# Melilite crystallization in the system CaO–MgO–Al$_2$O$_3$–SiO$_2$

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SUMMARY. The solidus temperatures (IPTS–68) and melilite compositions (mole %) determined for some four-phase assemblages in the system CaO–MgO–Al$_2$O$_3$–SiO$_2$ are: anorthite, diopside, spinel, melilite ($\text{Åk}_{81}\text{Geh}_{19}$), 1236·5 °C; diopside, spinel, forsterite, melilite ($\text{Åk}_{83}\text{Geh}_{17}$), 1238 °C; forsterite, spinel, monticellite, melilite ($\text{Åk}_{82}\text{Geh}_{18}$), 1351 °C; monticellite, merwinite, spinel, melilite ($\text{Åk}_{52}\text{Geh}_{48}$), 1378 °C; dicalcium-silicate, Ca$_5$MgSi$_3$O$_{12}$, spinel, melilite ($\text{Åk}_5\text{Geh}_{95}$), ca. 1412 °C; dicalcium-silicate, Ca$_6$MgAl$_8$SiO$_{21}$, spinel, melilite ($\text{Åk}_4\text{Geh}_{96}$), ca. 1347 °C.

MELILITES have a compositional range that crosses the quaternary system

$$\text{CaO–MgO–Al}_2\text{O}_3\text{–SiO}_2$$

from gehlenite to åkermanite. Melilite-bearing solid assemblages in the system have been revised by O'Hara and Biggar (1969a) and Biggar (1971). Data presented here, based on experimental results for compositions in the plane Ca$_3$Al$_2$O$_6$–MgO–SiO$_2$ define the melilite compositions in some of the solid assemblages.

The quenching technique and the preparation of coprecipitated gels, used as starting materials, have been described (Biggar and O'Hara, 1969a, b) except that the 1968 temperature scale is employed with secondary calibration points at the liquidus of lithium metasilicate (1208 °C) and of diopside (1395 °C) as suggested by Biggar (1972b). Published temperatures for which previous authors claimed an accuracy of better than ±3 °C are converted to the 1968 scale.

Values of $d_{211}$ for melilite solid solutions were determined by X-ray powder diffraction (Cr-$K\alpha$ radiation). Sodium chloride was added as an internal standard and six oscillations over the 211 melilite and 200 sodium chloride peaks were made. Values of $d_{211}$ were calculated assuming $d_{200}$ NaCl = 2·821 Å. Melilite compositions that differed by 0·0005 Å in $d_{211}$ were considered to be experimentally distinguishable.

*The stability of åkermanite.* A gel made up to be of åkermanite composition crystallized as åkermanite and merwinite at temperatures up to at least 1372 °C but was homogeneous melilite at 1427 °C (Table I). This behaviour is similar in nature to the appearance of pseudowollastonite below 1385 °C in a sample of åkermanite previously converted to glass (Schairer *et al.*, 1967). These results suggest that both laboratories had prepared starting materials that were slightly 'off-composition'. A series of isothermal sections of the system CaO–MgO–SiO$_2$ to explain these observations have been published (Biggar, 1972a). An important conclusion was that åkermanite solid solutions occupy an area in the ternary system that has a range of silica content giving rise to detectable changes in $d_{211}$ for different åkermanite solid solutions.

*The join åkermanite–gehlenite.* Systematic studies were not undertaken but a few experiments with 'gel' compositions were designed to obtain standards with which to relate $d_{211}$ to melilite composition. This was started before the range in values of $d_{211}$ of åkermanite in the alumina-free system $CaO–MgO–SiO_2$ was appreciated.

All compositions are expressed in mole %. In two of the samples, $Åk_{95}Geh_5$ and $Åk_{90}Geh_{10}$, traces of merwinite were present and the gels were assumed to be slightly silica-deficient. Homogeneous melilites were obtained from the compositions $Åk_{66\frac{2}{3}}Geh_{33\frac{1}{3}}$, $Åk_{33\frac{1}{3}}Geh_{66\frac{2}{3}}$ and $Geh_{100}$ (Table I). The melilite that coexists with a

TABLE I. *The join åkermanite–gehlenite*

| %Åk | %Geh | Starting material* | Temp. | Time | $d_{211}$ | Result |
|---|---|---|---|---|---|---|
|  |  | gel | 1372 °C | 17 days | $2·871_1$Å | Mel Merw |
|  |  | gel | 1427 | 3 | $2·870_0$ | Mel |
|  |  | glass† | 1427 | 3 | $2·870_7$ | Mel |
| 100 | 0 | gel | 1442 | 3 | $2·871_0$ | Mel Merw Liq |
|  |  | glass† | 1442 | 3 | $2·870_9$ | Mel Merw Liq |
|  |  | gel | 1455‡ | 4 | $2·872_3$ | Mel Liq |
|  |  | gel | 1459‡ | 0·5 |  | Liq |
| 95 | 5 | gel | 1372 | 17 | $2·869_7$ | Mel Merw |
| 90 | 10 | gel | 1371 | 21 | $2·867_8$§ | Mel Merw |
| 66⅔ | 33⅓ | gel | 1382 | 15 | $2·861_6$§ | Mel |
| 33⅓ | 66⅔ | gel | 1400 | 15 | $2·852_7$§ | Mel |
| 0 | 100 | gel | 1581 | 0·8 | $2·845_6$§ | Mel |

* The possibility that 'gel' starting materials nucleated metastable phases that did not subsequently react was checked by totally melting some samples and quenching. The product was glass, which was reloaded side by side with a second capsule containing a sample of the 'gel'. The greatest discrepancies between these starting materials is in the values of $d_{211}$ in samples quenched from 1427 °C.

† Prepared at 1468 °C for 2 days.

‡ Osborn and Schairer quote 1454 °C, equivalent to 1458 °C (IPTS–68).

§ Values used subsequently to assign melilite compositions in the system $CaO–MgO–Al_2O_3–SiO_2$.

silica-rich phase differs in silica content from that coexisting with a silica-poor phase. For åkermanite solid solutions differences in values of $d_{211}$ are as much as 0·0023 Å, which is more than four times the precision of measurement. It is not possible to use $d_{211}$ or other X-ray data to determine melilite composition. For ease in discussion of melilite crystallization, however, melilite compositions in mole % Åk will be assigned using an entirely arbitrary linear interpolation between selected values of $d_{211}$ (Table I, footnote). This method in effect ignores variation in silica content but is probably a fair assessment of $2Al^{3+}$ substitution for $Mg^{2+}+Si^{4+}$.

The melilite join in the system $CaO–MgO–Al_2O_3–SiO_2$ is shown in fig. 1 as a cylindrical volume to represent its range of silica content. Abbreviations are listed in the legend to fig. 1. The stable joins anorthite–spinel and diopside–spinel are shown above the melilite volume. Stable joins from spinel to each of forsterite, monticellite, merwinite, $Ca_5MgSi_3O_{12}$, dicalcium silicate, gehlenite, $C_{12}A_7$, CA, $CA_2$, $CA_6$ are shown. For clarity other joins are omitted. At subsolidus temperatures the volume

of the tetrahedron is occupied by subsolidus assemblages some of which are cut by the plane $Ca_3Al_2O_6$–MgO–$SiO_2$ in which lie the other compositions experimentally studied.
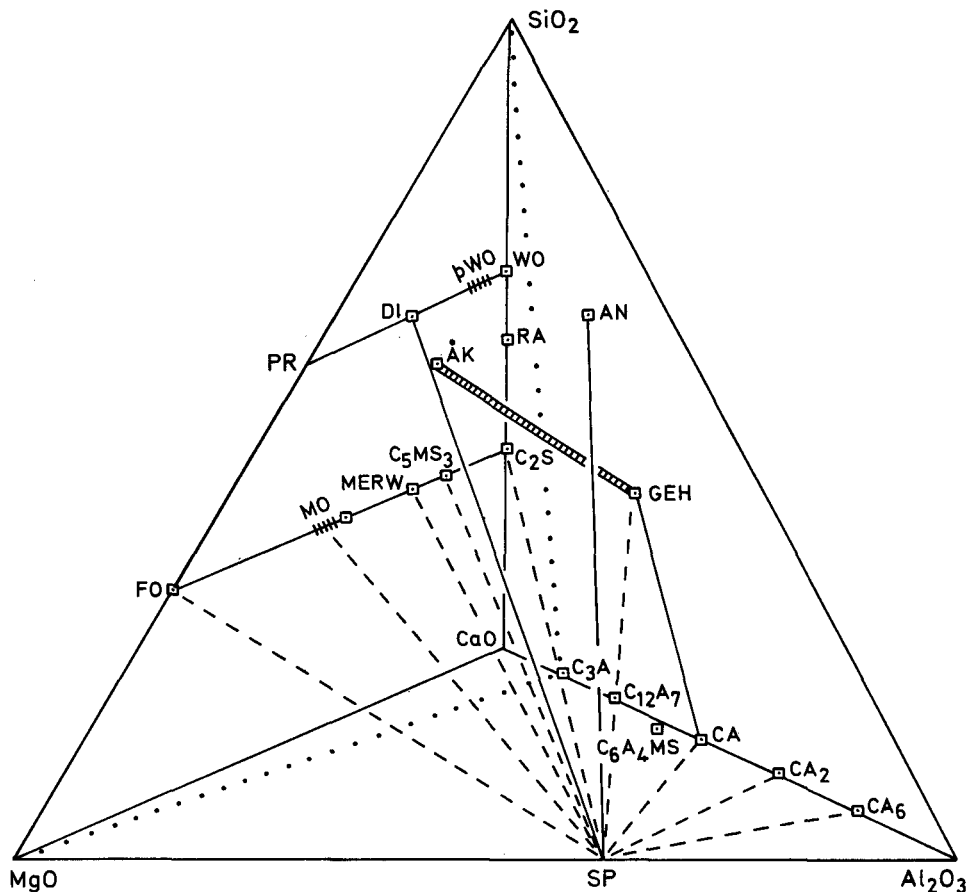


FIG. I. The system CaO–MgO–$Al_2O_3$–$SiO_2$ showing some of the stable subsolidus joins and the range of melilite solid solutions. Åkermanite, Åk; anorthite, An; diopside, Di; forsterite, Fo; gehlenite, Geh; merwinite, Merw; monticellite, Mo; protoenstatite, Pr; rankinite, Ra, spinel, Sp; wollastonite, Wo; pseudowollastonite, pWo. Other compositions are abbreviated using C for CaO, A for $Al_2O_3$, S for $SiO_2$, and M for MgO. The abbreviation Qy is used in fig. 2 for a quaternary compound close to $Ca_6MgAl_8SiO_{21}$ shown as $C_6A_4MS$ in this figure.

*Results from the plane* $Ca_3Al_2O_6$–MgO–$SiO_2$. These are plotted in fig. 2 along with piercing areas calculated from the compositional range of coexisting phases if these are known. Fig. 2 is polythermal, representing stable solidus assemblages in the temperature range just below the beginning of melting of the recorded assemblages. The four-phase assemblage $Ca_5MgSi_3O_{12}$–merwinite–spinel–melilite was not encountered by the compositions studied but its existence is not in doubt since the
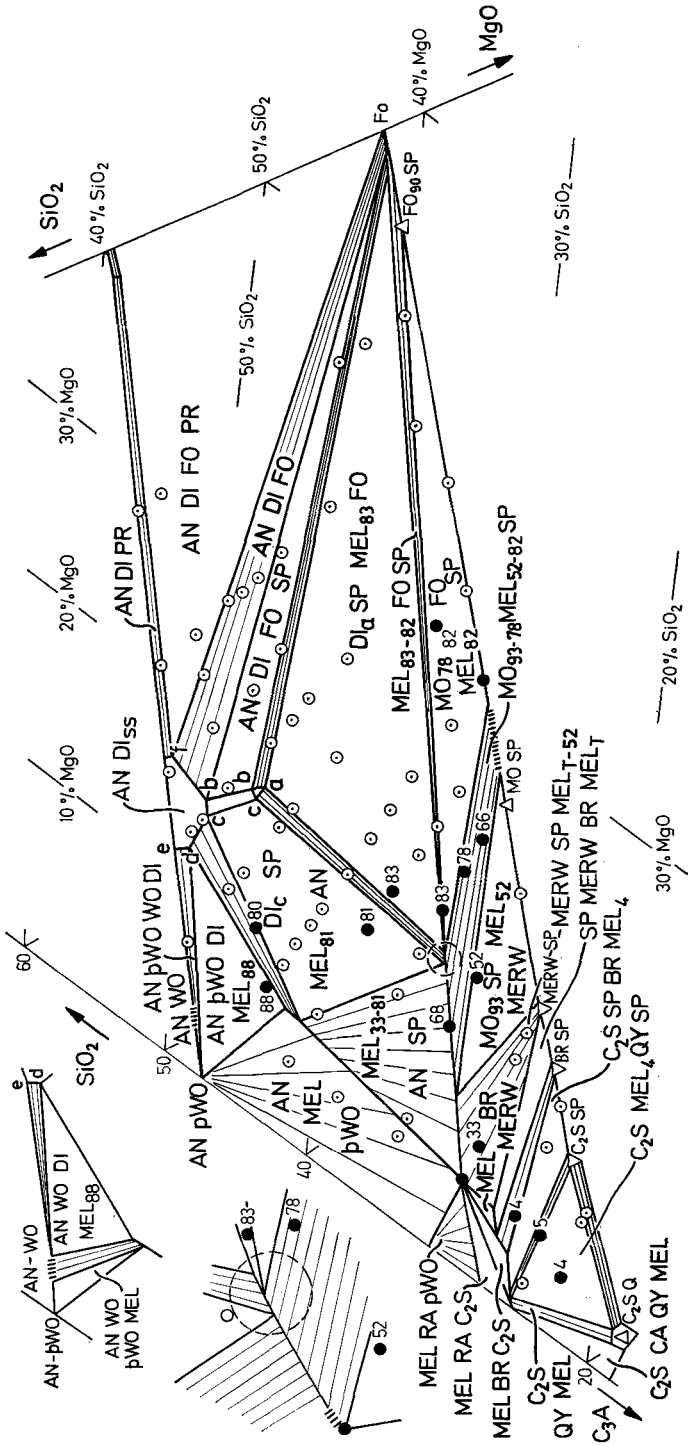
FIG. 2. Polythermal section showing experimentally determined subsolidus phase relationships in part of the plane $Ca_3Al_2O_6$–$MgO$–$SiO_2$ (in wt %), showing mainly areas in which melilite is one of the stable phases based on results from compositions indicated by circles. Abbreviations as in fig. 1 except bredigite ($C_5MS_3$), Br. The experimentally determined values of $d_{211}$ of melilite were converted to assumed molar % Åk and these are shown as figures beside the bulk composition (filled circle) on which the determination of $d_{211}$ was made. Monticellite compositions are from unpublished work but are based on determinations of $d_{130}$ converted to molar compositions according to the assumptions made by Biggar and O'Hara (1969c). Diopside compositions are based on Biggar (1969, p. 97). The equilibria involving wollastonite and pseudowollastonite are insufficiently known but one alternative is shown in an inset. Stoichiometric piercing points are indicated by triangles. The assemblage Sp–Merw–$Ca_5MgSi_3O_{12}$–Mel was not encountered by the limited number of composition studied and the melilite composition involved was designated $Mel_T$.

three-phase assemblages $Ca_5MgSi_3O_{12}$–melilite–spinel and merwinite–melilite–spinel were encountered. Values of $d_{211}$ appear in Table II.

*The melilite polyhedron.* Just as åkermanite solid solutions under isobaric, isothermal conditions occupy an area of the system $CaO-MgO-SiO_2$ (Biggar, 1972a), melilite compositions in the system $CaO-MgO-Al_2O_3-SiO_2$ will occupy a volume such as that

TABLE II. *Values of $d_{211}$ for melilites from the system* $CaO-MgO-Al_2O_3-SiO_2$

| Molar composition | | | | Temp | Time | Products | Melilite | |
|---|---|---|---|---|---|---|---|---|
| M | C | A | S | | | | $d_{211}$ | %Åk† |
| 7 | 3 | I | 5 | 1329 °C | 3 days | Fo Mo Sp Mel | 2·8658Å | 82 |
| 1½ | 3 | I | 4½ | 1232 | 28 | An Di Mel | 2·8650 | 80 |
| 1 | 3 | I | 4 | 1236 | 21 | An Mel* | 2·8672 | 88 |
| 2 | 3 | I | 3½ | 1210 | 30 | An Di Sp Mel | 2·8654 | 81 |
| 2½ | 3 | I | 3½ | 1236 | 21 | Di Sp Fo Mel | 2·8659 | 83 |
| 2½ | 3 | I | 3 | 1238 | 30 | Fo Sp Mo Mel | 2·8659 | 83 |
| 3 | 3 | I | 3 | 1340 | 14 | Mo Sp Mel | 2·8647 | 78 |
| 3½ | 3 | I | 3 | 1340 | 14 | Mo Sp Mel | 2·8613 | 66 |
| 1½ | 3 | I | 2½ | 1340 | 14 | Sp Mel | 2·8620 | 68 |
| 2 | 3 | I | 2½ | 1375 | 5 | Sp Mo Merw Mel | 2·8577 | 52 |
| ¾ | 3 | I | 2 | 1400 | 14 | Merw Sp Mel | 2·8528 | 33 |
| ½ | 3 | I | 1⅔ | 1400 | 14 | $C_5MS_3$ Sp Mel | 2·8464 | 4 |
| ½ | 3 | I | 1½ | 1414 | 8 | $C_2S$ Sp Mel | 2·8465 | 5 |
| ⅓ | 3 | I | 1⅓ | 1310 | 31 | Mel $C_6A_4MS$ Sp $C_2S$ | 2·8464 | 4 |

* Di and either Wo or pWo or liquid are present but in quantities too small for accurate identification.

† Based on arbitrary linear interpolation of values from Table I and used to draw figs. 2 and 3.

represented by the cylinder in fig. 1. In detail the cylinder will in fact be a polyhedron with distinct corners, edges, and faces (which may be curved). In the solidus at a fixed temperature each corner of the polyhedron represents the composition of a unique melilite of a four-phase assemblage. With the data of Table II it is possible to draw the polyhedron (fig. 3A). Each edge represents the range of melilite compositions in a three-phase assemblage and each face is the range of melilite compositions of a two-phase assemblage. The name of the coexisting phase appears on each face. Each face can be regarded as the solvus of melilite with respect to the other phase. Since dicalcium silicate is stable with åkermanite and all intermediate melilites to gehlenite the dicalcium silicate face is continuous and is, for convenience, used as a base in fig. 3A and therefore not seen. The rankinite face is also continuous and is used as the back face of fig. 3A. Melilite compositions at apices are derived from the X-ray diffraction data (Table II) but the gehlenite-rich end is speculative since there are no data for equilibria involving CA, $CA_2$, and $CA_6$. The spinel face is not expected to reach the gehlenite end of the polyhedron.

*Melting temperatures of assemblages containing melilite.* The join åkermanite–gehlenite contains a melting loop, with a minimum near 73% Åk (Osborn and

Schairer, 1941). From their data approximate solidus temperatures are shown along the mole % scale just below fig. 3A. The orientation of the polyhedron is random with respect to the stoichiometric join. For the present it can be imagined that the join lies
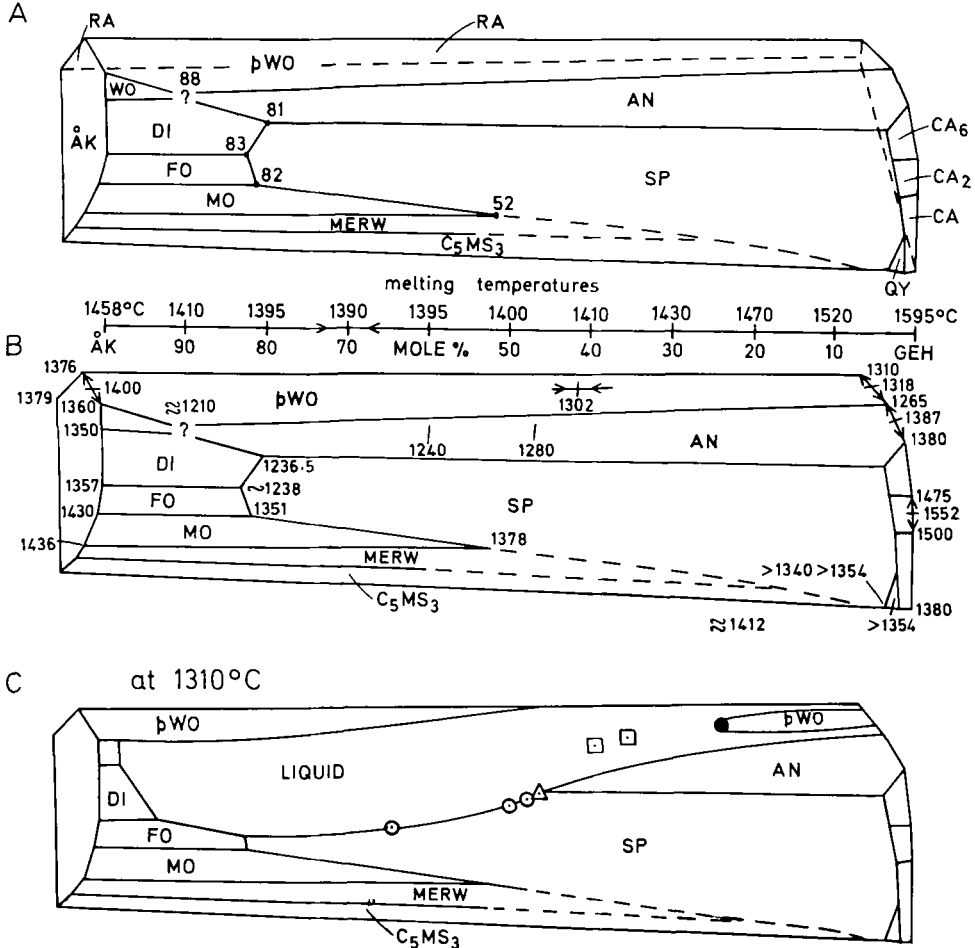


FIG. 3. A. Melilite solid solution polyhedron in the system $CaO-MgO-Al_2O_3-SiO_2$ diagrammatically shown with arbitrarily assigned values in mole %Åk. The scale below is in mole % with solidus temperatures from Osborn and Schairer (1941) for the join åkermanite–gehlenite. B. Similar to A but with melting temperatures shown. C. Isothermal polyhedron of melilite compositions at 1310 °C. Melilites from various assemblages are shown by symbols; ⊙ from melilite, spinel, liquid; △ from melilite, anorthite, spinel, liquid; ⊡ from melilite, liquid; ● from melilite, pseudowollastonite, liquid.

centrally within the polyhedron. Compositions that lie infinitesimally beyond the surface of the polyhedron will develop liquid at temperatures appropriate to either 2-, 3-, or 4-phase assemblages of the system $CaO-MgO-Al_2O_3-SiO_2$. Fig. 3B is a copy of fig. 3A with the temperature at which liquid develops at each of the 4-phase assem-

blages shown at each apex (data from Table III). There are no data for temperatures of beginning of melting of intermediate 3-phase assemblages (such as anorthite–melilite–spinel). Temperatures of beginning of melting of the 2-phase assemblage melilite–pseudowollastonite were given by Osborn and Schairer (1941) who reported a minimum at 1302 °C close to $\text{Åk}_{42}\text{Geh}_{58}$. This temperature from their data appears

TABLE III. *Melting temperatures of some four phase assemblages containing melilite*

|  | Original | Conversion to 1968 IPTS* | Reference |
|---|---|---|---|
| Mel Sp Di An | 1230±0·5 °C | 1236·5±0·5 | O'Hara and Biggar, 1969a |
|  | 1238±3 | 1241±3 | Schairer and Yoder, 1970 |
|  | 1238±2 | 1241±2 | Yang et al., 1972 |
| Mel Sp Di Fo | > 1230 < 1233·5 | > 1236·5 < 1240 | O'Hara and Biggar, 1969a |
|  | 1238±3 | 1241±3 | Schairer and Yoder, 1970 |
|  | 1240±2 | 1243±2 | Yang et al., 1972 |
| Mel Sp Fo Mo | 1348 | 1351 | Schairer and Yoder, 1970 |
| Mel Sp Mo Merw | 1380 |  | Osborn et al., 1969 |
| Mel Sp $C_2S$ $C_5MS_3$ | about 1412 |  | Biggar, 1971 |
| Mel Sp $C_2S$ $C_6A_4MS$ | > 1337 < 1351 | > 1340 < 1354 | Biggar, 1971 |

* For results of ±3 °C or better and also allowing for redetermined melting point of lithium metasilicate (Biggar, 1972b).

on the pseudowollastonite face. Likewise on the anorthite face appear some temperatures suggested by O'Hara and Biggar (1969b, p. 85). These temperatures fall from 1387 °C to 1236·5 °C with no minimum. It would obviously be possible with more data to contour the polyhedron with temperatures of beginning of melting. An isothermal view of the polyhedron is presented in fig. 3C to show the range of experimentally determined values of $d_{211}$ (converted to assumed melilite compositions) from melilites in equilibrium with liquid at 1310 °C. Some unpublished data for compositions on the plane $Ca_3Al_2O_6$–MgO–$SiO_2$ are used. As melting continues increasingly extensive liquid faces develop on the polyhedron. Alternatively, the crystallization behaviour of compositions from which melilite solid solutions of changing composition grow as crystallization proceeds can be followed from a series of isothermal polyhedra.

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