices (1.629–1.652) abnormally low for a pyroxene. The analysis of the hydrous augite reports 8.50 %  $\text{H}_2\text{O}$ , which Tomkeieff considered was not attributable to alteration due to weathering but formed an integral part of the molecule. He believed that two kinds of augite exist in the olivine nodules, a normal type and a hydrous type, and that they are possibly members of a continuous series of pyroxenes. Petrogenetically Tomkeieff concluded that the magnesium-rich nature of the nodules, together with their angular character and resorption borders, suggested that they are fragments of a pre-existing peridotite formed under plutonic conditions.

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The aim of the present work was to investigate in detail the chemistry and mineralogy of these nodules, as well as of the basaltic host rocks, to provide more evidence as to the origin of the nodules. It was also felt that the so-called 'hydrous augite' earlier reported as a constituent mineral of these olivine nodules should be re-examined.

Olivine nodules have been reported from many localities of the world: to their study, Ross, Foster, and Myers (1954) have contributed much. After discussing earlier works by Zirkel (1904), Heritsch (1908), Ernst (1936), Turner (1942), and others, and after reviewing host rocks relative to the nodules, Ross, Foster, and Myers concluded that in all occurrences olivine nodules contain the same four minerals: olivine, orthopyroxene, clinopyroxene, and chromian spinel. The relatively large size of the individual mineral grains and the high content of Cr in the spinels and clinopyroxenes seem to be an improbable concentration from a basaltic magma. The structure of the nodules is considered to indicate that they have been subjected to orogenic stress. In view of this, these authors believe that the most probable origin of these nodules is that they are derived from the peridotite zone of the earth's crust and that most of them at least came directly from that zone.

Brothers (1960), however, investigating the mineralogy and the fabric of olivine nodules in a volcanic neck at Kirikiripu, New Zealand, suggested that the nodules are xenoliths formed during the early stages in the magmatic history of the enclosing basalt, probably by continued gravitative sinking and consequent accumulation of successive mineral phases.

#### *Field occurrence and petrography.*

*The olivine nodules* are randomly distributed throughout the basaltic host rock in oval and rounded shapes. They are green in colour and have a medium to coarsely granular texture. The size of the nodules varies considerably, with an average of 1-1½ in. in diameter. They are quite fresh and have sharp boundaries against the enclosing basalt.

In thin section the nodules are seen to consist of four minerals: olivine, orthopyroxene, clinopyroxene, and spinel; there is a considerable range in the proportions of these minerals; this is shown in the modal analyses for seven sections, table I. Olivine is the most dominant mineral, with some grains undergoing slight serpentinization. In some grains iron ore is found as inclusions. Many of the grains show the twinning described and figured by Arnold-Bemrose, but it is the simple and not the multiple twinning. Some of the crystals are surrounded by

TABLE I. Modal analyses of olivine nodules and an average modal analysis of basaltic host rocks (vol. %).

<i>Olivine nodules.</i>										
Olivine	...	...	...	70.0	58.1	74.2	64.7	62.7	81.4	84.3
Orthopyroxene	...	...	...	15.7	18.6	7.6	18.4	17.6	9.9	8.6
Clinopyroxene	...	...	...	9.4	17.4	10.0	13.4	17.0	4.9	6.5
Spinel	...	...	...	3.3	—	3.8	1.4	0.6	0.5	0.5
Iron ore	...	...	...	1.7	5.8	4.4	2.1	2.2	3.3	0.2

<i>Host rock.</i>				
Phenocrysts:		Groundmass:		
Augite	6.1	Plagioclase (An <sub>64</sub> )	63.2	
Olivine	6.1	Olivine	} 16.6	
Chlorite	2.1	Pyroxene		
Analcime	2.1	Magnetite	2.9	
		Accessories	0.9	

orthopyroxene grains and have convex borders towards them, which suggests that olivine was the first mineral to crystallize. In one section magmatic reaction is well developed along the margins of olivine and the invariable product is an interstitial fine-grained aggregate of clinopyroxene. The orthopyroxene is almost colourless, with high relief and distinct cleavage. The clinopyroxene is faintly green and non-pleochroic with an average extinction angle of 45°. Spinel is sparse, ranging in different sections from almost none to 3.8 %; it is brown in colour and isotropic.

The basaltic host rocks are fine-grained in texture, greyish black, and seem to be quite unaltered and compact. They appear to be invading the lava, overlying the tuffs, and breaking off great masses of the lava. They are characterized by the presence of the relatively abundant olivine nodules and small infillings of dark green chlorite and pinkish white analcime. In thin section they consist of olivine and augite phenocrysts embedded in a groundmass of feldspar laths, and an aggregate of idiomorphic augite, magnetite, and traces of limonite. The olivine of the phenocrysts occurs as rounded and irregular grains, sometimes altered to serpentine and iron ore along the cracks. Many of the grains have a reaction border of augite. The latter also occurs as aggregates, sometimes associated with large grains of analcime. The chlorite occurs as aggregates of fibrous spherulites (cf. Tomkeieff, 1926), while the analcime exists as spherules and as irregular turbid patches having a greyish appearance. The outer part of these crystals is bordered by microlites of feldspar and augite. The plagioclase in the groundmass has the composition An<sub>64</sub> (labradorite).

On the whole the basalt represents a quickly chilled liquid while the olivine nodules are products of slow crystallization.

*The chemistry of olivine nodules and host rocks.*

Analyses and C.I.P.W. norms of these rocks are given in table II.

TABLE II. Chemical analyses and C.I.P.W. norms of olivine nodules and their host rocks. (Norms of nos. 3 and 5 recalculated.)

	1.	2.	3.	4.	5.	
SiO <sub>2</sub> ...	45.14	43.94	41.72	43.82	45.52	
TiO <sub>2</sub> ...	1.96	2.03	2.73	tr.	abs.	
Al <sub>2</sub> O <sub>3</sub> ...	16.54	15.44	13.04	2.26	7.50	
Fe <sub>2</sub> O <sub>3</sub> ...	2.58	3.90	2.68	3.15	—	
Cr <sub>2</sub> O <sub>3</sub> ...	0.05	—	0.06	0.30	0.17	
FeO ...	9.13	8.25	10.00	5.85	7.92	
MnO ...	0.12	tr.	0.18	0.11	0.37	
MgO ...	7.68	9.64	9.00	39.83	33.62	
CaO ...	9.29	10.56	10.82	2.44	3.85	
Na <sub>2</sub> O ...	2.72	2.81	3.74	0.22	tr.	
K <sub>2</sub> O ...	1.16	1.34	0.88	tr.	tr.	
P <sub>2</sub> O <sub>5</sub> ...	0.22	—	0.58	0.03	—	
H <sub>2</sub> O+	2.81	2.33	0.92	1.17	1.45	
H <sub>2</sub> O-	0.84	0.19	0.27	0.56	0.11	
Total ...	100.24	100.43	100.02	100.06	100.51	
D ...	2.907	2.968	—	3.188	3.277	
<i>C.I.P.W. norms.</i>						
or ...	6.84	7.95	5.23	—	—	
ab ...	20.59	9.72	23.06	1.83	—	
an ...	29.47	25.52	17.01	5.20	19.13	
ne ...	1.31	7.60	3.75	—	—	
di {	wo ...	6.37	11.23	5.37	2.81	—
	en ...	3.82	7.65	3.31	2.28	—
	fs ...	2.22	2.71	1.76	0.20	—
ol {	fo ...	10.72	11.58	13.31	53.49	39.35
	fa ...	7.22	4.52	7.83	5.14	9.59
hy {	en ...	—	—	—	20.52	27.50
	fs ...	—	—	—	1.78	2.65
mt ...	3.74	5.66	3.90	4.57	—	
cm ...	0.07	—	0.09	0.45	0.25	
il ...	3.72	3.86	5.18	—	—	
ap ...	0.50	—	1.38	0.07	—	

1. Analcime and chlorite basalt, Calton Hill, Derbyshire. Anal.: S. el D. Hamad.

2. Analcime-basalt, Calton Hill, Derbyshire (Tomkeieff, 1928).

3. Olivine-basalt, Finkenbergl, Siebengebirge, Germany (Frechen, 1948). Analysis includes 3.19 % CO<sub>2</sub>, 0.11 % Cl, 0.07 % BaO, 0.03 % ZrO<sub>2</sub>, and norm contains 0.18 % halite, 7.25 % calcite, and 0.04 % zircon.

4. Olivine nodule, Calton Hill, Derbyshire. Anal.: S. el D. Hamad. Analysis includes 0.32 % NiO.

5. Olivine nodule, Calton Hill, Derbyshire (Tomkeieff, 1928). Norm includes 0.48% corundum.

The volume percentage modes are listed in table I. Modal analyses were carried out by the point-counting method, 100–400 points being determined for the nodules whereas 1600 points were determined on the basaltic host rock.

The basalt (1) is relatively rich in alumina and CaO and poor in magnesia, bringing in large amounts of plagioclase in the norm. The nodule (4) is predominantly magnesia-rich and the low amount of  $\text{Al}_2\text{O}_3$  and CaO it contains is reflected in the low amount of clinopyroxene present. The ratio of total iron relative to magnesium in the basalt is approximately 0.6 compared with about 0.2 in the nodule. Although the host rock contains appreciable amounts of titania and alkalis, the nodules contain only traces of these oxides. This is reflected in the norm and mode by the presence of ilmenite and analcime. The presence of 0.30 %  $\text{Cr}_2\text{O}_3$  in the nodule compared with 0.05 % in the host rock indicates that the basaltic magma does not contain enough chromium to produce those minerals of the nodules that contain high percentages of that element. This is against the hypothesis that the nodules are magmatic segregations from the basalt.

The relatively high water content of the basalt may be attributed to the presence of chlorite whereas the small amount present in the nodules is due to the presence of traces of limonite adhering to the constituent minerals. Analysis (5) of the nodule given by Tomkeieff is relatively high in alumina and CaO, and low in magnesia.

#### *Mineralogy of the nodules.*

*Methods.* Olivine, orthopyroxene, clinopyroxene, and spinel have been separated from the olivine nodules of Calton Hill with the aid of an isodynamic magnetic separator followed by treatment with heavy liquids. The final purity of the minerals was 99.8 % or better. Refractive indices were measured in sodium light with an estimated accuracy of  $\pm 0.001$  for the three silicate minerals and  $\pm 0.002$  for spinel. Measurements of  $2V$  values were made on the universal stage on mounted grains and by direct rotation from one optic axis to another. The accuracy was in the range  $\frac{1}{4}^\circ$  to  $\frac{1}{2}^\circ$ . In the chemical analyses both classical and rapid methods were used. Special care was taken over the analysis of spinel and its parent rock,  $\text{Na}_2\text{O}_2$  being used for the decomposition of the rock (Rafter, 1950) after the sample was ground to an exceedingly fine powder. Spinel was brought into solution by fusing with potassium pyrosulphate, silica being determined separately by rapid methods. For the estimation of FeO in these samples the method of Shein (1937)

was employed. The samples were left to dissolve in the  $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4$  acid mixture for 20 minutes at  $360^\circ\text{-}380^\circ\text{C}$ . with frequent stirring. NiO and  $\text{Cr}_2\text{O}_3$  were determined colorimetrically (Sandell, 1950): NiO by the wine-red nickelic dimethylglyoxime complex and  $\text{Cr}_2\text{O}_3$  by the red-violet Cr-diphenylcarbazide complex. Co, Mo, and V were determined spectrographically.

The cell-sizes of the minerals were measured using a Philips X-ray diffractometer with Ni-filtered Cu- $K\alpha$  radiation for olivine, and Fe-filtered Co- $K\alpha$  radiation for spinel and the pyroxenes. The accuracy is estimated to be  $\pm 0.010\text{ \AA}$ .

*The olivines.* Chemical analyses, physical properties, and formulae of two samples are given in table III (6 and 7). They are highly magnesian, with 90-91 % of the  $\text{Mg}_2\text{SiO}_4$  molecule, and lie in the forsterite region. The compositions were also determined by using the X-ray determinative curves of Yoder and Sahama (1957), using the reflection 130, and of Jackson (1960), using the distance between the olivine 062 peak and LiF 220 peak. Both methods were found to be satisfactory and the compositions of the olivines vary less than 1 % from those obtained by chemical analysis. The intensity of the 062 reflection is less than that of 130 and this can be subject to small random and measurable error.

The olivine of Calton Hill, unlike those reported by Ross, Foster, and Myers, contains minor amounts of  $\text{Fe}_2\text{O}_3$ . This should not be attributed to impurities but is probably an oxidation product of the mineral during its growth. It is conceivable that this alteration product exists in the mineral on a submicroscopic scale. The olivine analysis (8) given by Tomkeieff has a remarkable high CaO content (4.70 %). Deer and Wager (1939) reported analyses of olivines that, although crystallized from a magma comparatively rich in CaO, remained almost pure members of the simple solid solution series  $\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ , being particularly free from  $\text{Ca}_2\text{SiO}_4$ . This suggests that, even if the olivines from the nodules of Calton Hill were differentiates of basaltic magma, the presence of the high CaO content reported by Tomkeieff would not be justified.

*The pyroxenes.* The analyses, properties, and structural formulae of the ortho- and clinopyroxenes are given in tables IV and V respectively. The formulae were calculated on the basis of 6 oxygens to the unit cell and the Ca:Mg:Fe ratios were recalculated to 100 %,  $\text{Fe}^{3+}$  and Mn being added to  $\text{Fe}^{2+}$ . The presence of the  $\text{CaSiO}_3$  molecule in the orthopyroxenes represents the solubility of the diopsidic molecule in

TABLE III. Chemical analyses, compositions, and physical properties of olivines from olivine nodules.

	6.	7.	8.	9.	10.				
SiO <sub>2</sub> ...	40.57	40.86	38.58	40.80	40.87				
TiO <sub>2</sub> ...	tr.	n.d.	nil	0.04	0.02				
Al <sub>2</sub> O <sub>3</sub> ...	0.00	0.00	nil	0.00	0.07		6A.	7A.	
Fe <sub>2</sub> O <sub>3</sub> ...	0.92	0.12	—	0.00	0.00	Si	0.99	0.99	
Cr <sub>2</sub> O <sub>3</sub> ...	tr.	tr.	n.d.	0.04	0.02				
FeO ...	8.72	8.41	14.00	8.61	8.72	Fe <sup>3+</sup>	0.017	0.002	} 2.00
MnO ...	0.03	0.00	—	0.13	0.15	Mg	1.799	1.823	
NiO ...	0.27	0.30	n.d.	0.38	0.34	Fe <sup>2+</sup>	0.177	0.171	
MgO ...	49.29	49.91	42.93	49.77	49.78	Ni	0.005	0.006	
CaO ...	0.00	0.00	4.70	0.20	0.07	Mn	—	—	
Na <sub>2</sub> O ...	0.05	0.14	—	0.00	0.01				
K <sub>2</sub> O ...	0.00	0.04	—	0.00	0.00				
P <sub>2</sub> O <sub>5</sub> ...	0.03	0.01	—	n.d.	n.d.				
H <sub>2</sub> O <sup>+</sup> ...	0.07	0.00	—						
				0.29	0.05				
H <sub>2</sub> O — ...	0.12	0.05	—						
Total ...	100.07	99.84	100.21	100.28	100.11				
α ...	1.658	1.659	—	—	—				
β ...	1.678	1.675	—	—	—				
γ ...	1.682	1.681	—	—	—				
2V <sub>γ</sub> ...	87°	86°	—	—	—				
a(Å) ...	4.749	4.743	—	—	—				
b(Å) ...	10.201	10.227	—	—	—				
c(Å) ...	5.990	5.993	—	—	—				
d <sub>130</sub> (Å) ...	2.7713	2.7708	—	—	—				
D ...	3.376	3.363	3.370	3.338	3.333				
% com- position (Fo)	90.3	91.4	84.6	90.7	90.6				

6 and 7. Olivine from olivine nodules, Calton Hill, Derbyshire. Anal.: S. el D. Hamad. (Also Co 98, 102; Mo 10, 226; V 148, 220 p.p.m. respectively for analyses 6 and 7.)

6A and 7A. Structural formulae of 6 and 7, numbers of ions on the basis of 4 oxygens.

8. Olivine from olivine nodules, Calton Hill, Derbyshire (Tomkeieff, 1928).

9. Olivine from olivine nodules, Camargo, Chihuahua, Mexico (Ross, Foster, and Myers, 1954). Analysis includes 0.02 % CoO.

10. Olivine from olivine nodules, Salt Lake Crater, Oahu, Hawaii (Ross, Foster, and Myers, 1954). Analysis includes 0.013 % CoO.

Mg-rich orthopyroxenes; with slow cooling this diopsidic material exsolves and forms lamellae.

The Al content in both ortho- and clinopyroxene is found to be quite sufficient to make the Z group 2.00 without the aid of Ti, the excess Al being added to the XY group. The amount of Al substituting for Si in the tetrahedral group in the clinopyroxene of Calton Hill is higher

TABLE IV. Chemical analyses, compositions, and physical properties of orthopyroxenes from olivine nodules.

	11.	12.	13.	14.		11A.	12A.
SiO <sub>2</sub> ...	55.24	55.04	55.04	55.38			
TiO <sub>2</sub> ...	tr.	tr.	0.10	0.05			
Al <sub>2</sub> O <sub>3</sub> ...	3.07	3.24	3.91	2.97	Si	1.909	1.901
Fe <sub>2</sub> O <sub>3</sub> ...	0.88	1.30	0.00	0.00	Al	0.091	0.099
Cr <sub>2</sub> O <sub>3</sub> ...	0.34	0.36	0.34	0.80			
FeO ...	5.59	5.85	5.93	5.66	Al	0.034	0.033
MnO ...	0.11	0.10	0.15	0.12	Fe <sup>3+</sup>	0.023	0.034
NiO ...	0.17	0.14	0.07	0.07	Cr	0.010	0.010
MgO ...	33.55	33.30	33.56	34.19	Fe <sup>2+</sup>	0.161	0.169
CaO ...	0.78	0.39	1.02	0.74	Mn	0.003	0.003
Na <sub>2</sub> O ...	0.15	0.14	0.00	0.06	Ni	0.005	0.004
K <sub>2</sub> O ...	tr.	tr.	0.00	0.00	Mg	1.739	1.723
P <sub>2</sub> O <sub>5</sub> ...	0.03	n.d.	—	—	Ca	0.029	0.015
H <sub>2</sub> O+ ...	nil	nil			Na	0.010	0.010
			0.20	0.14			
H <sub>2</sub> O—...	0.04	0.15					
Total ...	99.95	100.01	100.34	100.18			
α ...	1.666	1.667	—	—			
β ...	1.669	1.671	—	—			
γ ...	1.670	1.673	—	—			
2V <sub>γ</sub> ...	85½°	84°	—	—			
a(Å) ...	18.250	18.255	—	—			
b(Å) ...	8.835	8.821	—	—			
c(Å) ...	5.194	5.192	—	—			
D ...	3.296	3.284	3.304	3.278			
Atomic %							
Ca ...	1.5	0.8	2.0	1.4			
Mg ...	89.0	88.6	89.0	90.0			
Fe ...	9.5	10.6	9.0	8.6			
% Al in Z	4.6	5.0	4.9	4.3			

11 and 12. Orthopyroxenes from olivine nodules, Calton Hill, Derbyshire. Anal.: S. el D. Hamad (also Co 76, 80; Mo 17, 8; V 30, 40 p.p.m. for anal. 11 and 12 respectively).

11A and 12A. Structural formulae of 11 and 12; numbers of ions on the basis of 6 oxygens.

13. Orthopyroxene from olivine nodules, Camargo, Chihuahua, Mexico. (Ross, Foster, and Myers, 1954). Analysis includes 0.02 % V<sub>2</sub>O<sub>5</sub>.

14. Orthopyroxene from olivine nodules, Salt Lake Crater, Oahu, Hawaii (Ross, Foster, and Myers, 1954). Analysis includes 0.005 % CoO.

than that in the clinopyroxenes analysed by Ross, Foster, and Myers. This may well contribute to its high refractive indices as compared with those of the orthopyroxene. The high alumina content also suggests crystallization or recrystallization under a fairly high pressure.

The orthopyroxene lies at the enstatite-bronzite boundary (En<sub>90</sub>). In view of the high content of Al in the tetrahedral position together



TABLE V. Chemical analyses, compositions, and physical properties of clinopyroxenes from olivine nodules.

	15.	16.	17.	18.		
SiO <sub>2</sub>	49.35	52.22	51.78	52.12		
TiO <sub>2</sub>	0.34	n.d.	0.38	0.80		15A.
Al <sub>2</sub> O <sub>3</sub>	4.92	5.59	5.14	4.08	Si	1.795
Fe <sub>2</sub> O <sub>3</sub>	0.77	—	1.75	0.82	Al	0.205
Cr <sub>2</sub> O <sub>3</sub>	1.06	n.d.	0.95	1.44		} 2.00
FeO	2.19	9.50	2.14	2.24	Al	
MnO	0.07	—	0.12	0.09	Ti	0.009
NiO	0.05	n.d.	0.04	0.04	Fe <sup>3+</sup>	0.021
MgO	19.86	20.45	16.04	16.48	Cr	0.030
CaO	19.75	4.29	20.32	19.34	Fe <sup>2+</sup>	0.066
Na <sub>2</sub> O	1.23	—	1.06	2.14	Mn	0.002
K <sub>2</sub> O	nil	—	0.08	0.08	Mg	1.083
P <sub>2</sub> O <sub>5</sub>	n.d.	n.d.	—	—	Ni	0.001
H <sub>2</sub> O+	0.17				Ca	0.770
		8.50	—	—	Na	0.086
H <sub>2</sub> O—	0.08					} 2.07
Total	99.84	100.55	99.84	99.70		
α ...	1.676	—	—	—		
β ...	1.689	—	—	—		
γ ...	1.690	—	—	—		
2V <sub>γ</sub>	58°	—	—	—		
a(Å)	9.743	—	—	—		
b(Å)	8.897	—	—	—		
c(Å)	5.184	—	—	—		
β ...	106°56'	—	—	—		
D ...	3.306	2.937	3.322	3.312		
Atomic %						
Ca ...	39.6	10.7	44.6	43.3		
Mg ...	55.8	70.8	48.8	51.3		
Fe ...	4.6	18.4	6.6	5.3		
% Al in Z	10.3	11.2	5.9	5.0		

15. Clinopyroxene from olivine nodules, Calton Hill, Derbyshire. Anal.: S. el D. Hamad.

15A. Structural formula of 15; number of ions on the basis of 6 oxygens.

16. Hydrous augite from olivine nodules, Calton Hill, Derbyshire (Tomkeieff, 1928).

17. Clinopyroxene from olivine nodules, Camargo, Chihuahua, Mexico (Ross, Foster, and Myers, 1954). Analysis includes 0.04 % V<sub>2</sub>O<sub>5</sub>.

18. Clinopyroxene from olivine nodules, Salt Lake Crater, Oahu, Hawaii (Ross, Foster, and Myers, 1954). Analysis includes 0.03 % V<sub>2</sub>O<sub>5</sub>.

with the substantial amount of Cr<sub>2</sub>O<sub>3</sub>, the clinopyroxene can be referred to as a chromian diopsidic augite.

*Spinel.* Analysis, properties, and structural formula calculated on the basis of four oxygens to the unit cell are given in table VI (19). The presence of a minute amount of Si in the tetrahedral position is not

TABLE VI. Chemical analyses and physical properties of spinels from olivine nodules.

	19.	20.	21.		
SiO <sub>2</sub> ... ..	0.59	0.46	0.44		
TiO <sub>2</sub> ... ..	nil	0.44	2.71		
Al <sub>2</sub> O <sub>3</sub> ... ..	45.45	47.63	41.68	Si	0.016
Fe <sub>2</sub> O <sub>3</sub> ... ..	5.84	2.67	7.96	Al	1.459
Cr <sub>2</sub> O <sub>3</sub> ... ..	16.85	19.24	18.34	Fe <sup>3+</sup>	0.119
FeO ... ..	11.69	9.86	8.64	Cr	0.363
MnO ... ..	0.05	0.15	0.13		
MgO ... ..	19.29	19.22	19.71	Mg	0.789
CaO ... ..	tr.	0.20	0.00	Fe <sup>2+</sup>	0.266
Na <sub>2</sub> O ... ..	0.02	0.00	—	Mn	—
K <sub>2</sub> O ... ..	nil	0.00	—		
H <sub>2</sub> O+ ... ..	—	—	—		
H <sub>2</sub> O— ... ..	0.02	—	—		
Total ... ..	99.80	99.91	99.61		
<i>n</i> ... ..	1.833	—	—		
<i>a</i> (Å) ... ..	8.149	—	—		
<i>D</i> ... ..	3.928	3.850	3.905		

19. Spinel from olivine nodules, Calton Hill, Derbyshire. Anal.: S. el D. Hamad.

19A. Structural formula of 19; number of ions on the basis of 4 oxygens.

20. Spinel from olivine nodules, Camargo, Chihuahua, Mexico (Ross, Foster, and Myers, 1954). Analysis includes 0.04 % V<sub>2</sub>O<sub>5</sub>.

21. Spinel from olivine nodule, Ludlow, California (Ross, Foster, and Myers, 1954).

considered to be an impurity but may be a minor substitution for Al<sup>3+</sup>. Since Cr<sub>2</sub>O<sub>3</sub> is a dominant constituent, the mineral can be referred to as chromian spinel.

Considering the minor constituents NiO, Cr<sub>2</sub>O<sub>3</sub>, and MnO in the silicate minerals, there is a progressive decrease in NiO content from olivine through the orthopyroxene to the chromian clinopyroxene. There is a marked increase in the Cr<sub>2</sub>O<sub>3</sub> content in the same series of minerals but the MnO content is roughly constant throughout.

As regards the ratio of total iron to magnesium in the three silicate minerals, the orthopyroxene is the most iron-rich ferromagnesian silicate, then comes the olivine and lastly the clinopyroxene. This agrees with the postulate of Ramberg and De Vore (1951) that iron usually has a greater affinity to pyroxene than to olivine. Accordingly, the tie-line joining the pair of pyroxenes (fig. 1), when extended, intersects the Ca-Mg side line of the triangular diagram at En<sub>30</sub> Wo<sub>70</sub>. This is in accord with the findings of Hess (1941). However, the tie-lines of pyroxenes analysed by Ross, Foster, and Myers, when extended, intersect the Ca-Fe side line at Fs<sub>2.7</sub>, the clinopyroxenes being unique in

having a higher  $Fe/(Fe+Mg)$  ratio than the associated orthopyroxenes. Muir and Tilley (1958) noted that pyroxenes from volcanic rocks have their clinopyroxenes relatively enriched in iron, a relation corresponding to a non-equilibrium condition, while O'Hara (1960) suggested that differences in the distribution of Ca, Mg, and Fe are probably due in part to variations in the conditions of formation.

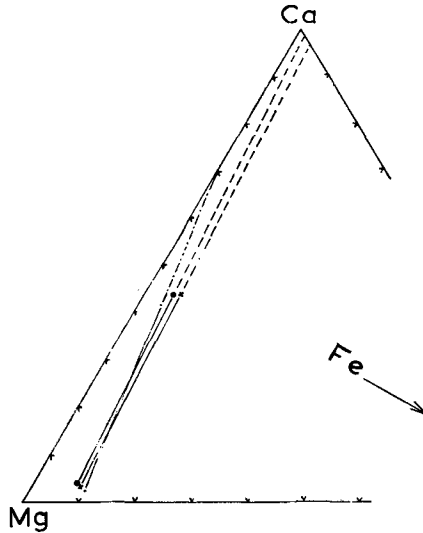


FIG. 1. Tie-lines joining coexisting ortho- and clinopyroxenes from olivine nodules. • Calton Hill, Derbyshire. × Camargo, Chihuahua, Mexico. ● Salt Lake Crater, Oahu, Hawaii.

Brown (1961) demonstrated that in coexisting igneous pyroxene pairs the orthopyroxene is enriched in  $Fe/(Fe+Mg)$  relative to the clinopyroxene, usually causing the tie-line to intersect the Ca-Mg side of the triangular diagram. Ross, Foster, and Myers (1954) claimed that dunites and olivine nodules in basaltic rocks were derived from the same source and had a similar genetic history, i.e. they considered the nodules as igneous rock fragments derived from the peridotite shell of the earth. As Brown (*loc. cit.*) has pointed out, the fact that the tie-lines for the coexisting pyroxenes from these basaltic olivine nodules of Ross, Foster, and Myers intersect the Ca-Fe side of the triangular diagram may provide even stronger evidence against the acceptance of anything like a standard value for igneous pyroxene tie-line intersections. Kretz (1961) has examined the distribution of Mg between coexisting

pyroxenes from a theoretical and thermodynamic aspect and has shown that the distribution coefficient  $K_D$  [ $= X_{Mg}^O(1 - X_{Mg}^C)/(1 - X_{Mg}^O)X_{Mg}^C$ , where  $X_{Mg} = Mg/(Mg + Fe^{2+})$  and  $X^O$  and  $X^C$  refer to ortho- and clinopyroxenes respectively] may differ for igneous and metamorphic assemblages, having typical values of 0.73 for the pyroxenes of the Skaergaard complex and 0.54 for the pyroxenes of the Madras charnockite series (Howie, 1955). However, the value now obtained for the pyroxenes from the Calton Hill nodules is 0.64, i.e. between the values for igneous and metamorphic pyroxenes. On the other hand  $K_D$  values for the pyroxenes from the nodules examined by Ross, Foster, and Myers are 0.76 for those from Mexico and 0.82 for the nodules from Hawaii, both values being higher than the average for igneous pyroxenes. These differences of  $K_D$  values may be due to compositional variations of elements other than Mg and Fe, and although Kretz had suggested that these variations are not great enough to change the distribution coefficient, De Vore (1957) concluded that the distribution of Mg and  $Fe^{2+}$  between coexisting pyroxenes is strongly controlled by the relative distribution of Al, Ti, and  $Fe^{3+}$  in sixfold co-ordination and by the level of influence these cations have on the octahedral position. In support of this hypothesis it should be noted that the clinopyroxenes from the nodules reported by Ross, Foster, and Myers are relatively rich in Al,  $Fe^{3+}$ , and Ti in the octahedral position. If, on the other hand, Kretz's hypothesis is considered, then it is possible that the variation in  $K_D$  is due to differences in pressure and that the pyroxenes from the nodules of Calton Hill reached equilibrium at greater depth.

On the whole, the writer considers that the variations of  $K_D$  for pyroxene pairs derived from different rocks are not only dependent on pressure and temperature but are also dependent on the compositional changes that take place in the minerals. The point where a tie-line intersects the left- or right-hand side of the diagram cannot be expected to be a measure of equilibrium conditions.

#### *Petrogenesis and conclusions.*

In order to reach a conclusion on the origin of the olivine nodules of Calton Hill, various features must be considered. First, the coarse-grained nodules, like many other nodules found throughout the world, contain the same four minerals: olivine, orthopyroxene, clinopyroxene, and spinel, while the host rock differs greatly in composition. The resorption reaction, the angular character, and the serpentinization of olivine together with the exsolution lamellae of the orthopyroxene

suggest a deep-seated crystallization-differentiation and do not indicate that the nodules are segregations from basaltic magma.

The minerals of the nodules are rich in magnesia, which gradually decreases in the order olivine, orthopyroxene, clinopyroxene. This feature is in line with the paragenetic sequence of crystallization differentiation in which the olivine was the first mineral to form. The distribution of Mg and Fe in the coexisting pair of pyroxenes differs from those of other nodules. This was explained previously by the fact that each mineral assemblage was, presumably, formed under different equilibrium conditions, e.g. temperature or pressure, or both. The presence of elements other than Ca, Mg, and Fe also affects the distribution coefficients of the pyroxenes.

Analysis of the clinopyroxene (15), table V, shows that it does not contain any appreciable amount of water and the mineral is a normal chromian diopsidic augite. This is in contrast to the earlier report that the clinopyroxene from the nodules of Calton Hill is abnormal in containing a large amount of water (16), table V.

The spinel appears to be of early crystallization since it is intergrown with the silicate minerals. The substantial amount of chromium found in the nodules suggests that Cr tended to be eliminated early both by the formation of chromian spinel and by its inclusion as a component of the clinopyroxene. Bowen (1928) suggested that spinel may be formed by the reaction of liquid with olivine and anorthite. He stated that a reverse reaction may take place with falling temperature, giving locally basic plagioclase with olivine and chromium-rich spinel, and that with further opportunity for reaction, the chromian spinel may disappear by incorporation in a notably chromian clinopyroxene. Since plagioclase is not found as a constituent mineral of the nodules, it is unlikely that the spinel is a product of the reaction of olivine and anorthite. A possible explanation is that the mineral developed as a primary phase during crystallization.

The presence of Cr-rich minerals in the nodules and the absence of  $\text{Cr}_2\text{O}_3$  in the host rock is further evidence that the nodules are improbable magmatic segregations from the basalt. It is considered likely that they are fragments of a deep-seated peridotite.

Various mechanisms by which olivine nodules reached the surface have been suggested and the problem arises as to their history after their departure from the peridotite layer. However, since the nodules of Calton Hill are found in an area that had undergone volcanic eruptions, the writer is inclined to accept Tomkeieff's view that they

are fragments from a deep-seated peridotite which were carried to the surface by the basaltic magma.

*Acknowledgements.* The author wishes to thank Dr. R. A. Howie for critically reading the manuscript and for his encouragement and advice during the progress of the research. This work is partly a fulfilment of M.Sc. requirements and the author is indebted to the University of Manchester for providing the facilities for the research and to the Sudan Government for a research studentship. Thanks are also due to The Derbyshire Stone Co. for permission to collect material for study from Calton Hill quarry.

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