X-RAY DATA ON SYNTHETIC MELILITES

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ABSTRACT

Using a Geiger-counter recording spectrometer, powder diffraction patterns were obtained for 10 mixtures in the akermanite-gehlenite series. Graphs plotting change in d-spacing against composition for 10 lines of these patterns are shown whereby the relative amounts of akermanite and gehlenite in a melilite may be calculated from its x-ray pattern. In addition, unit cell dimensions for these tetragonal minerals were calculated, which show an increase in a and a decrease in c on proceeding from gehlenite to akermanite. These changes are explained on the basis of the known atomic structure of melilite.

INTRODUCTION

The melilites are a group of tetragonal minerals appearing in igneous rocks, in metamorphic assemblages, and in synthetic products such as crystallized blast furnace slags. Complete solid solution exists at high temperatures between the two principal melilite compounds, gehlenite, $Ca_2Al_2SiO_7$, and akermanite, $Ca_2MgSi_2O_7$ (1)(2). Other cations are also commonly present, especially sodium and divalent iron. The role of sodium in melilite crystals is not clear, as recently emphasized by Goldsmith (3). Divalent iron substitutes for magnesium in akermanite, replacement being complete in "iron-akermanite" (4).

The structure of a natural melilite crystal, which was largely an akermanite-gehlenite solid solution, was analyzed by Warren (5) who found two molecules in the unit cell with $a = 7.74$ Å and $c = 5.02$ Å.* The structure has SiO_4 tetrahedra linked in pairs, calcium is in eightfold coordination, aluminum and magnesium in fourfold.

As the present study was being completed, the work of Andrews (6) on the d-spacings and cell dimensions in akermanite, in gehlenite, and in three akermanite-gehlenite solid solutions appeared. The results given herein, insofar as they overlap the findings of Andrews, are in very good agreement with his data.

RESULTS

Ten mixtures in the gehlenite-akermanite series were prepared from the pure oxides, melting four times with intermediate quenching to a glass and crushing. Each was crystallized by holding for several days at the temperature of the solidus, followed by several more days at a lower

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* Throughout this paper true ångstrom units are used, calculated according to the new grating wave lengths (Cu $K\alpha_1 = 1.5405$Å). Warren's values, actually in kX units, have been converted to ångstrom units (factor 1.002).

temperature. The glasses were shown to be uniform by their uniform refractive index, and the uniformity and complete crystallinity of the crystallized samples were checked petrographically.

Powder diffraction patterns for the crystallized samples were obtained on the Norelco recording spectrometer using Cu-Kα radiation. The *d*-spacings thus obtained were assigned indices (*hkl*) and then used to calculate unit cell dimensions, which are shown in Table 1 and Fig. 1. Using these values for *a* and *c*, *d*-spacings were calculated for each plane

TABLE 1. UNIT CELL DIMENSIONS IN ÅNGSTROM UNITS AND RATIO *c:a* FOR THE AKERMANITE-GEHLENITE SOLID SOLUTION SERIES

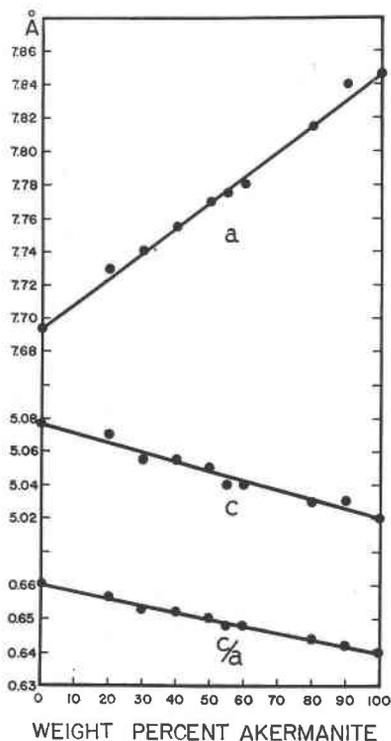| Wt. % Aker-manite	0	20	30	40	50	55	60	80	90	100
a	7.694	7.73	7.74	7.755	7.77	7.775	7.78	7.815	7.84	7.846
c	5.077	5.07	5.055	5.055	5.05	5.04	5.04	5.03	5.03	5.020
c/a	0.660	0.656	0.653	0.652	0.650	0.648	0.648	0.644	0.642	0.640

FIG. 1. Unit cell dimensions *a* and *c* in ångstrom units and ratio *c:a* for the akermanite-gehlenite solid solution series.

whose reflections were intense enough to appear. Table 2 gives, for pure gehlenite and akermanite, the d-spacings thus calculated together with the observed d-spacings and their estimated relative intensities showing the extent of agreement of the patterns with the assigned cell dimensions.

For the purpose of using x-ray patterns to determine the proportions of akermanite and gehlenite in a melilite, it is desirable to employ a simpler criterion than the change in unit cell dimensions, since the determination of these involves indexing a number of lines and making calculations. Correlating composition with d-spacing is the obvious simple procedure, but because of the simultaneous decrease in c with increase in a, as shown in Fig. 1, some pairs of lines in the pattern reverse their relative positions, while others show little change with composition. On the other hand, no one line would serve as a sufficiently precise measure of composition. Ten lines were selected which were distinct from any others throughout the range of compositions. These showed moderately large changes and were at the same time strong enough to appear in the majority of the patterns. In Fig. 2 the spacings for these 10 lines are plotted against composition, the solid line showing the d-spacings calculated
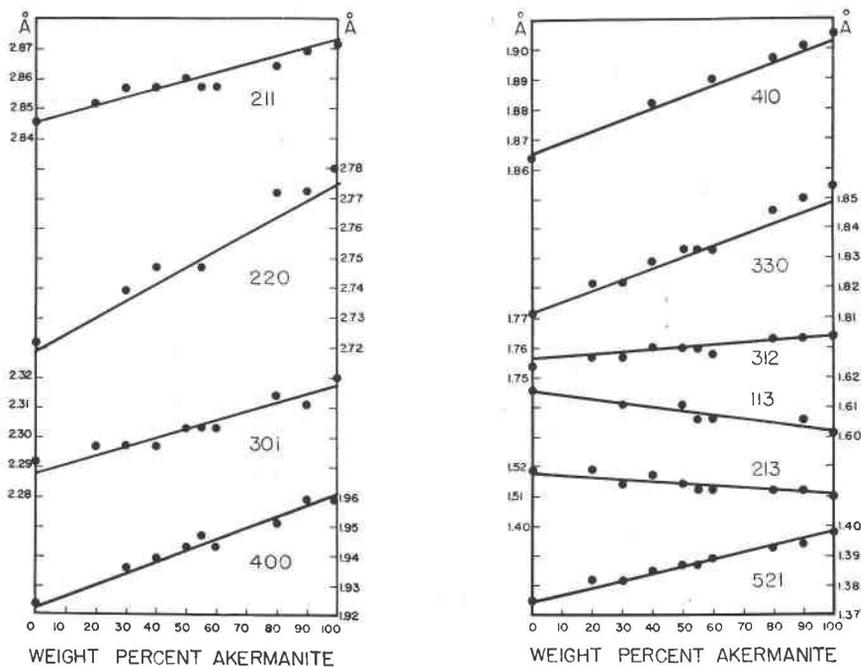

Fig. 2. Graphs showing manner of change in d-spacings of planes (hkl) in akermanite-gehlenite solid solutions. Circles represent experimentally determined points. The straight lines were drawn through points representing d-spacings calculated from the unit cell dimensions.

from the unit cell dimensions and the circles the observed d-spacings for each composition. Some points are missing where lines were too weak to be observed.

TABLE 2. CALCULATED AND OBSERVED d-SPACINGS IN
GEHLENITE AND AKERMANITE

hkl	Calcu-lated	Gehlenite Observed	Relative Intensity	Calcu-lated	Akermanite Observed	Relative Intensity
110	5.440	5.456	4	5.555	5.55	11
001	5.071	5.082	4	5.013		
101	4.234	4.218	3	4.224	4.22	9
200	3.846			3.929	3.91	4
111	3.707	3.67	20	3.721	3.73	13
210	3.440	3.430	1	3.514	3.51	4
201	3.064	3.070	25	3.092	3.091	27
211	2.846	2.846	100	2.873	2.871	100
220	2.719	2.722	4	2.780	2.780	2
002	2.536	2.535	6	2.505⎫	2.488	16
310	2.432	2.435	18	2.484⎭		
102	2.409⎫	2.404	22	2.387	2.391	9
221	2.396⎭			2.429	2.429	5
301	2.288	2.292	13	2.321	2.320	9
311	2.193	2.195	1	2.225		
320	2.134⎫	2.126	1	2.178		
202	2.117⎭			2.112		
212	2.042	2.043	14	2.040	2.039	19
321	1.966	1.967	1	1.997		
400	1.923	1.924	6	1.963	1.959	5
410	1.866	1.864	4	1.905	1.905	7
330	1.813	1.812	8	1.851	1.854	9
312	1.756	1.754	34	1.764	1.764	27
420	1.720	1.723	5	1.756		
331	1.707			1.736	1.735	4
003	1.691			1.673	1.673	3
322	1.633	1.632	1	1.644	1.643	3
113	1.615	1.616	3	1.599	1.601	4
203	1.547			1.537	1.537	1
213	1.518	1.519	14	1.508	1.510	7
332	1.474	1.475	1	1.489	1.471	3
223	1.436	1.437	5	1.431	1.435	7
521	1.375	1.375	8	1.400	1.398	9
440	1.360	1.361	3	1.388	1.384	4
323	1.325	1.327	1	1.325		
502	1.316	1.316	1	1.332	1.335	3
600	1.282	1.282	1	1.309	1.308	3
004	1.268	1.267	3	1.253⎫	1.256	9
413	1.253⎫	1.253	4	1.255⎭		
104	1.251⎭			1.235	1.242	3

To use these graphs the percentage akermanite is read off for each of the 10 lines of the pattern or as many of the ten as show up. The average of these 10 (or less) percentages is taken as the final value. The precision of this method is estimated at $\pm 2.5\%$ akermanite.

DISCUSSION

The above data agree very closely with those of Andrews. One discrepancy is that his curves of a and c against composition show a slight curvature. In our case, these plots are straight lines, within experimental error. However, the closeness of fit is probably not good enough to justify definite conclusions about adherence to Vegard's law and ideality of melilite solid solutions. It is clear, nevertheless, that no large departure from ideality exists.

The deviation of Warren's values for a and c is outside of the experimental error. That is, his value of 7.74 Å for a indicates about 25% akermanite while his value for c is equal to that for pure akermanite. Some of Warren's intensities deviate very markedly from those found for the gehlenite-akermanite series. Inasmuch as Warren used a crystal of natural melilite which would contain other ions in addition to those present in akermanite and gehlenite, the explanation for these differences is undoubtedly related to the presence of these other ions.* An analysis of the structures of pure gehlenite and akermanite might result in a change in some of the coordinates and interatomic distances but probably not in any of the fundamental features of the structure.

The seemingly remarkable decrease in the c dimension which accompanies the increase in a on going from gehlenite to akermanite has a simple explanation on the basis of Warren's structure. Close study of the structure (5), (7), shows that in the 001 plane the atoms are in close contact in the planes passing through the Mg positions. In the c direction, however there are gaps in the structure in the axes passing through the Mg positions. Consider now the effect of substituting Mg+Si for 2Al. In the first place, the a dimension should be increased by an amount approximating the difference between the increase in ionic radius of Mg over Al and the decrease in ionic radius of Si over Al, because of the close packing in the a direction. A purely geometrical calculation based on the ionic radii given by Evans (8), corrected for fourfold coordination, gives an increase of 0.23 Å for a as compared with 0.152 Å actually observed. The effect of the larger Mg ion on c, however, is nullified by the presence

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* The melilite crystal used by Warren was from Capo di Bove. The composition of a representative melilite from this locality analyzed by Damour and discussed by Schaller (*U. S. Geol. Survey, Bull.* **610**, 124 (1916)) is as follows: 38.34 SiO_2, 8.61 Al_2O_3, 32.05 CaO, 2.12 Na_2O, 6.71 MgO, 10.02 Fe_2O_3, 1.51 K_2O. It is considered possible by Schaller that a part of the iron existed in the melilite in the ferrous state.

of the gaps in the structure between the Mg ions in the c direction, into which the oxygen ions surrounding the Mg can move without expanding the cell dimensions in that direction. Thus the only effect is the contraction due to substitution of Si for Al which is calculated as 0.14 Å compared with 0.057 Å actually found. The lack of a quantitative check could be due to polarization effects, which have not been taken into account.

Densities calculated from these unit cell dimensions are compared below with the experimental values determined by Ferguson and Buddington (1):

	gehlenite	akermanite
Calculated density	3.031 ± 0.01	2.922 ± 0.01
Experimental density	3.038	2.944

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