# Subsolidus data for the join $Ca_2SiO_4$—$CaMgSiO_4$ and the stability of merwinite.[1]

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*Summary.*—A study of phase equilibria among the orthosilicates on the $Ca_2SiO_4$—$CaMgSiO_4$ join was undertaken with the use of hydrothermal techniques in the temperature range 600–900° C. at water pressures from 1000 to 15000 psi.[2] Monticellite, merwinite, and $Ca_2SiO_4$ crystallize as pure phases throughout this temperature range, and intermediate compositions contain mixtures of the end members. Powder X-ray diffraction data obtained on the mixtures indicate no change in lattice dimensions from the end members. Hence, very little or no solid solution is indicated at these temperatures. $Ca_2SiO_4$ was crystallized as the $\gamma$-form below 675° C. (at 2000 psi) and the $\beta$-form above this temperature (presumably having inverted from the $\alpha'$-form on cooling to room temperature). Infra-red absorption spectra obtained on the compounds $\gamma$-$Ca_2SiO_4$, $\beta$-$Ca_2SiO_4$, merwinite, and monticellite show characteristic differences in the pattern within the 9–13 micron region. All the data thus appear to confirm merwinite as a unique compound stable in the temperature range studied.

ONE of the most elusive problems within the complex system CaO—MgO—$SiO_2$ has been the determination of the equilibria on the orthosilicate join $Ca_2SiO_4$—$Mg_2SiO_4$. On the basis of similarity in crystal structure, partial or complete solid solution might be expected between forsterite and monticellite, and similarly between monticellite and $\gamma$-$Ca_2SiO_4$, all of which possess the olivine structure. When O'Daniel (1942) assigned the olivine structure to $\gamma$-$Ca_2SiO_4$ he predicted that extensive solid solution should exist between $\gamma$-$Ca_2SiO_4$ and monticellite; and Bredig (1950) later suggested that this solid solution should be continuous. Recent work of Ricker and Osborn (1954) on the subsolidus region of the join $CaMgSiO_4$—$Mg_2SiO_4$ has shown that a solid solution series extends to a maximum of about 30 weight % from each compound at solidus temperatures, but the amount of solid solution decreases rapidly with decrease in temperature.

The presence of the intermediate compound merwinite ($Ca_3MgSi_2O_8$)

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[2] Pounds per square inch; this contraction is used throughout this paper.

must be explained, however, for it is a naturally occurring mineral (Larsen and Foshag, 1921), and has been shown by Phemister *et al.* (1942) and by Osborn (1943) to be a unique (incongruently melting) compound having a stability field in the system $CaO$—$MgO$—$SiO_2$. The presence of merwinite on the join $Ca_2SiO_4$—$CaMgSiO_4$ was explained by Bredig (1950) as a composition in the $\alpha'$ solid solution series, i.e. he considered merwinite to be merely an end point in a solid solution series extending from $\alpha'$–$Ca_2SiO_4$[1] to the composition $Ca_3MgSi_2O_8$. Complete solid solution was presumed by Bredig to exist between the lower temperature polymorph ($\gamma$–$Ca_2SiO_4$) and monticellite. However, the possibility of a complete solid solution series between $\gamma$–$Ca_2SiO_4$ and monticellite, as well as the proposed $\alpha'$–$Ca_2SiO_4$—merwinite solid solution series, was considered unlikely by Ricker and Osborn (1954) on the basis of theoretical considerations. A recent summary of the current knowledge on the chemistry and polymorphism of $Ca_2SiO_4$ is that of Nurse (1954), who believed that single-crystal X-ray data and powder X-ray data obtained at elevated temperatures favour the designation of monoclinic merwinite as a distinct compound, not a solid solution of orthorhombic $\alpha'$–$Ca_2SiO_4$. Bredig (1954, see Nurse, 1954), in discussion of the above paper, suggested that merwinite (monoclinic, pseudo-orthorhombic) may be considered to be a 'fifth polymorphous form of calcium orthosilicate, related to $\alpha'$, and stabilized by large amounts of $Mg_2SiO_4$', presumably formed on cooling from high temperatures.

The present study was undertaken with the application of hydrothermal techniques in order to aid crystallization and in the hope of attaining equilibrium at subsolidus temperatures. It was hoped to establish more positively the character of merwinite and its equilibrium relations with the other orthosilicates, as well as to obtain new information on the polymorphism of $Ca_2SiO_4$.

*Experimental procedure*

Briefly, the experimental procedure was as follows: One or more samples contained in individual gold envelopes in a bomb were quickly brought up to the desired temperature. Water was pumped into the

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[1] The complexity of the relations among polymorphic forms of $Ca_2SiO_4$ is, of course, involved in the equilibria; recent papers of Newman and Wells (1946), Van Valkenburg and McMurdie (1947), Trömel (1949), Trömel and Möller (1949), and Bredig (1950) give evidence of four polymorphic forms, from the highest to lowest temperature, respectively, hexagonal $\alpha$, orthorhombic $\alpha'$, monoclinic $\beta$, and the olivine $\gamma$. Bredig (1950) has further suggested that the $\beta$-modification is only metastable.

bomb through pressure tubing to reach the desired water pressure. The bomb was then heated at this regulated pressure and temperature for a period varying from a few hours to several days. Most runs were made at low pressures, about 2000 psi, in an attempt to avoid entering an area of hydrate stability in the $Ca_2SiO_4$-rich mixtures. After completion of the run the water pressure was released to zero and after $\frac{1}{2}$ to 1 minute the bomb was quenched in water. The samples were examined by X-ray diffraction and the petrographic microscope, and in a few cases infra-red absorption spectra were obtained.

The hydrothermal equipment used was similar to that described by Roy, Roy, and Osborn (1950), and Roy and Osborn (1952). Stellite 'test-tube' bombs were used almost exclusively, and the water pressure was released just before quenching, as described above, in order to prevent hydrate formation during heating or cooling. A few 'dry' runs were made in a Pt-wound quenching furnace.

Starting materials used included mixed $CaCO_3$, $MgCO_3$, and silicic acid reacted at high temperatures, but most frequently a type of mixture which is much more intimate and almost 'amorphous to X-rays', prepared in the following manner: weighed amounts of $CaCO_3$ and MgO (or $MgCO_3$) were dissolved in dilute $HNO_3$ and added to an excess of absolute alcohol. Ethyl orthosilicate was measured out with a burette and dissolved in alcohol and the two solutions mixed, evaporated at 110° C., then heated to about 400° C. for a few hours, then to 700° to 900° C. over-night. Chemical analyses of the final products were not made, but compounds formed from stoichiometric ratios were found to be quite free from other phases when studied microscopically or by X-ray diffraction.[1]

## Results and discussion.

A summary of pertinent hydrothermal quenching data is given in table I, indicating phases present as detected by a combination of X-ray diffraction and optical data. The results are represented diagrammatically in fig. 1, which shows the phases present at the various temperatures in equilibrium with $H_2O$ at a constant pressure of 2000 psi. The three orthosilicate compounds $Ca_2SiO_4$, $Ca_3Mg(SiO_4)_2$, and $CaMgSiO_4$ crystal-lize as unique phases in the temperature range studied, 600–1000° C., and intermediate compositions show a mixture of monticellite and merwinite in the one case, and in the other a mixture of merwinite and $Ca_2SiO_4$ (the $\gamma$-form below 675° C. and $\beta$ above).[2] Runs made at temperatures as low

[1] Mixtures of CaO or $CaCO_3$ and silica gel were found to be less satisfactory with respect to attainment of equilibrium.

[2] New information obtained on the polymorphism of $Ca_2SiO_4$ is the subject of a separate paper to be published soon. Briefly, the data obtained using 'amorphous' starting materials inbicate that $\gamma$–$Ca_2SiO_4$ crystallizes below 675° C. (at 2000 psi) and that $\beta$ forms above this temperature. The $\beta$–$Ca_2SiO_4$, however, is probably

TABLE I.
Summary of hydrothermal quenching data for the join $Ca_2SiO_4$—$CaMgSiO_4$.

The pressure was 2000 psi except for the runs at 475° C., for which it was 15 000 psi, and at 1472° and 1455°, for which it was atmospheric.

Abbreviations used: X = $Ca_2SiO_4$-hydrate, not completely identified.
$C_2S$ = $Ca_2SiO_4$; tr. = trace; Mer. = Merwinite; Mont. = Monticellite.

| Mol. % $Ca_2SiO_4$. | Temp. ° C. | Time hrs. | Phases present. |
|---|---|---|---|
| 100 | 640 | 24 | $\gamma$–$C_2S$+tr. X |
| 100 | 662 | 48 | $\gamma$–$C_2S$+some X |
| 100 | 670 | 96 | $\gamma$–$C_2S$+$\beta$–$C_2S$+some X |
| 100 | 685 | 48 | $\beta$–$C_2S$+X |
| 100 | 705 | 24 | Mostly $\beta$–$C_2S$ |
| 100 | 870 | 24 | $\beta$–$C_2S$ |
| 100 | 1472 | 20 | $\gamma$–$C_2S$ on quench |
| 75 | 655 | 96 | Mer.+$\gamma$–$C_2S$+X |
| 75 | 665 | 72 | Mer.+$\gamma$–$C_2S$+tr. X |
| 75 | 685 | 48 | Mer.+$\gamma$–$C_2S$+$\beta$–$C_2S$ |
| 75 | 743 | 24 | Mer.+$\beta$–$C_2S$ |
| 75 | 885 | 96 | Mer.+$\beta$–$C_2S$ |
| 50 | 475 | 168 | Mont.+hydrate |
| 50 | 625 | 96 | Mer.+tr. Mont.? |
| 50 | 645 | 24 | Mer. |
| 50 | 650 | 96 | Mer. |
| 50 | 744 | 120 | Mer. |
| 50 | 870 | 20 | Mer. |
| 50 | 1472 | 20 | Mer. |
| 25 | 655 | 96 | Mont.+Mer. |
| 25 | 750 | 24 | Mont.+Mer. |
| 25 | 850 | 72 | Mont.+Mer. |
| 0 | 475 | 168 | Mont. |
| 0 | 610 | 72 | Mont. |
| 0 | 705 | 24 | Mont. |
| 0 | 860 | 24 | Mont. |
| 0 | 1455 | 2 | Mont. |

as 475° C. at 15 000 psi indicated that monticellite is stable under these conditions. Merwinite was not formed at 475° C. and 15 000 psi from an 'amorphous' mixture of the merwinite composition, which gave a mixture of monticellite and a dicalcium silicate hydrate. This is not positive evidence, however, that merwinite is no longer stable under these conditions.

formed only metastably, through a fairly rapid inversion on cooling, from $\alpha'$–$Ca_2SiO_4$. A further complication is the formation of a small amount of a lime-silica hydrate below about 700° C., both in pure $Ca_2SiO_4$ mixtures and the 75 mol. % $Ca_2SiO_4$ mixture.

Within the experimental error, the transition temperature from $\gamma$ to $\alpha'$ Ca$_2$SiO$_4$ is unchanged in the 75 mol. % Ca$_2$SiO$_4$ mixtures from that for pure Ca$_2$SiO$_4$, i.e. $675 \pm 10°$ C. at 2000 psi. The $d$-spacings of phases present in the intermediate mixture show no change (within the experimental error of $\pm 0.02°$ in $2\theta$) from those of the pure components Ca$_2$SiO$_4$ and merwinite. There is similarly no change in the spacings of merwinite and monticellite found in the 25 mol. % Ca$_2$SiO$_4$ mixture from those of the pure end-members.

Measurements from typical X-ray diffraction patterns of the end member compounds and intermediate compositions are given in table II. Most of these data were obtained with less than maximum precision in recording, but they demonstrate clearly that the intermediate compositions contain mixtures of the end-members, not an intermediate solid solution. More precise measurements obtained with slower speed of recording of a few selected reflections, which are diagnostic,[1] and in which there is no shift due to overlapping of peaks, demonstrate that very little, if any, solid solution exists among the various compounds and polymorphs.

Although the crystals formed, especially at low temperatures, are too small for accurate determination of optical properties, the differences in index of refraction are distinctive. The low index ($c$. 1·644) crystals of monticellite stand out clearly against the higher index ($c$. 1·700) merwinite crystals in the mixture with 25 mol. % Ca$_2$SiO$_4$, and the low index ($c$. 1·650) $\gamma$–Ca$_2$SiO$_4$
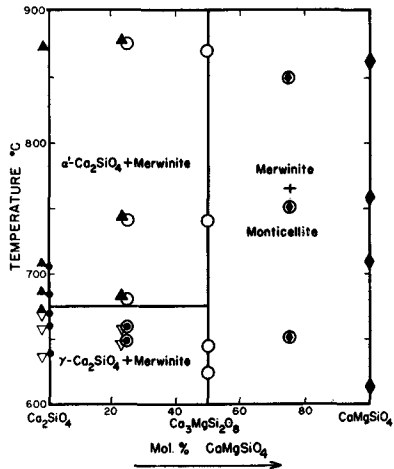


FIG. 1. Subsolidus phase equilibrium diagram for the join Ca$_2$SiO$_4$—CaMgSiO$_4$ at a water pressure of 2000 psi. Symbols used: $\bigcirc$ = merwinite, $\blacklozenge$ = monticellite, $\nabla$ = $\gamma$–Ca$_2$SiO$_4$, $\blacktriangle$ = $\alpha'$–Ca$_2$SiO$_4$ (inverted to $\beta$ at room temperature), $\bullet$ = hydrate.

[1] Peaks at $2\theta$ values (Cu-$K\alpha$) of 50·10° and 30·405° for monticellite, at 34·35°, 32·60°, 32·02°, and 32·16° for $\beta$–Ca$_2$SiO$_4$, at 32·86° and 29·715° for $\gamma$–Ca$_2$SiO$_4$, and at 48·445°, 33·78°, and 33·43° for merwinite were unchanged within the experimental error of $\pm 0.03°$ in $2\theta$ in intermediate compositions showing mixtures of merwinite plus one of the other phases.

TABLE II. X-ray diffraction data for phases on the $Ca_2SiO_4$—$CaMgSiO_4$ join. Spacings measured on Norelco High-angle diffractometer using filtered Cu radiation.

| $\beta$-$Ca_2SiO_4$ | | $\gamma$-$Ca_2SiO_4$ | | $\gamma$-$Ca_2SiO_4$ + Merwinite | | $\beta$-$Ca_2SiO_4$ + Merwinite | | Merwinite | | Merwinite + Monticellite | | Monticellite | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ |
| 3·807 | 0·05 | 5·62 | 0·2 | 5·62 | 0·05 | 3·818 | 0·02 | 3·883 | 0·05 | 5·55 | 0·05 | 5·56 | 0·1 |
| 3·381 | 0·05 | 4·33 | 0·4 | 4·33 | 0·1 | 2·876 | 0·3 | 3·633 | 0·05 | 5·12 | 0·02 | 4·19 | 0·3 |
| 3·243 | 0·1 | 4·058 | 0·3 | 3·824 | 0·3 | 2·790 | 0·7 | 3·340 | 0·1 | 4·20 | 0·1 | 3·640 | 0·8 |
| 3·048 | 0·05 | 3·821 | 0·5 | 3·345 | 0·2 | 2·782 | 0·7 | 3·173 | 0·1 | 3·898 | 0·05 | 3·192 | 0·4 |
| 2·876 | 0·1 | 3·014 | 1·0 | 3·043 | 0·3 | 2·744 | 0·8 | 2·868 | 0·1 | 3·645 | 0·4 | 2·939 | 0·4 |
| 2·791 | 1·0 | 2·898 | 0·1 | 3·010 | 0·35 | 2·730 | 0·5 | 2·749 | 0·2 | 3·326 | 0·4 | 2·771 | 0·05 |
| 2·783 | 0·9 | 2·840 | 0·2 | 2·990 | 0·1 | 2·722 | 0·5 | 2·682 | 1·0 | 3·199 | 0·1 | 2·676 | 1·0 |
| 2·746 | 0·9 | 2·750 | 0·1 | 2·780 | 0·1 | 2·681 | 1·0 | 2·675 | 0·9 | 3·169 | 0·05 | 2·598 | 0·6 |
| 2·726 | 0·4 | 2·750 | 0·9 | 2·750 | 0·4 | 2·671 | 0·9 | 2·652 | 0·3 | 3·052 | 0·05 | 2·546 | 0·15 |
| 2·607 | 0·4 | 2·728 | 1·0 | 2·726 | 0·3 | 2·655 | 0·2 | 2·618 | 0·02 | 2·997 | 0·05 | 2·404 | 0·3 |
| 2·545 | 0·1 | 2·686 | 0·1 | 2·685 | 1·0 | 2·609 | 0·3 | 2·589 | 0·05 | 2·940 | 0·25 | 2·359 | 0·05 |
| 2·449 | 0·05 | 2·589 | 0·1 | 2·660 | 0·1 | 2·547 | 0·1 | 2·398 | 0·05 | 2·873 | 0·1 | 2·213 | 0·1 |
| 2·406 | 0·2 | 2·536 | 0·1 | 2·522 | 0·05 | 2·283 | 0·2 | 2·318 | 0·1 | 2·755 | 0·2 | 1·920 | 0·02 |
| 2·283 | 0·2 | 2·519 | 0·2 | 2·321 | 0·1 | 2·214 | 0·2 | 2·306 | 0·1 | 2·714 | 0·1 | 1·819 | 0·3 |
| 2·189 | 0·4 | 2·475 | 0·1 | 2·212 | 0·1 | 2·189 | 0·3 | 2·214 | 0·1 | 2·686 | 1·0 | 1·777 | 0·02 |
| 2·164 | 0·1 | 2·327 | 0·1 | 2·032 | 0·05 | 2·166 | 0·1 | 2·171 | 0·1 | 2·679 | 0·9 | 1·749 | 0·02 |
| 2·047 | 0·05 | 2·249 | 0·05 | 1·911 | 0·4 | 2·027 | 0·05 | 2·060 | 0·05 | 2·656 | 0·4 | 1·725 | 0·1 |
| 2·022 | 0·1 | 2·189 | 0·1 | 1·879 | 0·2 | 1·983 | 0·1 | 2·030 | 0·1 | 2·592 | 0·3 | 1·689 | 0·02 |
| 1·985 | 0·2 | 2·026 | 0·15 | 1·809 | 0·1 | 1·910 | 0·25 | 1·909 | 0·3 | 2·549 | 0·1 | 1·600 | 0·2 |
| 1·895 | 0·05 | 1·910 | 0·8 | 1·757 | 0·1 | 1·878 | 0·1 | 1·877 | 0·2 | 2·517 | 0·05 | 1·508 | 0·05 |
| 1·804 | 0·02 | 1·806 | 0·3 | 1·689 | 0·1 | 1·630 | 0·1 | 1·722 | 0·02 | 2·465 | 0·05 | 1·390 | 0·05 |
| 1·708 | 0·05 | 1·755 | 0·05 | 1·535 | 0·15 | 1·610 | 0·1 | 1·705 | 0·02 | 2·405 | 0·1 | — | — |
| 1·631 | 0·05 | 1·689 | 0·2 | — | — | 1·535 | 0·1 | 1·579 | 0·05 | 2·317 | 0·05 | — | — |
| 1·608 | 0·1 | 1·637 | 0·2 | — | — | 1·414 | 0·05 | 1·549 | 0·05 | 2·216 | 0·1 | — | — |
| 1·526 | 0·02 | — | — | — | — | — | — | 1·535 | 0·1 | 2·173 | 0·05 | — | — |
| 1·486 | 0·02 | — | — | — | — | — | — | — | — | 2·029 | 0·3 | — | — |
| — | — | — | — | — | — | — | — | — | — | 1·912 | 0·2 | — | — |
| — | — | — | — | — | — | — | — | — | — | 1·882 | 0·05 | — | — |
| — | — | — | — | — | — | — | — | — | — | 1·781 | 0·05 | — | — |
| — | — | — | — | — | — | — | — | — | — | 1·752 | 0·05 | — | — |
| — | — | — | — | — | — | — | — | — | — | 1·724 | 0·05 | — | — |
| — | — | — | — | — | — | — | — | — | — | 1·602 | 0·05 | — | — |
| — | — | — | — | — | — | — | — | — | — | 1·535 | 0·05 | — | — |

crystals are distinct from those of merwinite in the 75 mol. % $Ca_2SiO_4$ mixture treated below 675° C. The higher index $\beta$-$Ca_2SiO_4$ crystals, formed in the latter mixture just above 675° C., are not easily distinguished optically from those of merwinite, but the X-ray diffraction
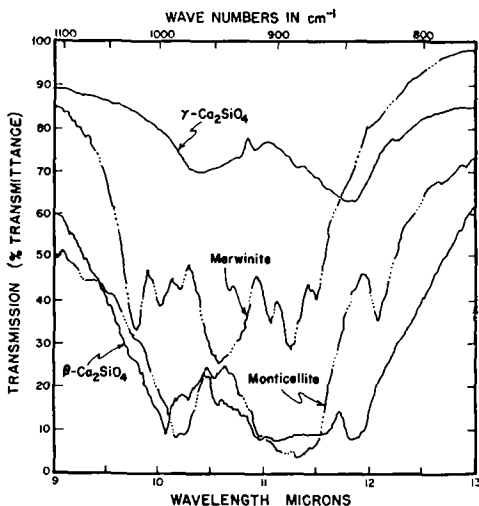


FIG. 2. Infra-red absorption spectra. Monticellite and $\beta$ $Ca_2SiO_4$ obtained using 0·4 % concentration in KBr pellet, merwinite 0·2 % in KBr; $\gamma$–$Ca_2SiO_4$ obtained from 'Nujol' mull on NaCl plates.

patterns of the two phases are readily identified in mixtures, as has been demonstrated above.

Another diagnostic property of these phases was the infra-red absorption spectrum. Spectra were obtained on the Perkin–Elmer model 21 double-beam instrument, using both the 'Nujol' mull technique and pressed KBr pellets.[1] Typical spectra of $\gamma$ $Ca_2SiO_4$, $\beta$-$Ca_2SiO_4$, merwinite and monticellite are shown in fig. 2. The diagnostic portion is mainly within the 9·5–12·5 micron range, although spectra were obtained from 2 to 15 microns. The four phases are seen to be quite distinct in their infra-red absorption spectra, and even structurally similar monticellite and $\gamma$ $Ca_2SiO_4$ exhibit differences.

[1] Standard techniques of sample preparation for crystalline materials include the suspension of a few milligrams of the sample in a mull with a high-boiling paraffin oil such as 'Nujol', smeared between polished flat NaCl plates. The paraffin oil has a few sharp characteristic absorption bands, but an alternative method employs KBr, which is completely infra-red transparent, as a suspending medium. A small concentration of sample (0·2–2 %) is mixed with finely ground KBr and pressed under a hydrostatic load of about 100 000 psi into a flat disk.

Although the KBr method generally gives better and more easily reproducible spectra, the pattern shown for $\gamma$-$Ca_2SiO_4$ is that obtained by the 'Nujol' method. The pattern obtained from the KBr pellet in this case was diffuse, which may be the result of a pressure-inversion. The spectra obtained by the 'Nujol' and KBr methods were comparable in the other three substances, although the KBr spectra were more sharp, more easily reproducible, and had no interfering absorption maxima.

## Conclusions.

Studies of phase relations among $Ca_2SiO_4$, $Ca_3MgSi_2O_8$, and $CaMgSiO_4$ in the temperature range 600°–900° C. confirm the existence of each of these compositions as a unique compound in the system CaO—MgO—$SiO_2$. X-ray diffraction, optical and infra-red absorption data on crystalline material obtained in the hydrothermal runs all point to the conclusion that no appreciable solid solution exists among the phases in this temperature range.

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