

The lattice parameters and interplanar spacings of some artificially prepared melilites.

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[Communicated by Dr. F. A. Bannister; read June 24, 1948.]

Introduction.—A laboratory investigation in connexion with some blast-furnace slags, led to the preparation of the five synthetic melilites for which X-ray data are provided. The five compounds represent gehlenite, åkermanite, and three members of the intermediate series of solid solutions, corresponding to 25, 50, and 75 % of åkermanite.

The binary system gehlenite-åkermanite was studied by Ferguson and Buddington,¹ who established relationships between refractive indices, density, and composition and determined solidus and liquidus curves. The crystal structure of the melilite group of compounds was investigated by Warren,^{2,3} who showed that the structure was based on a tetragonal lattice. In åkermanite the magnesium atoms occupy the centres and corners of the (001) faces, whilst the silicon atoms are at the centres of silicon-oxygen tetrahedra joined together in pairs by a common oxygen atom, thus forming Si_2O_7 groups. In going from åkermanite to gehlenite magnesium atoms are replaced by aluminium and some of the silicons by aluminium also. The composition of gehlenite is reached when all the magnesium atoms and half the silicon have been replaced in this manner. The replacement may be represented by $\text{Mg}^{2+} + \text{Si}^{4+} \rightleftharpoons \text{Al}^{3+} + \text{Al}^{3+}$. We are not here concerned with the similar replacement of $\text{Ca} + \text{Mg}$ by $\text{Na} + \text{Al}$, which would account for the presence of the sodium atoms usually included in the general formula for melilite.

Experimental Work.—The samples were prepared from pure component oxides of 'analytical reagent' or similar quality. The calcium oxide was prepared by calcining calcium carbonate at a temperature of

¹ J. B. Ferguson and A. F. Buddington, The binary system åkermanite-gehlenite. Amer. Journ. Sci., 1920, ser. 4, vol. 50, pp. 131-140. [M.A. 1-167.]

² B. E. Warren, The structure of melilite $(\text{Ca}, \text{Na})_2(\text{Mg}, \text{Al})_1(\text{Si}, \text{Al})_2\text{O}_7$. Zeits. Krist., 1930, vol. 74, pp. 131-138. [M.A. 4-367.]

³ W. L. Bragg, Atomic structure of minerals. London, 1937, p. 177. [M.A. 7-7.]

about 950° C., but all oxides were heated at this temperature immediately before weighing out the quantities required. Samples of a total weight of approximately one gram each were prepared. A technique of careful and prolonged mixing and grinding together was followed, and the mixtures then rammed into cylindrical pellets, ready for firing.

TABLE I. Compositions and lattice parameters of standard compounds.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
% Gehlenite	100	75	50	25	0
% Åkermanite	0	25	50	75	100
Molecular percentage composition.					
CaO	50.00	47.06	44.44	42.11	40.00
Al ₂ O ₃	25.00	17.65	11.11	5.26	—
MgO	—	5.88	11.11	15.79	20.00
SiO ₂	25.00	29.41	33.33	36.84	40.00
CaO/SiO ₂	2.00	1.60	1.33	1.143	1.00
Weight percentage composition.					
CaO	40.94	41.00	41.04	41.12	41.20
Al ₂ O ₃	37.19	27.96	18.65	9.34	—
MgO	—	3.64	7.41	11.09	14.77
SiO ₂	21.87	27.40	32.90	38.45	44.03
Lattice parameters, kX units.					
<i>a</i>	7.674	7.703	7.738	7.772	7.828
	±0.002	±0.002	±0.003	±0.003	±0.002
<i>c</i>	5.057	5.044	5.034	5.016	5.000
	±0.002	±0.002	±0.003	±0.002	±0.002
<i>c/a</i>	0.659 ₀	0.654 ₈	0.650 ₅	0.645 ₁	0.638 ₇
	±0.0004	±0.0004	±0.0006	±0.0005	±0.0004
Lattice parameters, Ångström units.*					
<i>a</i>	7.690	7.719	7.754	7.787	7.843 ₅
<i>c</i>	5.067 ₅	5.054 ₅	5.044 ₅	5.026 ₅	5.010

* The values in Å. are obtained by multiplying the kX values by a factor of 1.00202.

The compositions of the samples are listed in table I. It is considered that the probable errors in composition arising from the method of preparation employed are less than would be obtained by ordinary chemical analysis of much larger samples. Samples of the size prepared are small enough to be thoroughly mixed by careful hand-mixing, but large enough for the components to be sufficiently accurately weighed, and for the effect of small losses (in any case practically nil) to be negligible in proportion.

The heating schedule was: The samples were heated from 20 to 1300° C. in approximately 4 hours, and then held at 1300° C. for approximately 3 hours, and finally cooled down with the furnace.

The samples were examined by the X-ray powder method in the 9 cm. diameter camera and the photographs which were taken with Co- $K\alpha$ radiation are illustrated in fig. 1. The photographs showed that the crystals were reasonably well developed, and sharp lines were generally

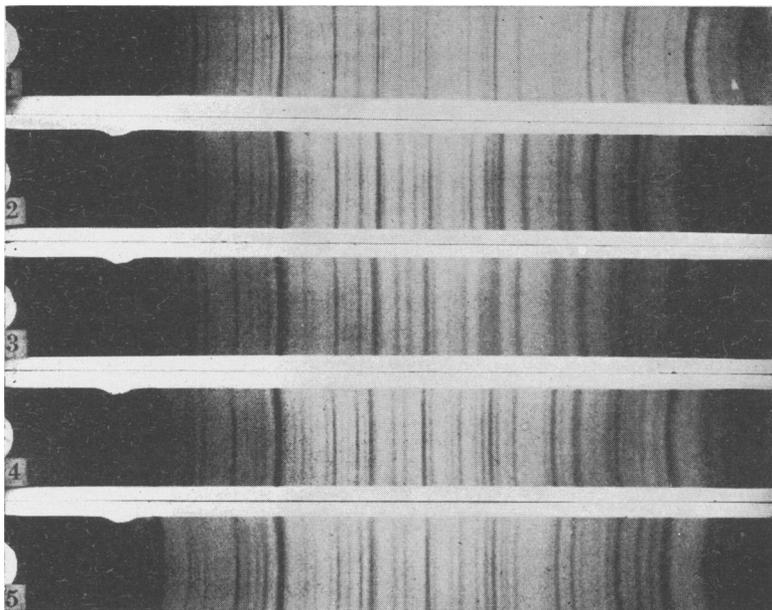


FIG. 1. X-ray powder photographs (reduced from 5 inches) of the two end-members and three mixed crystals of the gehlenite-åkermanite series.

			1.	2.	3.	4.	5.
Gehlenite	100	75	50	25	0
Åkermanite	0	25	50	75	100

obtained up to high angles. The sample representing 50 % gehlenite, and 50 % åkermanite in mutual solid solution (no. 3), however, showed somewhat poorer lines at high angles than the others. No change was observed after prolonged periods of heating with this or the other samples, and the photographs provided the accuracy desired.

The values of the lattice parameters and axial ratios corresponding to the five synthetic samples are included with the composition data in table I. The results are plotted against composition in fig. 2, which shows how, proceeding from gehlenite to åkermanite, the replacement of 2Al by Mg+Si leads to an increase in the a spacing and a decrease in the c spacing, with a corresponding decrease in axial ratio.

Measurements were made in kX units and converted to Ångström units as indicated in table I. The a and c parameters were then used to calculate interplanar spacings which are recorded in table II, together

TABLE II. Values of interplanar spacings in Ångström units.

Indices	No. 1.		No. 2.		No. 3.		No. 4.		No. 5.	
	<i>hkl</i>	<i>d_{hkl}</i>								
101	vw	4.232	vw	4.229	vw	4.228	vw	4.223	vw	4.222
111	wm	3.708	wm	3.708	w	3.712	w	3.712	w	3.717
210	vvw	3.439	vvw	3.452	vvw	3.468	vvw	3.483	vw	3.508
201	wm	3.063	wm	3.067	wm	3.074	m	3.078	m	3.088
211	s	2.846	s	2.851	s	2.858	s	2.863	s	2.874
220	vvw	2.719	vvw	2.736	vvw	2.742	vvw	2.753	—	—
002	vvw	2.534	vvw	2.527	vvw	2.522	vvw	2.513	vvw	2.505
310	m	2.432	m	2.441	m	2.452	m	2.463	m	2.480
102	m	2.407	m	2.402	w	2.399*	wm	2.392*	wm	2.386*
221	m	2.396	m	2.401	wm	2.409*	w	2.415*	w	2.426*
112	m	2.297	m	2.293	vw	2.291*	vw	2.286*	w	2.283*
301	—	2.287	—	2.293	wm	2.300*	wm	2.306*	wm	2.318*
311	vw	2.193	vw	2.198	vvw	2.205	vvw	2.211	vvw	2.223
202	vvw	2.116	vvw	2.114	vvw	2.114	vvw	2.112	vvw	2.111
212	wm	2.040	wm	2.039	wm	2.040	m	2.038	m	2.039
321	vw	1.966	vw	1.971	vvw	1.978	vw	1.984	vw	1.996
400	wm	1.922	wm	1.930	wm	1.939	wm	1.947	wm	1.961
410	w	1.865	w	1.872	w	1.881	w	1.889	wm	1.902
222	w	1.854	vw	1.854	vw	1.856	vw	1.856	vw	1.859
330	wm	1.813	wm	1.819	wm	1.828	wm	1.836	wm	1.849
312	s	1.755	s	1.756	ms	1.758*	ms	1.759*	ms	1.763*
411	—	1.752	—	1.756	ms	1.762*	wm	1.768*	wm	1.779*
420	w	1.720	w	1.726	vw	1.734	vw	1.741	—	—
331	vvw	1.707	vvw	1.712	vw	1.718	vw	1.724	w	1.734
003	—	—	vvw	1.685	vvw	1.682	vvw	1.675	vvw	1.670
322	w	1.632	w	1.634	w	1.636*	w	1.638*	w	1.643*
421	—	1.628	—	1.633	w	1.640*	w	1.645*	vvw	1.655*
113	vw	1.613	vw	1.610	vw	1.608	w	1.603	w	1.599
203	vvw	1.547	vvw	1.544	vvw	1.543	vw	1.539	vw	1.537
412	—	—	—	—	—	—	—	—	vw	1.515
213	m	1.516	m	1.514	m	1.513	m	1.510	wm	1.508
332	vw	1.474 _s	vw	1.476 _s	vw	1.480	vw	1.482	vw	1.487 _s
511	vvw	1.445 _s	vvw	1.450 _s	vvw	1.456	vw	1.461 _s	w	1.470 _s
520	—	—	—	—	—	—	—	—	vvw	1.456 _s
223	w	1.435	w	1.433 _s	wm	1.433 _s	—	1.431 _s	—	1.431*
422	vw	1.423	vvw	1.425 _s	vw	1.429	wm	1.431 _s	wm	1.436 _s *
303	vvw	1.410 _s	vvw	1.409 _s	vw	1.409 _s	vw	1.407 _s	w	1.407 _s
313	vw	1.387 _s	vw	1.386 _s	vw	1.386 _s	vvw	1.385*	vvw	1.385 _s *
521	m	1.374 _s	m	1.379	m	1.384 _s	m	1.390*	m	1.398 _s *
440	w	1.359 _s	w	1.364 _s	vw	1.371	w	1.376 _s	w	1.386 _s *

I intensity: s strong, m medium, w weak, &c.

* Lines whose relative positions are reversed by axial ratio change.

with the corresponding indices and relative intensities. These calculated interplanar spacings are expected to be useful for the identification of members of this series of solid solutions. The actual calculated values are retained (rather than a mean value) where two lines are too close together to be resolved. It will thus be observed how some pairs of lines

such as 102 and 221, or 312 and 411, approach, coincide, and then separate on the opposite side of each other, as the axial ratio changes

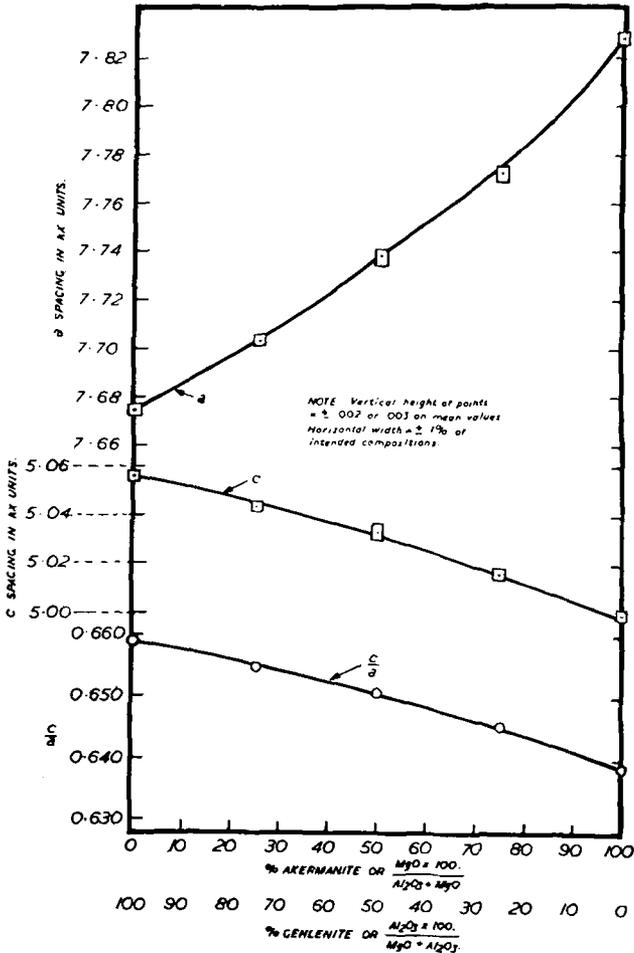


FIG. 2. Lattice spacing relationships in the gehlenite-åkermanite series.

from one end of the series to the other. Lines which as a result are displaced in the otherwise strict order of decreasing magnitude of d_{hkl} in the table, are therefore indicated by an asterisk.

Conclusions.—The five members of the solid solution series examined have been sufficient to indicate to a reasonable degree of accuracy the

lattice parameter variations accompanying the isomorphous substitution represented by $\text{Mg} + \text{Si} \rightleftharpoons \text{Al} + \text{Al}$. The ionic radii are in the order $\text{Mg} > \text{Al} > \text{Si}$, and commencing with åkermanite the replacement of Mg by Al would be expected to lead to a contraction of the lattice, whilst the replacement of some of the Si atoms by Al would result in an increase in the dimensions of the silicon-oxygen tetrahedra linked in pairs. The combination of these two tendencies leads to the resultant decrease of the a parameter and increase of the c parameter proceeding from åkermanite to gehlenite (i.e. from right to left in fig. 2).

Interplanar spacing data are provided, and are expected to be of use for the identification of members of this series of solid solutions, providing that isomorphous substitution of ions other than those considered is not large enough to affect the spacings seriously. The presence of sodium ions in melilites has been referred to in the introduction. The replacement of magnesium by divalent iron (and possibly also by manganese) and of aluminium by trivalent iron is expected. In the mineral hardystonite $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ the Mg of åkermanite is completely replaced by zinc. The possibility of other substitutions is not excluded providing the ionic radii are of a similar order to the radii of the ions referred to.

Acknowledgements.—The author wishes to thank Mr. F. H. Saniter, Director of Research, The United Steel Companies Limited, for permission to publish these data. He would also like to record his gratitude to the late Dr. A. H. Jay under whose direction the work was commenced, and his thanks to Mr. N. Marshall for assistance with some of the calculations.