

*Two new pyroxenes included in the system clinoenstatite,
clinoferrosilite, diopside, and hedenbergite.*

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TWO monoclinic pyroxenes from the Skaergaard Halvoen intrusion,¹ Kangerdlugssuak, East Greenland, have been separated and analysed. They occur in a strongly differentiated gabbro complex which ranges from a hypersthene-olivine-gabbro at the base to a fayalite-quartz-gabbro of unique composition at the top. The differentiation has proceeded with a steady increase in iron and a corresponding decrease in magnesia, while the other major oxides remain relatively constant throughout. The clinopyroxenes in the lower horizons are in equilibrium with labradorite, normal olivine and hypersthene, and are fairly normal varieties as shown by the following optical properties:—

(1)... α 1.672, β 1.678, γ 1.701, $2V$ 42°, $\gamma:c$ 39°, sp. gr. 3.34.

(2)... α 1.695, β 1.702, γ 1.722, $2V$ 43°, $\gamma:c$ 41°, sp. gr. 3.38.

In ascending to higher horizons both the orthorhombic and monoclinic pyroxenes become progressively richer in the ferrosilite molecule; in the later differentiates hypersthene ceased to form as a separate phase. Analyses and optical properties of two pyroxenes from rocks high in the series where orthorhombic pyroxene is absent are presented here (tables I and II). As will be seen these pyroxenes are low in sesquioxides, and it is possible as a first approximation to regard them as members of the system wollastonite, clinoenstatite, and clinoferrosilite.

Pyroxene I occurs in one of the earlier rocks of the differentiation series which contains no hypersthene. It is titaniferous and is of special interest in that the aluminium is insufficient to bring the value of the

¹ L. R. Wager, Geological investigations in East Greenland, Part I. Meddel. om Grønland, 1934, vol. 105, no. 2, pp. 36-37.

TABLE I. Analyses and optical data¹ of pyroxenes. (Analyst, W. A. Deer.)

	I.	II.		I.	II.
SiO ₂ ...	42.32	42.62	2V (positive)	44°	58°
TiO ₂ ...	4.42	1.69	$\gamma:c$	39°	47°
Al ₂ O ₃ ...	2.25	5.24	Refr. indices	α 1.721	1.743
Fe ₂ O ₃ ...	4.72	3.74		β 1.728	1.751
FeO ...	25.13	31.54		γ 1.749	1.772
MnO ...	0.22	0.78	Pleochroism	α yellow-brown	pale-green
MgO ...	8.33	0.47		β violet-brown	green
CaO ...	12.07	12.27		γ violet-brown	green
Na ₂ O ...	0.61	1.02	Dispersion	$r > v$	$r > v$
K ₂ O ...	trace	0.23			
H ₂ O+ ...	0.12	0.48			
H ₂ O- ...	0.25	0.22			
	100.44	100.30	Weight% ²	Wo. 27.2	30.0
				En. 22.5	1.5
				Fe. 50.3	68.5
Sp. gr. ³ ...	3.50	3.65			

I. Pyroxene from hortonolite-quartz-gabbro (E. G. 1907).

II. Pyroxene from fayalite-quartz-gabbro (E. G. 1881).

TABLE II. Calculation of formulae of pyroxenes I and II.

	Mol. ratios.	No. of metal atoms on basis of 6(O,OH).		Mol. ratios.	No. of metal atoms on basis of 6(O,OH).		
		I.			II.		
SiO ₂ ...	0.7046	1.720	} 1.96	0.7096	1.785	} 2.00	
Al ₂ O ₃ ...	0.0220	0.107		0.0513	0.258		{ 0.215
TiO ₂ ...	0.0552	0.135	} 2.08	0.0211	0.053	} 2.02	
Fe ₂ O ₃ ...	0.0296	0.144		0.0234	0.118		{ 0.043
FeO ...	0.3497	0.853		0.4390	1.105		
MnO ...	0.0031	0.008		0.0110	0.028		
MgO ...	0.2066	0.503		0.0117	0.029		
CaO ...	0.2152	0.525		0.2188	0.550		
Na ₂ O ...	0.0098	0.048		0.0164	0.083		
K ₂ O ...	—	—		0.0024	0.012		

I. (Mg,Fe'',Fe''',Ca,Mn,Na)₂₋₁ [(Si,Al,Ti)₂O₆].II. (Mg,Fe'',Fe''',Ca,Mn,Na,K,Ti,Al)₂[(Si,Al)₂O₆].

¹ Determinations of 2V and $\gamma:c$ ($\pm 2^\circ$) were made on the universal stage. We wish to thank Mr. N. F. M. Henry for confirming certain of these determinations. Refractive indices ± 0.002 .

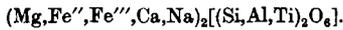
² Disregarding sesquioxides, titania, and alkalis.

³ Determined by matching in Clerici solution and measuring density of solution with a hydrostatic balance.

(Si,Al) group to 2. Machatschki¹ suggested as the general monoclinic pyroxene formula: $XY(\text{Si,Al})_2(\text{O,OH,F})_6$, in which X = Ca, Na, (K), (Mn), (Mg), and Y = Mg, Fe, Mn, Al, (Zn), (Ti). Although this formula appears to be applicable to many augite analyses,² it fails to satisfy a number of titaniferous pyroxenes when these are low in sesquioxides, especially alumina. This point was made by Dixon and Kennedy,³ who listed a number of titaniferous pyroxenes in which the combined silicon and aluminium is insufficient to satisfy the silicon chains of the pyroxene structure. There seems to be no way out of the assumption that silicon may be replaced by titanium in spite of the difference in size of the ionic radii, and in the co-ordination numbers of the two quadrivalent cations. This question has been discussed by Barth in connexion with the titaniferous augite from Hiva Oa, Marquesas Islands,⁴ and, although he calculates the analysis into the constituent molecules, he concludes that Ti^{++++} as well as Al^{+++} may replace Si^{++++} in the pyroxene structure. The analysis, optical properties, and calculation of the Hiva Oa pyroxene on the basis of six oxygens to the unit cell are given below (table III) for comparison with the pyroxene from Kangerdlugssuak. Barth has also

TABLE III. Pyroxene from Hiva Oa, Pacific Ocean. (T. F. W. Barth, 1931.)

	Wt. %	Mol. ratios.	No. of metal atoms on basis of 6(O,OH).
SiO_2 ...	47.11	0.7843	1.754
TiO_2 ...	3.75	0.0469	0.105
Al_2O_3 ...	3.00	0.0294	0.132
Fe_2O_3 ...	3.84	0.0240	0.107
FeO ...	12.20	0.1698	0.380
MgO ...	16.65	0.4105	0.918
CaO ...	13.54	0.2414	0.540
Na_2O ...	0.22	0.0355	0.016
K_2O ...	0.03	0.0032	0.002
	100.34		



Sp. gr. 3.32, α 1.695, β 1.701, γ 1.728, 2V 46°, $\gamma:c = 39^\circ$.

¹ F. Machatschki, Über die Formel der monoklinen Amphibole und Pyroxene. Zeits. Krist., 1929, vol. 71, pp. 219-236. [M.A. 4-202.]

² B. E. Warren and J. Biscoe, The crystal structure of the monoclinic pyroxenes. Zeits. Krist., 1931, vol. 80, pp. 391-401. [M.A. 5-186.]

³ B. E. Dixon and W. Q. Kennedy, Optically uniaxial titanaugite from Aberdeenshire. Zeits. Krist., 1933, vol. 86, pp. 112-120. [M.A. 5-440.]

⁴ T. F. W. Barth, Pyroxen von Hiva Oa, Marquesas-Inseln und die Formel titanhaltiger Augite. Neues Jahrb. Min., Abt. A, 1931, Beil.-Bd. 64, pp. 217-224. [M.A. 5-219.]

demonstrated experimentally that diopside is capable of incorporating 10% $\text{CaMgTi}_2\text{O}_6$ without destroying the essential structure of the pyroxenes. Machatschki's¹ suggestion that titanium may replace silicon at high temperatures and that crystals so formed would be metastable at ordinary temperatures does not appear to be valid in the case of the Kangerdlugssuak pyroxene I. This pyroxene is very rich in ferrous iron, an unusual condition in titaniferous pyroxenes; all titaniferous augites quoted by Doelter² are low in iron, and most of the later analyses confirm this observation. It has crystallized in stable equilibrium with the other phases under conditions of slow cooling, and since the magma is rich in iron the temperature of the crystallization was probably low. On the basis of six (O,OH,F) atoms to the unit cell it is necessary to assume, if the pyroxene structure is to be maintained, that the whole of the titanium in the Kangerdlugssuak pyroxene is replacing silicon, and Machatschki's formula must be modified to: $\text{XY}(\text{Si,Al,Ti})_2(\text{O,OH,F})_6$ for titaniferous pyroxenes in which TiO_2 is greater than Al_2O_3 . Kunitz³ has recently discussed the role of titanium in garnets and came to the conclusion that Ti may replace Si in those garnets containing an appreciable amount of titanium.

Pyroxene II is an almost pure member of the hedenbergite-clinoferrosilite solid solution series prepared by Bowen, Schairer, and Posnjak,⁴ and it has almost identical refractive indices: for the natural pyroxene α 1.743, γ 1.772; and for the artificial melt pyroxene containing 70% FeSiO_3 and 30% CaSiO_3 α 1.744, γ 1.772. Although occurring in the gabbro in patches of approximately the same size and shape as the other Kangerdlugssuak pyroxenes these patches consist of variously orientated grains, a feature which is also well displayed in other rocks of about the same position in the differentiation series. This texture is a clear indication that the pyroxene has formed by inversion from some other mineral. The work of Bowen, Schairer, and Posnjak on the system CaO-FeO-SiO_2 suggests that the higher-temperature mineral was a β -wollastonite solid solution. Tilley⁵ has recently shown that an iron-bearing wollastonite with probably about 25 wt. % of FeSiO_3 is present in the hybrid zone at Scawt Hill, whereas the more iron-rich wollastonite solid solution, which was presumably the high-temperature

¹ F. Machatschki, *Centr. Min., Abt. A*, 1930, p. 192.

² C. Doelter, *Handbuch der Mineralchemie*. 1914, vol. 2, p. 559, nos. 132-137.

³ Kunitz, *Neues Jahrb. Min., Abt. A*, 1936, Beil.-Bd. 70, p. 395. [M.A. 7-30.]

⁴ N. L. Bowen, J. F. Schairer, and E. Posnjak, *The system CaO-FeO-SiO₂*, *Amer. Journ. Sci.*, 1933, ser. 5, vol. 26, pp. 193-284. [M.A. 5-454.]

⁵ C. E. Tilley, *Min. Mag.*, 1937, vol. 24, pp. 569-572.

form of the Kangerdlugssuak pyroxene II, has inverted to a hedenbergite solid solution. The melt work of Bowen and his collaborators had suggested (*loc. cit.*, pp. 217–221, 260–261) that such contrasted behaviour would probably occur in nature.

The titaniferous pyroxene from the hortonolite-quartz-gabbro and the ferrous pyroxene from the fayalite-quartz-gabbro are both of considerable interest as they represent an extension of the field of naturally occurring pyroxenes. Winchell¹ recently stated that the maximum tenor of iron in pyroxenes could be expressed by the formula $MgFeSi_2O_6$, and that under ordinary magmatic conditions mixed crystals of the system clinoenstatite, clinoferrosilite, and diopside, with more than about 50 % $FeSiO_3$ would not be formed. Bowen (*loc. cit.*, p. 198) has shown experimentally that a much higher tenor of iron is possible in pyroxenes of artificial melts. Thus in the system hedenbergite-ferrosilite a pyroxene containing as much as 80 % $FeSiO_3$ has been obtained, and in the system $MgSiO_3-FeSiO_3$ a pyroxene with 87 % of $FeSiO_3$. The two natural iron-rich pyroxenes I and II from Kangerdlugssuak contain 50 % and nearly 70 % $FeSiO_3$ respectively.

Tomita² in 1934 drew up a valuable series of diagrams showing the relationship between composition and optical properties in the clinoenstatite-clinohypersthene-diopside-hedenbergite system. Since then further data have been obtained which justify revision of the diagram for the α and γ refractive indices. The new diagrams, figs. 1 and 2, are based on the data used by Tomita, together with Bowen, Schairer, and Posnjak's optical data (*loc. cit.*, pp. 259–261) on the synthetic clinoenstatite-clinohypersthene series, Bowen's determinations on natural clinoferrosilite,³ our determinations on the Kangerdlugssuak pyroxenes, and the data collected in table IV. The two analysed augites C and D (table IV) are complexly zoned and not ideally suited for plotting on the diagrams as their properties are variable, but in each case the lowest values for α and γ have been used, these fitting moderately well with the other data. The revised diagrams (figs. 1 and 2) show the greatest amount of change from the middle of the field diopside, hedenbergite clinoferrosilite, clinoenstatite, towards the ferrosilite component. The

¹ A. N. Winchell, Further studies in the pyroxene group. *Amer. Min.*, 1935, vol. 20, p. 566. [M.A. 6-294.]

² T. Tomita, Variations in optical properties, according to chemical composition, in the pyroxenes of the clinoenstatite-clinohypersthene-diopside-hedenbergite system. *Journ. Shanghai Sci. Inst.*, Sect. 2., 1934, vol. 1, pp. 41-58. [M.A. 6-71.]

³ N. L. Bowen, Ferrosilite as a natural mineral. *Amer. Journ. Sci.*, 1935, ser. 5 vol. 30, pp. 481-494. [M.A. 6-260.]

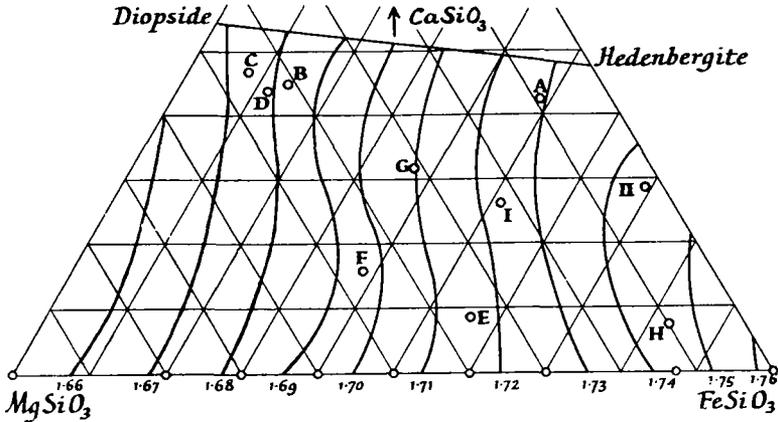


FIG. 1. Variation in chemical composition and the refractive index α in the system diopside, hedenbergite, clinoenstatite, and clinoferrosilite. The Roman numerals refer to the analyses of the Kangerdlugssuak pyroxenes (table I); A, B, C, and D to the pyroxene analyses on page 21; E to pigeonite from Mull, Scotland (A. F. Hallimond, *Min. Mag.*, 1914, vol. 17, p. 97); F to pigeonite, Åland Islands, Finland (W. Wahl, *Min. Petr. Mitt. (Tschermak)*, 1907, vol. 26, p. 18); G to pigeonite, Lake Onega, Russia (W. Wahl, *ibid.*, p. 27); H to artificial mineral from a slag (N. L. Bowen, *Journ. Washington Acad. Sci.*, 1933, vol. 23, p. 83 [M.A. 5-454]).

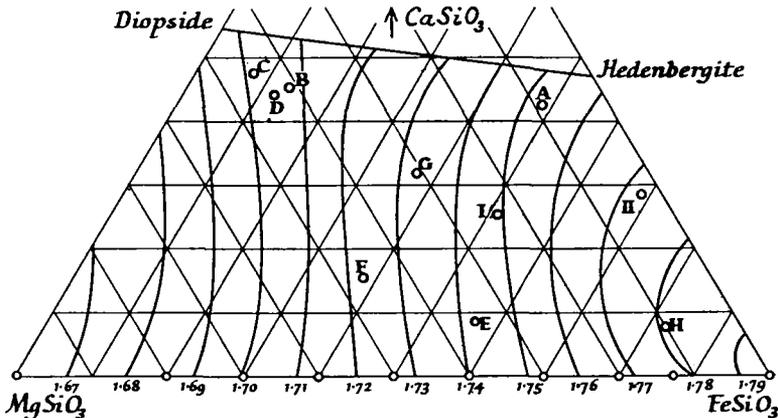


FIG. 2. Variation in chemical composition and in the refractive index γ in the system diopside, hedenbergite, clinoenstatite, and clinoferrosilite. For meaning of the letters and numbers see fig. 1.

new values for the refractive indices of the clinoenstatite-clinohypers-
thene series have made the curves for both α and γ much flatter than
those given by Tomita.

TABLE IV. Pyroxene analyses and optical data.

	A.	B.	C.	D.
SiO ₂ ...	47.58	50.40	49.86	50.10
TiO ₂ ...	0.37	1.13	0.41	0.70
Al ₂ O ₃ ...	1.16	1.63	5.48	4.57
Fe ₂ O ₃ ...	2.60	2.06	2.42	2.34
FeO ...	24.21	9.74	4.23	7.14
MnO ...	0.59	0.09	0.15	0.32
MgO ...	3.34	13.37	15.02	14.20
CaO ...	18.80	20.65	22.34	20.18
Na ₂ O ...	0.47	0.66	nil	0.32
K ₂ O ...	0.21	0.23	nil	trace
H ₂ O+ ...	0.34	0.48	0.20	0.24
H ₂ O- ...		0.03	0.11	0.10
	99.67	100.47	100.22	100.21
Wo. ...	42.5	45.2	47.8	44.0
Fo. ...	9.1	41.3	45.0	43.3
Fe. ...	48.4	13.5	7.2	12.7
α ...	1.730	1.691	1.680-1.698	1.684-1.700
... ..	1.736	1.697	1.687-1.704	1.692-1.708
γ ...	1.755	1.718	1.706-1.723	1.707-1.721
2V ...	60°	51-66°	58°2'-59°9'	50°41' 57°55'
$\gamma:c$...	45°	43°	43-44°	41-43°

- A. Hedenbergite from Percy quadrangle, New Hampshire. R. W. Chapman and C. R. Williams, Evolution of the White Mountain magma series. Amer. Min., 1935, vol. 20, p. 512. [M.A. 6-215.] (Analyst, F. A. Gonyer.)
- B. Phenocryst in pumice, Komagataké, Japan. (Calculated analysis from mixed analysis of pyroxene and hypersthene, and analysis of the hypersthene.) S. Kôzu, The great activity of Komagataké in 1929. Min. Petr. Mitt. (Tschermak), 1934, vol. 45, pp. 133-174. [M.A. 6-21.]
- C. Augite from Wadaki, Idu, Japan. H. Kuno and M. Sawatari, On the augites from Wadaki, Idu, and from Yoneyama, Etigo, Japan. Japanese Journ. Geol. Geogr., 1934, vol. 11, pp. 327-343. [M.A. 6-19.] (Analyst, S. Tanaka.)
- D. Augite from Yoneyama, Etigo, Japan. Ibid. (Analyst, S. Tanaka.)

Tomita's diagram showing the variations of the optical axial angle and the extinction-angle $\gamma:c$ is given here unchanged except for the addition of circles marking the position of the newly analysed pyroxenes (fig. 3). It will be seen that the diagram does not fit at all closely the values of 2V and $\gamma:c$ which have been found for the Kangerdlugssuak

pyroxenes. The discrepancies will probably be found to be due to the fact that these values, unlike the refractive indices, are very sensitive to variations in the amounts of the other constituents occurring in natural pyroxenes.

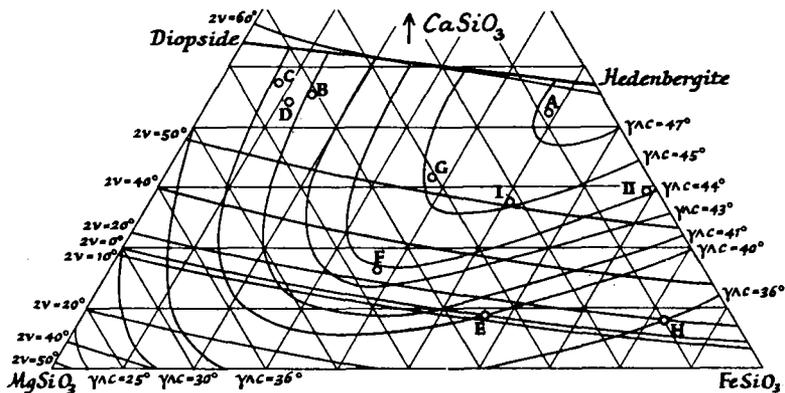


FIG. 3. Variation in chemical composition and in the values $2V$ and $\gamma:c$ in the system diopside, hedenbergite, clinenstatite, and clinoferrosilite (after T. Tomita, 1934).

The rocks containing the analysed pyroxenes from the Skaergaard Halvoen gabbro complex will be described in a later paper and the petrological significance of the iron-rich rocks and pyroxenes discussed.