

that the sum of the chemical analysis (Table 3) does not quite total 100 per cent, implying that certain components are probably too low, all of the calculated densities therefore represent a minimum value. If we allow for slight increases in these calculated densities (perhaps as much as 0.01), the calculated density of (1) would fit very well, whereas those of (2) and (3) would be too high.

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STABILITY AND PROPERTIES OF THE
SYNTHETIC PYROXENE $\text{CaAl}_2\text{SiO}_6^1$

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Clark, *et al.*, (1962) report the synthesis of a clinopyroxene having the composition $\text{CaAl}_2\text{SiO}_6$, which they refer to as "lime Tschermak's mole-

¹ Published under the auspices of the committee on Experimental Geology and Geophysics and the Dept. of Geological Sciences, Harvard University.

cule" (Tschermak, 1914). They give unit cell parameters for this phase and for a series of synthetic clinopyroxenes with compositions lying on the join $\text{CaMgSi}_2\text{O}_6$ — $\text{CaAl}_2\text{SiO}_6$. In the course of the author's study of phase equilibria in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ at high pressures and temperatures, the new pyroxene phase appeared as a product in a number of runs. Optical and x-ray data for the new phase and some observations on its synthesis field and stability are reported here.

Starting material for most of the syntheses was a nearly homogeneous glass with composition $\text{CaO } 25.71\%$, $\text{Al}_2\text{O}_3 \text{ } 46.75\%$, $\text{SiO}_2 \text{ } 27.54\%$ in weight per cent, corresponding to the proposed formula $\text{CaAl}_2\text{SiO}_6$. The glass was prepared by the author under the supervision of J. F. Schairer and using the methods and materials described by Schairer (1959). At the maximum temperature of the platinum furnace used (about 1600°C .), it was not possible to dissolve completely the Al_2O_3 starting material, so

TABLE 1. OPTICAL DATA

α	$1.709 \pm .002$	
β	$1.714 \pm .002$	(Na light, 25°C)
γ	$1.730 \pm .002$	
$2V$ (calculated)		$59^\circ \pm 15^\circ$
Birefringence (calculated)		$.021 \pm .004$
Extinction angle	not determined	

that the final product contained a few crystals of corundum and $\beta\text{-Al}_2\text{O}_3$ in an otherwise homogeneous glass. This was true of the starting material used by Clark *et al.* as well (Schairer, pers. comm.).

Most of the high pressure runs were made in the single-stage piston and cylinder apparatus described by Boyd and England (1960). The crystals on which optical and x-ray measurements were made were synthesized in a similar device of larger dimensions, also designed by Boyd and England.

The product of the high pressure runs was a dense, white, fine-grained aggregate. The specimen was crushed and examined optically by the immersion method. Average grain size is less than ten microns. A few grains are as large as fifty microns. Indices of refraction measured in sodium light at 25°C . are given in Table 1. Although the blocky grains tended to lie on a prominent cleavage face (presumably 110), there were many irregular grains and grains partially imbedded in polygranular fragments, so that the indices determined are believed to be the true principal indices. Extinction angle and $2V$ were not determined. Calculated $2V$ and birefringence are given in Table 1. The calculated bire-

fringence agrees well with interference colors observed in the larger grains. The optical data in Table 1 are consistent with data on aluminous diopsides given by Zvetkov (1945), but the extrapolation is not linear.

A portion of the specimen was examined in filtered Cu radiation on an *x*-ray diffractometer using a silicon internal standard. The diffractometer charts were indexed with the aid of *d*-values calculated from the cell constants of Clark *et al.* and by comparison with a diopside powder pattern. The data of Clark *et al.* on pyroxenes of intermediate compositions are strong evidence that the new phase has the diopside structure. Unfortunately, no crystals large enough for single crystal *x*-ray work have yet been synthesized.

The *d*-values observed were used to refine the unit cell with the aid of the Burnham (1962) least squares computer program. Both the Clark

TABLE 2. X-RAY DATA

<i>a</i>	$9.619 \pm .003 \text{ \AA}$
<i>b</i>	$8.659 \pm .003 \text{ \AA}$
<i>c</i>	$5.278 \pm .002 \text{ \AA}$
β	$73.86 \pm .02 \text{ degrees}$
V	$422.3 \pm .2 \text{ \AA}^3$
ρ	$3.431 \pm .002 \text{ g/cm}^3$

Errors given refer to least squares fit of *d*-spacings used and do not include other possible sources of error.

et al. cell and the diopside cell were used as initial arguments with identical results. The unit cell parameters given in Table 2 are in good agreement with those of Clark *et al.* Table 3 is a comparison of the observed powder pattern with the pattern computed from the unit cell of Table 2.

Density of the aggregate was measured in two ways for comparison with the density calculated from the *x*-ray data. A 67 mg disc measured on a Berman balance had a density of $3.42 \pm .02 \text{ g/cm}^3$. The entire sample (335 mg) measured in a pycnometer had a density of $3.43 \pm .01 \text{ g/cm}^3$. The calculated *x*-ray density is $3.43 \pm .005 \text{ g/cm}^3$.

An electron microprobe analysis of the $\text{CaAl}_2\text{SiO}_6$ pyroxene was made by C. Klein of Harvard University, using as a standard a natural anorthite crystal from Franklin, N. J., assumed to have the composition reported by Palache (1935). Results of the analysis as given in Table 4 are in fair agreement with the composition of the starting glass and the pyroxene structural formula. Scanning photographs on $\text{CaK}\alpha$, $\text{AlK}\alpha$, and $\text{SiK}\alpha$ on scales of 45 microns and 360 microns show no apparent inhomogeneities.

TABLE 3. X-RAY POWDER PATTERN

hkl	d(calc)	d(obs)	I/I ₀	hkl	d(calc)	d(obs)	I/I ₀
200	4.62	4.62	4	313	1.662	1.662*	9
111	4.38	—	—	223	1.624	1.624*	12
020	4.33	4.33	5	441	1.597	1.596	20
$\bar{1}11$	3.63	3.63	3	531	1.596		
220	3.16	3.16	†	440	1.580	1.580*	11
221	2.94	2.94	100	600	1.540	1.540	3
310	2.902	2.904	36	602	1.516	1.516	
311	2.862	2.863	45	402	1.511	1.512	27
202	2.540			350	1.510	1.510	
002	2.535	2.535	38	133	1.497	1.497*	20
112	2.524			$\bar{5}31$	1.399	1.399	18
131	2.510	2.509	28	$\bar{3}51$	1.396		
$\bar{2}21$	2.478	2.478*	48	$\bar{2}23$	1.385		
$\bar{1}31$	2.341	2.340*	4	352	1.382	1.382	32
$\bar{3}11$	2.275	2.274*	19	$\bar{1}52$	1.381		
$\bar{1}12$	2.212	2.212	12	$\bar{3}13$	1.318	1.316	7
312	2.219			712	1.317		
222	2.188	2.188	16	710	1.305	1.305	10
022	2.191			314	1.292		
330	2.106	2.105*	17	114	1.291	1.292	7
331	2.091	2.090*	21	641	1.288		
421	2.075	2.075*	12	262	1.255		
402	2.008	2.007	17	640	1.255	1.254	5
$\bar{2}02$	2.003	2.002		062	1.254		
041	1.991	1.991	35	170	1.226	1.226	7
132	1.948	1.948*	12	$\bar{3}52$	1.226		
$\bar{2}22$	1.816			171	1.202	1.202	1
510	1.807	1.808	6	$\bar{1}71$	1.182	1.182	1
332	1.796			370	1.148	1.147	2
150	1.702	1.703	15	604	1.148		
$\bar{3}12$	1.701						

Philips x-ray unit and diffractometer, Ni filtered CuK α radiation, 45 kV, 20 ma, 1° slits. Smear mount on glass slide with silicon internal standard. Scan 1/4 deg/min, chart speed 1/2 inch/min, time constant 8 seconds. Intensities given are measured areas under peaks relative to area under 221 peak.
 † Partially masked by silicon peak.
 * Indicates d-value used for least squares refinement.

TABLE 4. ELECTRON MICROPROBE ANALYSIS
 Weight per cent

SiO ₂	25.1
Al ₂ O ₃	47.6
CaO	26.3
	—
	99.0

Fe and Mg looked for but not detected.
 Structural formula (6 oxygen basis)

	VI	IV			
Ca	Al	Al	Si	O	
1.04	1.00	1.07	.93	6	

Analyst: C. Klein.

All syntheses of the $\text{CaAl}_2\text{SiO}_6$ pyroxene were made above 12 kilobars and above 1050°C . Table 5 shows the results of some pertinent runs in which crystalline starting materials prepared from synthetic glasses were used. The stability of the new pyroxene at lower pressure is precluded by the assemblage

anorthite + gehlenite + corundum,

and stability at higher pressure and lower temperature is precluded by the assemblage

grossular + corundum.

The stability of the new pyroxene within a portion of its synthesis field is established relative to both these alternative assemblages. The geologically unusual combination of high temperature, high pressure, and absence

TABLE 5. EXPERIMENTAL RUNS USING CRYSTALLINE STARTING MATERIALS

Run	T($^\circ\text{C}$)	P(kb)	Duration (hours)	Starting Material	Products
082	1250	7	4.6	CaTs	An+Geh+Cor
083	1250	27	11.3	CaTs	Gros+Cor
084	1300	13	11.3	An+Geh+Cor	CaTs+starting material
095	1250	15	2.5	Gros+Cor+CaTs	CaTs+trace Cor (CaTs grew)

An=anorthite, Geh=gehlenite, Cor=corundum, Gros=grossular, CaTs= $\text{CaAl}_2\text{SiO}_6$ pyroxene.

All phase identifications by optical examination and x-ray powder patterns.

of iron and magnesium, required for the formation of this phase explains its apparent non-occurrence as a natural mineral.

The $\text{CaAl}_2\text{SiO}_6$ pyroxene (indicated by "CaTs." for "lime Tschermak's molecule") occurs in the following synthetic assemblages:

anorthite + gehlenite + CaTs.

anorthite + grossular + CaTs.

Further work is in progress to determine the stability relationships of these phases and to locate precisely the equilibrium curves.

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X-RAY CRYSTALLOGRAPHY OF RINKITE

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INTRODUCTION

The name rinkite was proposed by Lorenzen (1884) for a mineral found at Kangerdluarssuk, Greenland. From the beginning, the symmetry of rinkite was very controversial. Lorenzen (1884) described it as monoclinic with

$$a:b:c = 1.569:1:0.292 \quad \beta = 88^\circ 47'$$

Optical axial plane normal to (010), $c \wedge \gamma = 7.5^\circ$. Frequent polysynthetic twin lamellae (100). Zambonini (1921) did not find these twin lamellae, and stated that $c \wedge \gamma = 0^\circ$ or, at the most, 0.5° . Gordon (1924) obtained