

The system diopside-anorthite-åkermanite.

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[Taken as read 23 January 1958.]

Summary. The high-temperature phase equilibrium relationships in the system diopside-anorthite-åkermanite have been investigated by the quenching method. This system may be regarded as essentially a simple eutectic system. The eutectic is located at the composition 9 diopside:44 anorthite:47 åkermanite (by weight) and at a temperature of 1226° C. Åkermanite is a stable phase at least as low as this temperature. Triclinic anorthite is the only form of $\text{CaAl}_2\text{Si}_2\text{O}_8$ encountered in the liquidus range of temperatures.

ONE of the most important four-component systems for the consideration of petrological and technological problems is the system lime-magnesia-alumina-silica. Much work has already been done on various portions of this system. Considerable work remains to be done before the relations in the system are fully understood.

The present investigation concerns the system diopside($\text{CaMgSi}_2\text{O}_6$)-anorthite($\text{CaAl}_2\text{Si}_2\text{O}_8$)-åkermanite($\text{Ca}_2\text{MgSi}_2\text{O}_7$), which constitutes a plane in the lime-magnesia-alumina-silica tetrahedron. Diopside, anorthite, and åkermanite are end-members in the important mineral solid-solution series pyroxene, plagioclase, and melilite, respectively. A number of investigators, including McCaffery, Oesterle, and Schapiro (1927), Janecke (1933), Nurse and Midgley (1951), Osborn, de Vries, Gee, and Kraner (1954), and Prince (1954), have indicated that pyroxene, anorthite, and melilite form a stable equilibrium phase-assembly. But no systematic study of the liquidus relations for the diopside-anorthite-åkermanite system has thus far been carried out.

The system diopside-anorthite has been studied by Bowen (1916) and by Osborn (1942). The diagrams resulting from these two studies are in essential agreement. Osborn, however, proposes a small departure from the true binary behaviour depicted by Bowen, because of the slightly aluminous character of the diopside. The diopside and anorthite liquidus curves meet at a composition of 42 anorthite:58 diopside, and a temperature of 1274° C.

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The diagram for the system diopside-åkermanite, as presented by Ferguson and Merwin (1919), is that of a simple binary system. The eutectic lies at the composition 42 åkermanite:58 diopside. The eutectic temperature was not specified, but appears from their diagram to be about 1365° C.

The anorthite-åkermanite system has recently been investigated by De Wys and Foster (1956). The liquidus relationships suggested a simple binary system, with the eutectic located at the composition 46 anorthite:54 åkermanite, and at a temperature of 1234° C. No evidence in support of the claim that åkermanite becomes unstable below 1325° C. (Osborn and Schairer, 1941) was encountered. It was also concluded that the tendency of åkermanite to abstract alumina from anorthite-åkermanite compositions to yield a melilite solid solution is negligible.

The foregoing investigations furnished the necessary liquidus data for the three limiting sides of the system diopside-anorthite-åkermanite. They also provided index of refraction measurements on the homogeneous glasses of each of the limiting systems. In addition, they yielded reliable values for the melting-points of the three compounds involved in the present study. These melting temperatures are: diopside, 1391.5° C.; anorthite, 1553° C.; and åkermanite, 1454° C.

Methods.

Thirty compositions were selected for the determination of the liquidus relations of the system under investigation. In each case a homogeneous glass was prepared from high-purity CaCO_3 , MgO , Al_2O_3 , and SiO_2 . Each mixture was rendered uniform by three fusions, each of which was followed by quenching in water, and by fine grinding of the resulting glass. The mixtures were fused in graphite crucibles in an Ajax-Northrup induction furnace. Previous tests on a number of mixtures with known liquidus temperatures had demonstrated that this method led to no detectable departures from the calculated compositions. A portion of each of the thrice-fused glasses was heated for 1-48 hours in a platinum crucible in the temperature range 900°-1200° C., in order to effect substantial devitrification.

The high-temperature equilibrium relations were determined by the quenching method outlined by Shepherd, Rankin, and Wright (1909). This method involves wrapping about 10 mg. of devitrified glass powder in platinum foil, and holding it at a selected temperature in a platinum-wound furnace for a time sufficient to ensure equilibrium. By quenching

the charge in mercury, the phases representing the equilibrium condition at the selected high temperature are retained at room temperature. The polarizing microscope, aided in selected instances by X-ray diffraction analysis, permits the ready identification of these phases.

Since the silicate liquids formed from these mixtures were moderately fluid, prolonged runs were not required to establish equilibrium in the charges. The individual runs varied, in length of time, from 30 to 50 minutes. Liquidus temperatures were established by bracketing between two temperatures 4° C. apart, one above and one below the actual liquidus. At suitable intervals the platinum: platinum-rhodium (10 % Rh) thermocouple was calibrated against the following reference melting-points: gold, 1063° C.; diopside, 1391.5° C.; and pseudowollastonite, 1544° C.

The optical constants of the three crystalline phases, diopside, anorthite, and åkermanite, as well as of their homogeneous glasses, are accurately known from previous investigations. It will suffice here to present only those characteristics which served to distinguish these phases from each other in the quenched charges.

Glasses. The index of refraction chart for glasses in the system diopside-anorthite-åkermanite is presented in fig. 1. A tentative chart of this type was immediately available by joining appropriate index values of the three limiting systems previously investigated. As each of the 30 glasses was prepared, its composition and homogeneity could be checked by reference to this chart. At the same time, the essential validity of the tentative chart was confirmed.

Diopside was readily distinguished from anorthite and åkermanite by its decidedly higher indices of refraction. Moderately high birefringence and a tendency to form lath-like elongated crystals, exhibiting large (40° maximum) extinction angles, were also characteristic. Positive relief with respect to the glassy matrix was shown in every instance.

Crystals of *anorthite* occurred usually as fine needles which invariably possessed lower indices of refraction than the enclosing glass. Inclined extinction as high as 40° was observed on these needles; interference colours did not exceed first order grey or white. In every instance the primary crystals appeared to be triclinic anorthite; the hexagonal and orthorhombic forms described by Davis and Tuttle (1952) and by Goldsmith and Ehlers (1952) were not encountered.

Åkermanite formed more or less equidimensional crystals with a pronounced tendency towards a blocky outline. Such blocky crystals displayed parallel extinction. The maximum interference colours observed

were grey-white. Like diopside, åkermanite showed positive relief against the surrounding glass.

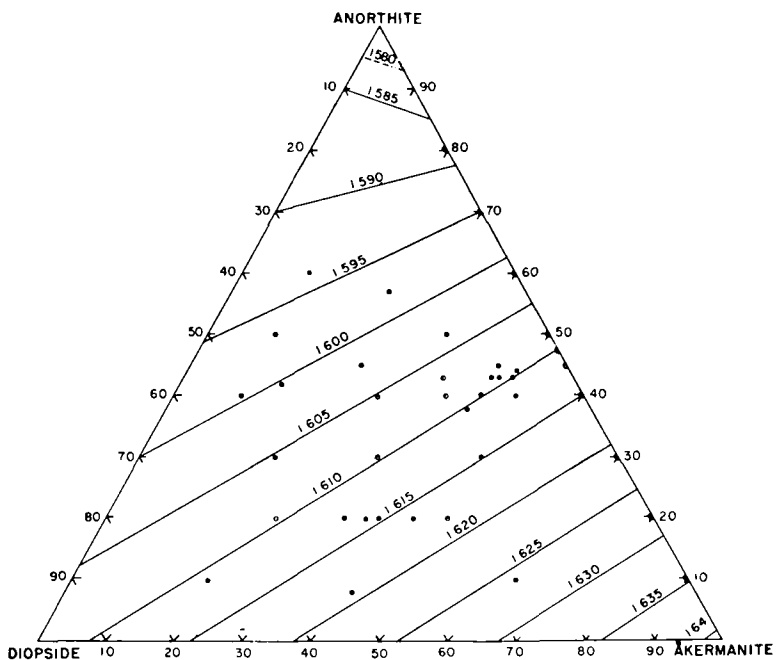


FIG. 1. Isofract diagram for glasses of the system diopside-anorthite-åkermanite (weight %).

Results.

Quenching data for the thirty selected compositions involved in the present study are presented in table I. For convenience, the data are arranged according to the identity of the primary phase obtained in the quenched charges. Only those runs which furnished limiting values of the liquidus temperatures have been included.

The data presented in table I were used to construct the phase diagram shown as fig. 2. Each of the compounds diopside, anorthite, and åkermanite is seen to possess a large primary phase area. It was concluded by de Wys and Foster (1956) that åkermanite had little if any tendency to abstract alumina from anorthitic mixtures to yield a gehlenite-bearing melilite. Such an effect, had it occurred, would cause a departure from ternary behaviour in the present system. According to the work of Osborn (1942), the diopside encountered in the diopside-anorthite

TABLE I. Thermal data for the system diopside-anorthite-åkermanite.

Weight %			Time (min.)	Temp. ° C.	Final condition*	Weight %			Time (min.)	Temp. ° C.	Final condition*
Di	An	Åk				Di	An	Åk			
<i>Primary phase diopside</i>						<i>Primary phase anorthite</i>					
50	40	10	30	1274	Gl	40	50	10	30	1312	Gl
			30	1270	Di, gl				30	1308	An, gl
43	42	15	30	1264	Gl	30	60	10	30	1382	Gl
			30	1260	Di, gl				30	1378	An, gl
70	10	20	30	1350	Gl	20	57	23	30	1342	Gl
			30	1346	Di, gl				30	1338	An, gl
50	30	20	30	1292	Gl	30	45	25	30	1266	Gl
			30	1288	Di, gl				30	1262	An, gl
55	20	25	45	1318	Gl	15	50	35	30	1284	Gl
			40	1314	Di, gl				30	1280	An, gl
30	40	30	30	1260	Gl	10	45	45	30	1240	Gl
			30	1256	Di, gl				30	1236	An, gl
45	20	35	40	1308	Gl	<i>Primary phase åkermanite</i>					
			30	1304	Di, gl	35	20	45	30	1308	Gl
35	30	35	30	1278	Gl				30	1304	Åk, gl
			30	1274	Di, gl	15	40	45	45	1240	Gl
42	20	38	30	1304	Gl				30	1236	Åk, gl
			40	1300	Di, gl	9	43	48	30	1230	Gl
19	43	38	30	1246	Gl				30	1226	Åk, gl
			30	1242	Di, gl	30	20	50	40	1318	Gl
30	38	32	30	1264	Gl				50	1314	Åk, gl
			30	1262	Di, gl	20	30	50	30	1288	Gl
40	20	40	30	1308	Gl				30	1284	Åk, gl
			40	1302	Di, gl	10	40	50	30	1254	Gl
20	40	40	30	1248	Gl				30	1250	Åk, gl
			40	1244	Di, gl	25	10	65	30	1380	Gl
50	8	42	30	1340	Gl				30	1376	Åk, gl
			30	1336	Di, gl	<i>Eutectic horizontal</i>					
18	38	44	40	1224	Gl	11	43	46	40	1228	Di, gl
			30	1240	Di, gl				30	1224	Di, An,
12	43	45	30	1234	Gl						Åk
			30	1230	Di, gl	10	45	45	30	1228	An, gl
11	43	46	50	1230	Gl				30	1224	Di, An,
			30	1226	Di, gl						Åk
						8	44	48	30	1228	Gl
									30	1224	Di, An,
											Åk

*Di, diopside; An, anorthite; Åk, åkermanite; Gl, glass.

system was slightly aluminous. The deviation from binary behaviour resulting therefrom would carry over unavoidably into the system diopside-anorthite-åkermanite. Since such a deviation would be only slight the present system may for all practical purposes be regarded as a simple ternary eutectic system.

Because of the simplicity of the system, the liquidus data on the thirty compositions studied were sufficient to permit the approximate location of the isotherms and boundary curves, as shown in fig. 2.

The boundary curves come together at the approximate composition 9 diopside:44 anorthite:47 åkermanite, and at a temperature which has been located at 1226° C. As suggested above, this intersection point may be regarded as essentially a ternary eutectic. It is significant that no

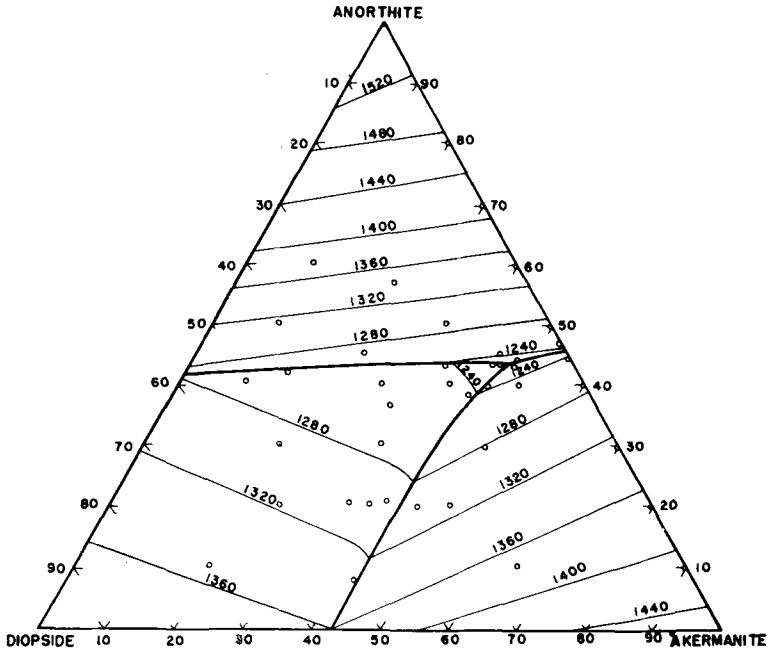


FIG. 2. Equilibrium diagram for the system diopside-anorthite-åkermanite, showing isotherms (weight %).

additional primary fields, which might reasonably be expected on the basis of the alleged instability of åkermanite below 1325° C., are found to occur in this system.

Discussion.

The experimental data of this study indicate that diopside, anorthite, and åkermanite form essentially a simple ternary system in the liquidus range of temperatures. Thus, a new plane has been added to those already known to participate in the subdivision of the system lime-magnesia-alumina-silica into subsystems. These data cannot fully explain the relationships between the pyroxenes, the plagioclase feldspars, and the melilites. However, a knowledge of this system serves to fill one of the existing gaps in our understanding of them.

The system sheds some light on the problem of the stability of åkermanite. It has long been held that åkermanite becomes unstable below 1325° C. (Osborn and Schairer, 1941). This claim is at variance with earlier work (Taylor and Williams, 1935) which recorded the solid-state synthesis of åkermanite in the temperature range 800–1200° C. Recently Nurse and Midgley (1953) and de Wys and Foster (1956) have reported studies purporting to show that åkermanite does not become unstable on cooling below 1325° C. The present study lends added support to these latter claims: åkermanite was found to crystallize from appropriate liquids of the system diopside–anorthite–åkermanite at least 100° C. below the alleged stability limit; if åkermanite were unstable in the liquidus range of temperatures of this system, the primary field of some phase or phases other than diopside, anorthite, and åkermanite might have been expected; no such additional phase was encountered.

The present study was incapable of disclosing the equilibrium relationships existing well below the eutectic. It is of interest in this connexion that subliquidus studies by Harker and Tuttle (1956) have shown that below about 700° C. åkermanite breaks down into wollastonite and monticellite. At the same time their results confirm rather than contradict those of this investigation. Thus, although Harker and Tuttle indicate that åkermanite possesses a low-temperature stability limit, their results confirm the stability of this phase above 700° C. Belief in its inherent instability on passing below 1325° C. must therefore be discarded.

The results of Harker and Tuttle are of further interest in connexion with the present study. They indicate that the system diopside–anorthite–åkermanite may exist as a dividing plane in the lime–magnesia–alumina–silica tetrahedron only above 700° C. Indeed, they suggest that all phase diagrams depicting the coexistence of åkermanite with other crystalline phases are valid only above 700° C., unless the intervention of solid solution phenomena lowers this limit. It would therefore appear that such additional diagrams as that of the anorthite–åkermanite system (de Wys and Foster, 1956) and the central portion of the lime–magnesia–silica system (Ferguson and Merwin, 1919; Ricker and Osborn, 1954) are valid only above 700° C.

No further data on the interrelationships between the hexagonal, orthorhombic, and triclinic forms of $\text{CaAl}_2\text{Si}_2\text{O}_8$ were obtained. Only the triclinic form, anorthite, was found to crystallize from the liquids of this system.

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