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The thermal transformation of datolite, $CaBSiO_4(OH)$, to boron-melilite

J. TARNEY, A. W. NICOL, and GISELLE F. MARRINER
Departments of Geology, Minerals Engineering, and Physics, respectively,
University of Birmingham

SUMMARY. A kinetic and X-ray study of the dehydroxylation of datolite, $CaBSiO_4(OH)$, has shown that the decomposition occurs very rapidly above 700 °C in air, with an activation energy for the reaction of the order of 200 kcal mole^{-1}. The transformation is topotactic, the dehydroxylated phase being tetragonal with a 7·14 Å, c 4·82 Å, and particularly well formed even at the lowest temperatures of decomposition. Single-crystal studies have shown that two orientations of the new phase exist and that the original a of datolite becomes the unique axis of the tetragonal phase while the tetragonal a axes are oriented either parallel to or at 45° to the b and c axes of datolite. The new phase appears to be a boron-containing analogue of the melilite structure, composition $Ca_2SiB_2O_7$, but is metastable. The basic sheet structure is preserved during the transformation but a reorganization of the tetrahedral layer from the 4- and 8-membered rings of datolite to the 5-membered rings of the new phase is involved, together with effective removal of protons and some silicon. The transformation can be explained in terms of an inhomogeneous reaction mechanism involving migration of calcium and boron into the new phase domains and counter-migration of silicon and protons, but with only minor readjustment of oxygens. The high activation energy of the reaction is explicable in terms either of the effort necessary to remove silicon from the domains of the new phase or of the difficulty of moving the large calcium ions through a relatively close-packed structure.

DATOLITE, $CaBSiO_4(OH)$, has been studied as part of an investigation into the kinetics and mechanics of dehydration of some hydrous minerals and hydrated natural glasses. Although invariably a secondary mineral frequently associated with other low-temperature hydrous minerals such as prehnite and various zeolites, datolite is unusual in retaining its water up to high temperatures (c. 700 °C). The water is firmly bound in the structure as OH groups linked to boron (Ito and Mori, 1953) contrasting with the hydrogen-bonded water molecules of associated zeolites, which are removed fairly easily.

Interest also centres on the behaviour of this OH group linked to boron (BO_3OH) during the dehydroxylation of a calcium borosilicate. In some hydrated calcium silicates, such as afwillite or tobermorite, where the hydroxyl is bound to silicon in the SiO_3OH group and also closely associated with bound water molecules in the structure, the water molecules are lost readily at about 300 °C and followed at rather higher temperatures by loss of hydroxyl groups (Megaw, 1952; Megaw and Kelsey, 1956; Taylor, 1955, 1957, 1959). It has been suggested that migration of calcium ions is involved in the resulting topotactic transformations (Taylor, 1955; Nicol, 1962, 1971). On the other hand, with calcium silicate hydrates such as xonotlite and foshagite, where the OH groups are not connected directly with silicon and there are no associated water molecules, thermal breakdown occurs at much higher temperatures (about 700 °C) and the topotactic transformations seem to involve migration of silicon rather than calcium (Dent and Taylor, 1959; Gard and Taylor, 1958, 1960).

Structure. The structure of datolite has been determined by Ito and Mori (1953) and refined by Pavlov and Belov (1957) and by Pant and Cruickshank (1967). Datolite is monoclinic (*a* 4·84, *b* 7·60, *c* 9·62 Å; β 90° 09′; space group $P2_1/c$) and consists of sheets of linked alternate SiO_4 and BO_3OH tetrahedra aligned parallel to (100) and separated by sheets of calcium atoms in eight-fold coordination with respect to oxygen and hydroxyl ions (fig. 8). The tetrahedral sheet is arranged in a pattern of 8-member and 4-member rings with calcium atoms lying above and below the larger rings. Pairs of boron tetrahedra capped by OH groups point alternately up and down and are linked by SiO_4 tetrahedra lying on edge.

The datolite used in this study was well crystallized material from the well-known locality at Westfield, Massachusetts. The X-ray powder patterns of the material agree with published data for datolite. The kinetic studies and X-ray work will be described separately, and the evidence will be combined in explaining the mechanism of datolite dehydroxylation.

Kinetics of datolite dehydroxylation. Reaction-rate studies were carried out in air on a Stanton HT-D recording thermobalance of 0·1 mg sensitivity fitted with a 1000 °C nichrome-wound furnace. An independent thermocouple was placed alongside the sample to check the temperature during isothermal runs, control being within $\pm 1\frac{1}{2}$ °C. The normal alumina sample support was replaced by a thin Kanthal wire with three projecting platinum prongs to support the sample holder. This had the effect of reducing buoyancy effects considerably and of allowing the sample to attain the furnace temperature independently of the support rod, factors very desirable when attempting to follow fast reactions. The sample itself was spread lightly over a thin platinum foil tray and was never more than 0·10 g in weight in the isothermal experiments and 0·20 g in the programmed heating runs. This arrangement allowed the sample to attain furnace temperature quickly during isothermal runs with minimum interference from self-cooling (due to loss of water vapour) or from 'back pressure' of water-vapour effects between the grains inhibiting the reaction. The system approaches closely Brindley and Nakahira's (1958) ideal of an infinitely thin disc. Crushed (200–300 mesh) material was used in all experiments.

The programmed runs were carried out at a heating rate of 4 °C per minute. Datolite dehydroxylates rapidly at just over 700 °C (fig. 1), the reaction being completed by 780 °C at the heating rate used. The extraordinary rapidity of this reaction is illustrated by the derivative thermogravimetric plot in fig. 2. The DTA curve is also shown. The actual weight loss from this sample is 6·07 % compared with a theoretical weight loss (as H_2O) of 5·60 %. This is normal for datolite, the excess probably being loosely held molecular water.

Isothermal runs were carried out in air between 700 °C and 780 °C by lowering the pre-heated furnace over the sample, weight changes being continuously recorded on the chart. Separate experiments, carried out by placing a fine thermocouple in the sample itself, showed that the sample reaches the furnace temperature in less than 40 seconds.

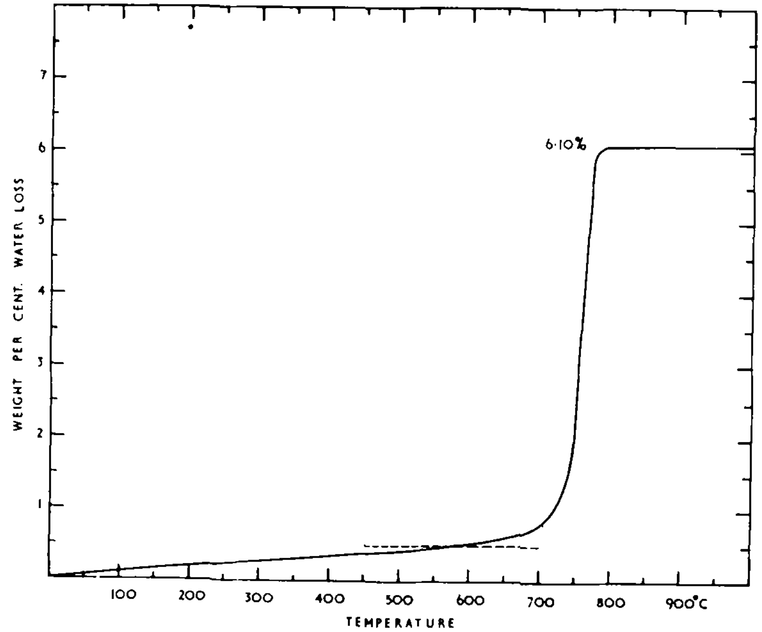


FIG. 1. Weight loss *v.* temperature curve for datolite from Westfield, Mass. The fraction below the dotted line is presumed to be non-structural water.

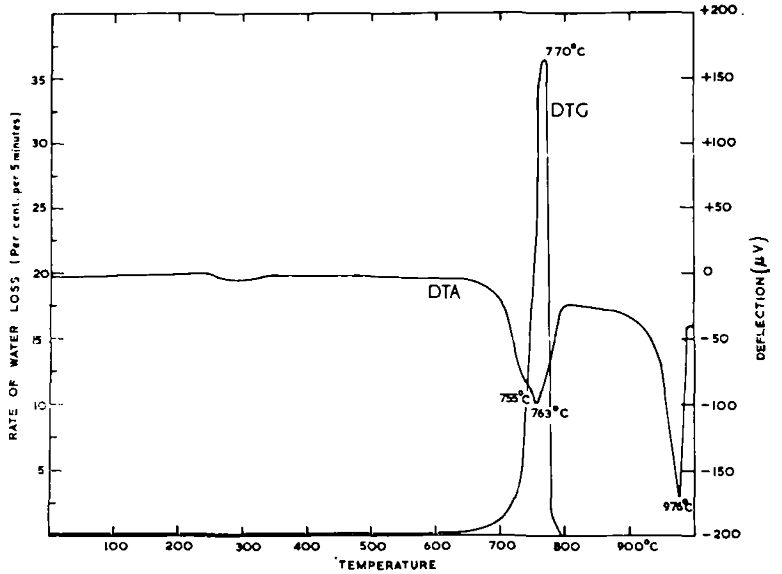


FIG. 2. Derivative thermogravimetric and differential thermal curves for datolite.

Below 700 °C the reaction is on a time scale measured in days and does not go to completion, while by 775 °C the half-life of the dehydroxylation reaction is less than 100 seconds and at about the limit of the response capability of the balance to record the weight loss accurately. It is obvious that at such fast decomposition rates the sample dehydroxylates before it reaches the furnace temperature; indeed, the self-cooling action of the rapidly escaping water vapour will also depress the sample temperature.

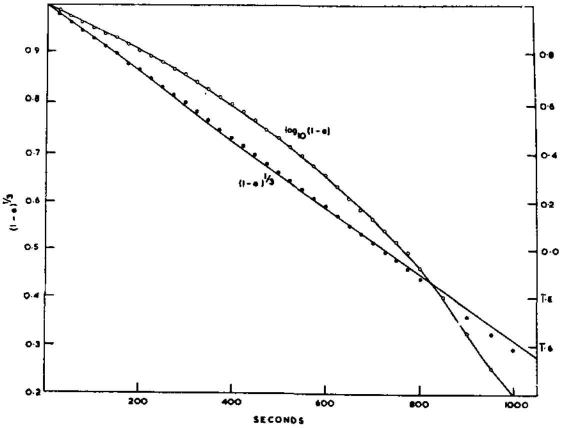
Owing to the large initial buoyancy effects that occur when the cool sample is placed in the hot zone of the furnace, blank repeat runs were made on a spent sample and the resulting trace subtracted from the apparent weight-loss curve to give the true weight-loss curve.

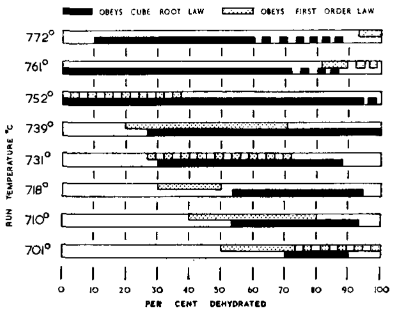
Many attempts have been made to fit the dehydration curves of hydrous minerals to rate equations. The first-order law has enjoyed great popularity, particularly with fine-grained clay minerals such as kaolinite (Murray and White, 1955; Brindley and Nakahira, 1958) but later detailed work on kaolinite and on serpentine (Brindley *et al.*, 1967*a*, *b*) has shown that the approximation to first-order kinetics is merely apparent, and that the rate of dehydroxylation of these two minerals is in fact diffusion controlled. More recently Johnson and Kessler (1969) have argued that even a diffusion model does not explain all the features of kaolinite dehydroxylation and that a pseudo-interface mechanism controls the dehydroxylation rate. The decomposition of brucite has given rise to a similar discussion on the details of the rate-controlling mechanism (Gregg and Razouk, 1949; Anderson and Horlock, 1962; Gordon and Kingery, 1967). In spite of these differences in interpretation, the basic mathematical expressions for first order, interface-controlled, or diffusion-controlled mechanisms for variously shaped particles are well known (Carter, 1961; Sharp *et al.*, 1966).

The dehydroxylation curves for datolite do not follow first-order kinetics. This is illustrated in fig. 3 where the 752 °C curve is replotted according to the integrated version of the first-order equation $ln\ (1-\alpha) = -kt$, where α is the fraction reacted at time t. The plot does not yield the expected straight line of slope proportional to k. On the same graph, however, is shown a plot of $(1-\alpha)^{1/3}$ against t which does give a straight line relationship corresponding to the expression $1-(1-\alpha)^{1/3} = kt$, which mathematically represents the inward movement of an interface at constant velocity into a spherical particle. In physical terms k is proportional to v/r where v is the velocity of movement of the interface in a particle of radius r.

The expression does not hold over the whole temperature range. An attempt is made to illustrate this in fig. 4, where the extent to which the reaction approximates either to moving-interface or to first-order kinetics is indicated. Deviations are greater at low temperatures and may be due to the fact that a moving interface is beset with difficulties of nucleation, preferential movement in one crystallographic direction, or interruption by defects, while such obstacles are 'steam-rollered' through at higher decomposition rates. In spite of these difficulties, values for the rate constant k, assuming the cube-root law, have been calculated for each run and have been plotted against the reciprocal of the absolute temperature in fig. 5 in accord with the logarithmic form of the Arrhenius expression $\log_{10} k = \log_{10} A - E/(2{\cdot}303RT)$, where T is the absolute temperature, R is the gas constant, E is the activation energy, and A is the pre-exponential constant or 'frequency' factor.

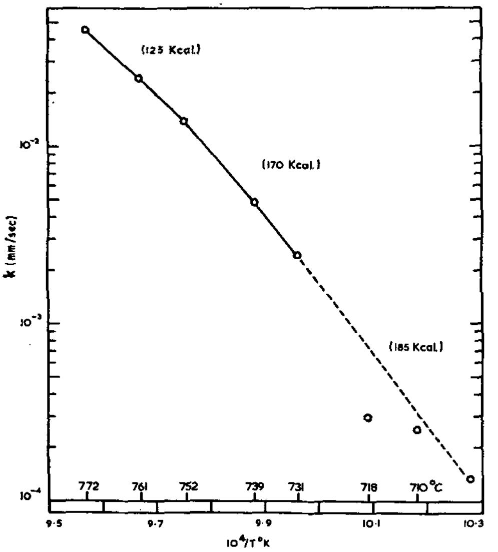
The results conform reasonably well to a straight line, but like most other plots of this type there is curvature at higher temperatures, due largely to experimental difficulties such as the failure of the sample to heat up quickly, self-cooling, back pressure of water vapour, and the limitations of balance response (all these factors being exacerbated by larger sample weights). The lower values for the activation energy, E, for this part of the curve can thus be discounted, the true value probably being in excess of 185 kcal mole^{-1}.

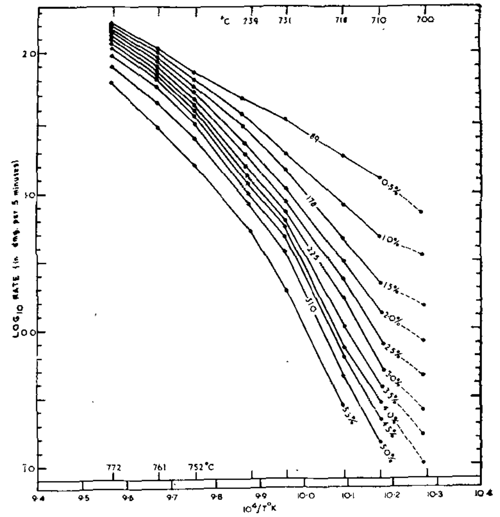




FIGS. 3 and 4: FIG. 3 (left). The 752 °C weight-loss dehydroxylation curve of datolite plotted against time according to the first-order law, $\log_{10}(1-\alpha)$, and the expression for the movement of an interface at constant velocity into a spherical particle, $(1-\alpha)^{1/3}$. FIG. 4 (right). Summary of dehydroxylation curves for datolite showing the extent to which the rate approaches the first-order law or the moving-interface expression over the temperature range investigated.

Further uncertainties in this sort of plot occur at lower temperatures where decomposition is incomplete and the observed weight loss is less than the theoretical value, thus affecting the absolute value of the rate constant, k. An alternative approach, which skirts round this problem, is to assume a constant 'law' of decomposition throughout the temperature range, i.e. that the rate of weight loss, $d\alpha/dt = k(f)$, where f is some (unspecified) function dependent on the fraction undecomposed $(1-\alpha)$. If the slope $d\alpha/dt$ from the initial data is then measured at constant intervals of water loss at each temperature and these values are then plotted against temperature in the normal Arrhenius fashion, a family of curves is produced as shown in fig. 6. These should be evenly, but not necessarily equally, spaced if the mechanism remains constant throughout each dehydroxylation run, and parallel if the mechanism remains constant with temperature. Departures from ideality are thus immediately obvious. The slopes of the lines are directly proportional to the activation energy (appropriate values are indicated), and it is apparent that more energy is required for the decomposition reaction at lower temperatures, particularly near the end of the reaction as the interface moves into the centres of the crystal fragments. This is probably a reflection of the extra energy needed to remove blockages, etc., as discussed above. The activation energy of the first 0·5 % water loss includes a major fraction of loosely held molecular water and is therefore of lower value (95 kcal). The remaining water loss requires a high activation energy of the order of 200 kcal, but it is clear that no precise figure can be given. The value of the frequency factor, A, in the Arrhenius equation is about 10^{36} cm sec^{-1}, which compares with a common value of 10^{11} litre mole^{-1} sec^{-1} for many gas reactions and reactions in solution and values of 10^{11} to 10^{13} cm sec^{-1} for the dehydration of hydrated compounds and simple hydroxides such as brucite (Garner, 1955; Gordon and Kingery, 1967). This high value may reflect the highly favourable geometric arrangements in the structure, so that the reaction can proceed with vigour once the energy to activate the reaction is provided (Lacy, 1965).





FIGS. 5 and 6: FIG. 5 (left). Arrhenius plot of dehydroxylation rates for datolite. FIG. 6 (right). Modified Arrhenius plot of dehydroxylation rates (dα/dt) at 0·5 % water loss intervals. Activation energies corresponding to the different slopes are indicated.

X-ray investigation

In attempting to explain the high activation energy for the thermal breakdown of datolite, powder and single-crystal X-ray studies were undertaken in order to establish the composition and structure of the new phase and its orientation with respect to the original datolite.

Powder diffractometry. The powders remaining after each isothermal run all gave the same well-crystallized powder pattern, which matched none of the known phases in the CaO–B_2O_3–SiO_2 system. Approximate cell dimensions were deduced from single-crystal photographs (see below) and these and the powder patterns could be indexed completely on a tetragonal cell with parameters *a* 7·140± 0·002 Å, *c* 4·823± 0·002 Å. Systematic absences were found for *h*00 with *h* odd, this being consistent with either space group $P\bar{4}2_1m$ or space group $P42_12$. No other crystalline phase could be detected. The indexed powder pattern for this phase is given in table I.

TABLE I. *d-spacings and approximate relative intensities for dehydroxylated datolite product (boron-melilite) indexed according to a tetragonal cell, a 7·140 Å, c 4·823 Å. Diffractometer trace,* $Cu\text{-}K_\alpha$ *radiation. The hkl reflections and relative intensities are comparable with those of åkermanite (J.C.P.D.S. file card 4·0681)*

d	*Int.*	*hkl*	*d*	*Int.*	*hkl*	*d*	*Int.*	*hkl*
3·48 Å	50	111	1·924 Å	50	212	1·524 Å	5	113
3·17	5	210	1·830	5	321	1·514	< 5	421
2·86	60	201	1·782	10	400	1·465	< 5	203
2·66	100	211	1·744	15	222	1·435	< 5	213
2·52	20	220	1·732	15	410	1·406	< 5	412
2·41	10	002	1·679	15	330	1·356	< 5	223
2·28	20	102	1·646	30	312	1·278	< 5	251
2·25	25	310	1·626	10	411	1·190	< 5	600
2·23	30	221	1·605	5	003	1·177	< 5	143
2·22	10	112	1·588	15	331	1·161	< 5	522
2·13	25	301	1·528	5	322	1·086	< 5	541
2·05	10	311						

The cell dimensions and axial ratios of the new phase are very similar to those of the melilite group (space group $P\bar{4}2_1m$):

New Phase		*a* 7·14 Å	*c* 4·82 Å	*c*/*a* 0·674
Åkermanite	$Ca_2MgSi_2O_7$	7·84 Å	5·01 Å	0·640
Gehlenite	$Ca_2Al_2SiO_7$	7·69 Å	5·08 Å	0·661

and apart from the small changes in line positions the powder patterns of all three phases are closely comparable. It seems likely, therefore, that the new phase is a boron-variety of melilite with the reduced cell parameters that one might expect from substitution of the small boron atom into the tetrahedral groups. Just how the boron and silicon atoms are distributed between the two types of tetrahedral site in the melilite structure needs to be elucidated. Smith (1953) has examined the intermediate members of the melilite group in some detail in order to assess the distribution of Mg, Al, and Si in the two types of tetrahedral site which he labels T_1 and (T_2, T_3). The melilite structure is essentially formed from pentagonal rings of tetrahedra joined together to form sheets; these are separated by the larger calcium cations, which are in eightfold coordination with oxygen. The T_1 sites are common to four pentagons, the (T_2, T_3) sites to three pentagons, the T_1 sites being the larger. In åkermanite, $Ca_2MgSi_2O_7$, the larger Mg ion (0·65 Å) occupies T_1 while Si (0·41 Å) occupies (T_2, T_3). With gehlenite, $Ca_2Al_2SiO_7$, two limiting cases of ordering were recognized with Al in T_1 and with Al and Si in (T_2, T_3) and with Si in T_1 and Al in (T_2, T_3), the latter probably being the more stable arrangement. The lack of obvious discontinuities in the cell parameters in members of the åkermanite–gehlenite series, however, suggests there is no abrupt change in the type of ordering such as would exist with the second arrangement.

Datolite cannot transform directly to a new melilite-like phase without removal of one in four of the tetrahedra in addition to water. This would involve either removal of silica or of boron oxide according to the equations: $2CaBSiO_4(OH) \rightarrow Ca_2BSi_2O_7 + BO_2 + H_2O$ or $2CaBSiO_4(OH) \rightarrow Ca_2B_2SiO_7 + SiO_2 + H_2O$.

The first reaction product is obviously not possible owing to charge imbalance and therefore datolite must break down to boron melilite plus silica. The structure of melilite (Warren, 1930; Smith, 1953) has limited flexibility and it is possible to calculate the size of the tetragonal cross-section using Si–O and B–O bond lengths such as have been deduced by Johansson (1959) in danburite, $CaB_2Si_2O_8$, and by Pant and Cruickshank (1967) in datolite itself. The products of both reactions fit neatly into a 7·14 Å-sided tetragonal cell, though there is slight distortion of the tetrahedra with the $Ca_2SiB_2O_7$ product. The slight distortion in the tetrahedral layer may result from the stretching of a much contracted tetrahedral sheet over the large calcium cations, and may account for the apparent metastable nature of this product (see below).

It is possible of course that both boron and silicon may be randomly distributed between the T_1 and the T_2, T_3 positions, though the weight of evidence from structural studies on the melilite group (Smith, 1953) suggests that the smaller ion favours the T_2, T_3 positions, in this case boron. A check was made to discover whether the observed powder pattern of the new phase could be generated in fact by a boron-melilite with boron and silicon distributed in this way. This was done using a computer programme written by Yvon, Jeitschko, and Parthe (1970), for producing numerical and graphical representations of powder diffraction patterns, complete with line intensities corrected for Lorentz and polarization effects, from a given structure. The fractional atomic coordinates used for the proposed boron-melilite were those of natural melilite (Smith, 1953) with calcium and oxygen in the positions given for the natural mineral, but with various distributions of silicon and boron between the various T_1, T_2, and T_3 tetrahedral sites. While it was realized that the model would probably differ in detail from the true atomic coordinates in the boron-containing phase owing to the smaller cell size, it was felt that such discrepancies would not be significant. Of the three combinations used, namely SiBB, BSiB, and BBSi in T_1, T_2, and T_3 respectively, the closest approximation to the observed powder pattern occurred with silicon in T_1 and boron in (T_2, T_3). Thus it appears likely that boron occupies the positions normally occupied by silicon in åkermanite.

The suggestion that boron can substitute for silicon in positions normally occupied by SiO_4 tetrahedra is not new. In bakerite and garrelsite for instance, Christ (1959) has suggested that they are related to datolite through $B \rightleftharpoons Si$ substitution:

Datolite	$Ca_4\,B_4\,(SiO_4)_4\,(OH)_4$
Bakerite	$Ca_4\,B_4\,(SiO_4)_3\,(BO_3OH)\,(OH)_4$
Garrelsite	$M_4\,B_4\,(SiO_4)_2\,(BO_3OH)_2\,(OH)_4$ (M = Ba, Ca, Mg)

A beryllium equivalent of the proposed boron-melilite structure has been described by Bartram (1969). This has the composition $Yt_2SiBe_2O_7$ and cell dimensions *a* 7·283 Å, *c* 4·755 Å, the former being slightly larger and the latter slightly smaller than in boron melilite, but just as might be expected through substituting the larger Be ion for B and the smaller Yt ion for Ca. Furthermore, Bartram has demonstrated unequivocally that the smaller Be atoms occupy the paired T_2, T_3 tetrahedral sites, while silicon occupies T_1.

The fact that datolite transforms to boron-melilite is not surprising in view of the similar features shown by the two types of structure over a wide range of compositions (Bakakin *et al.*, 1970). The rare-earth mineral, nordite, is closely related to the structures of melilite and datolite-gadolinite and has been considered to show an unusual combination of features of both (Bakakin *et al.*, 1970).

Attempted synthesis of boron-melilite. Attempts to increase the crystallinity of boron-melilite by heating the datolite dehydroxylation product for long periods at successively higher temperatures were unsuccessful. At about 870 °C lines due to wollastonite appeared, and the two patterns persisted together up to 950 °C, when the material melted incongruently to give wollastonite, calcium borate, and liquid, as expected from the published phase diagram for the system (Flint and Wells, 1936). Only wollastonite could be detected in material heated to 1080 °C, again in accordance with the phase diagram.

Attempts were made to synthesize the new phase by reacting together finely mixed $CaCO_3$, H_3BO_3, and precipitated SiO_2 in the required proportions in the solid state at 750 °C. At this temperature only tri-calcium borate and dicalcium silicate formed, but by 850 °C these had disappeared and were replaced by wollastonite and minor calcium borate. Similar experiments were repeated using carefully calcined gels, made by adding $Si(OEt)_4$ to solutions containing $Ca(NO_3)_2$ and H_3BO_3 (Roy, 1956), and these also gave the products expected from the phase diagram both on heating dry and heating hydrothermally under a water pressure of 1 kb at 700 °C. It seems likely that boron-melilite is metastable, albeit quite markedly so, and can be produced only by dehydroxylating datolite.

Single-crystal studies. X-ray diffraction studies were carried out on single crystals of the same sample of datolite to determine the detailed nature of the crystalline phases formed on dehydroxylation and their crystallographic orientations, if any, relative to the original material, using methods based essentially on those described by Taylor (1955) and Dent and Taylor (1956). Thus, a small crystal of datolite, showing well-developed (011), $(0\bar{1}1)$, and (001) faces and a sharp, straight (011):$(0\bar{1}1)$ edge, was positioned in a Unicam S25 single-crystal camera with its *b*-axis parallel to the rotation axis and the orientation of its crystallographic axes relative to these faces confirmed using 5° and 10° oscillation photographs. The crystal was removed from its mount and carefully dehydroxylated without decrepitation by slowly heating it through the range 700° to 830 °C on the thermobalance. Some slight shrinkage occurred, with associated slight crack development due to escaping water vapour, but the basic shape of the crystal was retained, apart from minor curvature adjacent to the cracks. The crystal was repositioned on the goniometer arcs in its original orientation and the cell dimensions and orientations of the axes of the new phase were found relative to the habit faces, again using oscillation photographs. The orientation relationships were further confirmed using Weissenberg photographs.

A final check on the relative orientations was obtained by cementing a datolite crystal to the bead of a Pt/Pt13Rh thermocouple, using a high alumina cement, and carefully heating it in situ on the Weissenberg goniometer, using a small nichrome-wound furnace, until the crystal had undergone only partial conversion to the dehydroxylated phase. Many crystals so treated split at the junction between the dehydroxylated and the unconverted portions of the crystal, but Weissenberg photographs from crystals in which the partial conversion had been successful contained reflections from both the unchanged datolite and its dehydroxylation product. Optical microscopic investigation of these crystals showed that they had not twisted during the dehydroxylation, and so the films showed the orientation relationship unambiguously. Orientation relationship data were collected from crystals oriented both with the datolite *a*-axis and the *b*-axis as rotation axis.

All reflections from the dehydroxylated phase were appreciably broader than those from the original datolite, indicating a smaller particle size, and were markedly streaked along powder directions, indicating an increase in the randomness of the mosaic structure of the crystal. This is in accord with almost all other studies of similar reactions. The absence of streaking radially in reciprocal space, however, indicates that the product phase contains little or no structural disorder.

The orientation relationships derived by all the methods used agreed exactly, within experimental error, and confirmed that the unit cell of the new phase is tetragonal with *a* 7·14 Å and *c* 4·82 Å. Two distinct orientations were found. In both, the unique tetragonal axis was parallel (within ±1°) with the direction of the original *a*-axis of datolite, and in one orientation the tetragonal *a*-axes coincided with the datolite *b*- and *c*-directions (Orientation I), while in the other they lay at 45° to the original *b*- and *c*-directions in the datolite (100) plane (Orientation II). All orientations are considered to be correct to within ±1°. No other crystalline products could be detected.

The transformation of datolite to boron melilite, therefore, shows a high degree of topotaxy, and the new phase has two possible orientations relative to the original. Taylor (1962b) has described a similar situation in the case of the dehydration of hemimorphite, where the first dehydration product, β-Zn_2SiO_4, appears in two orientations with respect to the host lattice, at 45° to one another, and finally transforms to α-Zn_2SiO_4 (willemite), with four possible orientations relative to the original structure. Similar studies on datolite crystals heated to more than 900 °C showed that the high temperature products had no obvious preferred orientation relative to the host.

Comparison of datolite and boron-melilite structures. Since the composition and the crystal structure of the boron-melilite phase derived from datolite have been identified, it is possible to compare the original and the product structures in their observed relative orientations and attempt to analyse the mechanism of the dehydroxylation reaction.

Fig. 7 shows how the real-space lattices of datolite and of boron-melilite are related in the two orientations, and 'transformation blocks' have been defined to represent volumes that are closely similar in shape and size in the two phases, and contain integral numbers of unit cells in the two structures. These may be thought of as 'unit cells of transformation' in the overall reaction. The diagram shows that, in the transformation block for Orientation I, 6 datolite cells convert into 8 melilite cells, whereas in the block for Orientation II, 6 datolite cells convert into 9 melilite cells. In both orientations there is a negligible (½ %) contraction along the datolite *a*-direction, perpendicular to the oxygen sheets in the original structure.

In the datolite (100) plane the fit is close but not exact. There is a contraction along the original *b*-direction for Orientation I and an expansion along the original *c*-direction for Orientation II, while there is a smaller contraction along datolite *c* for Orientation I and smaller expansion along datolite *b* for Orientation II. This amounts to an overall contraction of 6·7 % in the volume of the transformation block of Orientation I and an expansion of 5·0 % in Orientation II. While these dimensional changes are of the same order of magnitude as those found in similar topotactic transformations (Katz, Nicol, and Roy, 1969; Nicol, 1964; Brindley, 1963), larger transformation blocks could be chosen to give an even closer fit (e.g. 42 datolite cells transforming to 60 melilite for both orientations).

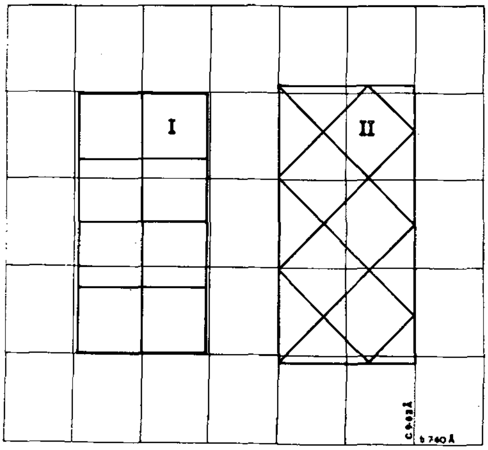


FIG. 7. Simplified unit cell transformation blocks showing the two orientations of boron melilite (I and II) superimposed on the datolite lattice.

TABLE II. *Comparison of ionic contents of proposed transformation blocks (see fig. 7). Note that in both orientations, separately and together, overall charge balance is maintained. Major differences in cation content are apparent, but there is little difference in oxygen content, because the apparent small changes are matched by equivalent expansion or contraction in the volumes of the two orientations during the transformation*

	Ca^{2+}	B^{3+}	Si^{4+}	O^{2-}	H^+	Σ +ve charge	Σ −ve charge	Area (Å^2)	Volume (Å^3)
Datolite (6 cells)	24	24	24	120	24	240	240	438	2123
Orientation I (8 cells)	32	32	16	112	0	224	224	408	1967
Difference	+ 8	+ 8	− 8	− 8	−24	− 16	− 16	− 30	− 156
				(6·7 %)				(6·7 %)	(7·3 %)
Orientation II (9 cells)	36	36	18	126	0	252	252	459	2213
Difference	+12	+12	− 6	+ 6	−24	+ 12	+ 12	+ 22	+ 89
				(5·0 %)				(5·0 %)	(4·2 %)

Table II lists the ionic contents of the two simplified transformation blocks in terms of the compositions of datolite and boron-melilite, and summarizes the changes in ionic content required to pass from datolite to its dehydroxylation product. The most significant point is that charge balance is maintained throughout the conversion in both transformation blocks. Secondly, although there is an apparent small loss of oxygen (6·7 %) from the transformation block for Orientation I and a small gain (5·0 %) for Orientation II, this corresponds exactly with the misfit in the volumes (−6·7 % and +5·0 % respectively) of the simplified transformation blocks. Hence there appears to be no net gain or loss of oxygen from the transformation blocks during the transformation. This accords with the fact that the oxygen densities of the two phases are very similar, datolite having 565 oxygens per 10^{-26} m^3 while boron melilite has 570 oxygens per 10^{-26} m^3. A third important point from table II is that the numbers of all other cations must change significantly in both transformation blocks.

The structures of the two phases may now be compared in order to ascertain the atomic rearrangements necessary for the transformation. The structure of datolite is shown projected on (100) in fig. 8 (*a*) while the equivalent projection of the tetrahedral layer of the proposed boron-melilite structure is shown in fig. 8 (*b*). The first point of interest is that there is very little change in the basic sheet structure of the two phases, there being only a minimal contraction from 4·84 Å to 4·82 Å in the repeat distance normal to the oxygen sheets. Since there is no net loss of calcium or of oxygen, the essential change appears to involve

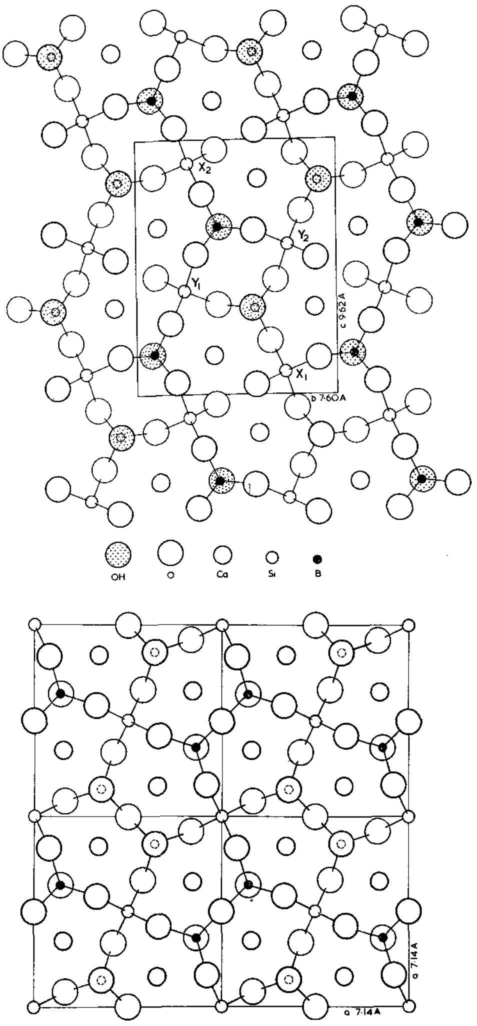


Fig. 8. *a*, top: Projection of the tetrahedral layer of datolite on (100). Labelling of the silicon atoms is discussed in the text. *b*, bottom: Projection of four cells of the tetrahedral layer of the proposed new phase, boron-melilite, on (001). The structure has been drawn assuming complete ordering of silicon and boron in T_1 and T_2, T_3 positions respectively. Note that the two types of chain which (at right angles) make up the datolite sheet are here present at 45° to each other.

reconstruction of the tetrahedral layer from the 8- and 4-membered rings of datolite to the 5-membered rings of boron melilite.

Examination of the tetrahedral sheets in datolite shows that the structure can be regarded as being composed of two sets of 'Viererketten' chains at right angles, one set lying parallel to the *b*-direction, with a repeat distance of 7·6 Å, and the other parallel to the *c*-direction, with a repeat of 9·6 Å. Similar 'Viererketten' chains can be distinguished in the melilite structure, and these occur in two pairs, the members of each pair lying at right angles to one another, as demanded by the tetragonal symmetry. One pair lies parallel to the *a*-axes, with a repeat distance of 7·14 Å, and the other lies parallel to (110), with a repeat of 10·1 Å. These are outlined in fig. 9 and represent, for the former pair, a contraction of 6 % relative to the chains in datolite parallel to *b*, and, for the latter, an expansion of 5 % relative to the chains parallel to *c*.

Examination of the calcium cation layers of datolite and of the new phase also reveals that, in the observed orientations, the majority of the calcium positions coincide in the two phases, and the calcium atoms that have to move to make up the required composition appear to do so from eight-fold sites in datolite to eight-fold sites in the melilite.

Transformation of datolite into boron-melilite involves loss of silicon as well as hydroxyl from the tetrahedral layer. It is, moreover, interesting to note that, if the silicons in a unit cell of datolite are labelled X_1, X_2, Y_1, and Y_2, as shown in fig. 8 (*a*), then movement of X_1+Y_1 or of X_2+Y_2 in any unit cell would effectively rupture alternate 7·6 Å chains and initiate the production of nuclei of the new phase with residual chains parallel to the axes of the host lattice. Movement of X_1+Y_2 or of X_2+Y_1, on the other hand, would rupture adjacent 9·6 Å chains resulting in nucleation of the new phase with its axes at 45° to the original axes. This is shown diagrammatically in fig. 9. It is evident therefore from a consideration of the details of the atomic movements required during a reconstruction of datolite to a boron-melilite structure that nuclei of the new phase form without disrupting the basic oxygen sheet structure and also that in the two orientations produced there is minimum disturbance of the pattern of oxygens and calciums within these sheets.

Reaction mechanism. Any proposed reaction mechanism must explain the formation of two orientations of the product phase, topotactically, and with general retention of a large proportion of the calcium and oxygen positions in the original phase. It must also explain how the overall composition can change, and it must account for the high activation energy derived from the kinetic studies.

Various possibilities are open for the actual mechanism of the transition, since silica could migrate through the structure with or without its attendant oxygens, and hydroxyl likewise might escape, in whole or in part, as protons or as water molecules. In both cases, however, the metastable nature of the melilite formed from datolite, and the fact that there is no net change in the oxygens during its formation, makes it difficult to envisage a mechanism whereby silica and water molecules could be removed from the structure, in the form of SiO_2 and H_2O respectively, without destroying the oxygen planes completely throughout the structure. Moreover, as Taylor (1961) has pointed out in many cases, migration of large SiO_2 and H_2O units through the relatively close-packed oxygens in datolite would further disrupt the structure, making an orderly change of the remaining material into the observed product virtually impossible to envisage.

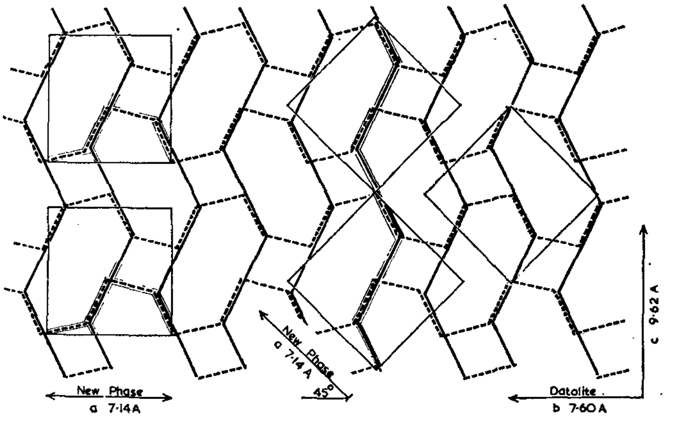


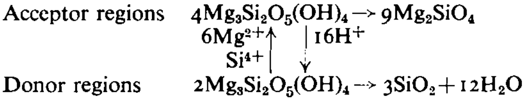
FIG. 9. Diagrammatic representation of the tetrahedral layer of datolite with its two basic linked-chain types shown lined and dashed respectively. Superimposed are unit cell outlines of the two orientations of the new tetragonal phase, the parts of the original datolite sheet common to each being indicated.

In contrast, Taylor (1962a) has suggested that very limited movement of the larger ions in the structure, notably oxygen and, to a somewhat lesser extent, calcium, occurs during thermally induced topotactic transformations in minerals, and that migration of the smaller cations, for example Si^{4+}, Al^{3+}, Mg^{2+}, B^{3+}, Zn^{2+}, H^{+}, occurs through the relatively immobile oxygen lattice. By this means, 'donor' and 'acceptor' regions are set up in the crystal, the former normally donating cations to the latter and receiving hydrogen ions in exchange. The 'acceptor' regions then recrystallize to form the observed product and the 'donor' regions lose water and remain either as pores or as regions of very poorly defined stoichiometry showing, usually, only short-range order.

Comparisons may be drawn with other layer-type minerals, such as kaolinite (Brindley and Nakahira, 1959; Taylor, 1962), pyrophyllite and talc (Nakahira, 1964; Ball and Taylor, 1963), muscovite (Eberhart, 1963; Nicol, 1964), serpentine (Ball and Taylor, 1963; Brindley and Hayami, 1965), and tremolite (Freeman and Taylor, 1960), which undergo reactions showing a high degree of topotaxy to give a silica-poor ordered product and a poorly crystalline silica-rich phase on thermal breakdown. In general it has been noted that, for the aluminium-silicate phases, the endothermic dehydroxylation peak in the DTA curve occurs at a temperature well below that of the exothermic, presumed recrystallization, peak, whereas for the corresponding magnesium-silicate phases, the exothermic peak follows quickly on the endotherm. In the present case, there is no evidence for an exothermic peak separate from the dehydroxylation endotherm (fig. 2). Moreover, in many alumino-silicates an anhydrous phase is formed on dehydroxylation, which may be very highly disordered, as in kaolinite, or of a structure closely similar to that of the hydrated mineral, as in pyrophyllite and muscovite. In the magnesium-silicates, on the other hand, a principal product of dehydroxylation is observed shortly after water loss occurs. With datolite the new product appears immediately on dehydroxylation.

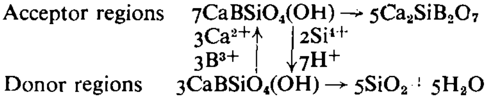
The behaviour of datolite would appear, therefore, to parallel the magnesio-silicates rather than the alumino-silicates. Nakahira, in comparing the dehydroxylation behaviour of pyrophyllite and talc, considers that pyrophyllite dehydrates by a homogeneous mechanism involving loss of water molecules evenly throughout the crystal structure, but that talc reacts by an inhomogeneous mechanism involving counter-migration of 4 magnesium and 8 hydrogen ions per unit cell of talc. The consensus view agrees with Nakahira's postulate of an inhomogeneous mechanism for magnesio-silicates in general, although other workers include silicon among the ions that move during the reaction, but there is much disagreement about the alumino-silicates, with Brindley, Nakahira, and Eberhart favouring homogeneous, and Nicol and Taylor favouring inhomogeneous, mechanisms. In addition, Nicol (1962, 1971) and Taylor (1962a) have argued strongly in favour of inhomogeneous mechanisms in the dehydrations of hydrated calcium silicate and related phases.

In interpreting new evidence on the breakdown of serpentine, Brindley and Hayami (1965) have argued that silica-depleted domains, comprising disorganized forsterite, and silica-enriched domains form in the postulated acceptor and donor regions, respectively, almost immediately on dehydroxylation and give a formalized stoichiometry for the overall reaction:



$$\begin{tikzcd}
\text{Acceptor regions} & 4Mg_3Si_2O_5(OH)_4 \arrow[r] \arrow[d, shift left=2, "16H^+"] & 9Mg_2SiO_4 \\
\text{Donor regions} & 2Mg_3Si_2O_5(OH)_4 \arrow[r] \arrow[u, shift left=2, "\begin{array}{c}6Mg^{2+}\\ Si^{4+}\end{array}"] & 3SiO_2 + 12H_2O
\end{tikzcd}$$

It is our opinion that a broadly similar scheme applies to the dehydroxylation of datolite, except that, instead of a one-way migration of cations compensated by counter-movement of hydrogen ions, calcium and boron cations migrate to the acceptor regions while silicon cations accompany the hydrogen ions in the opposite direction. Thus we can write, formally,



$$\begin{tikzcd}
\text{Acceptor regions} & 7CaBSiO_4(OH) \arrow[r] \arrow[d, shift left=2, "\begin{array}{c}2Si^{4+}\\ 7H^+\end{array}"] & 5Ca_2SiB_2O_7 \\
\text{Donor regions} & 3CaBSiO_4(OH) \arrow[r] \arrow[u, shift left=2, "\begin{array}{c}3Ca^{2+}\\ 3B^{3+}\end{array}"] & 5SiO_2 + 5H_2O
\end{tikzcd}$$

Although silica is shown with water as one of the products of reaction in the donor regions, it is probable that the material actually remaining after the reaction has no well-defined stoichiometry but contains appreciable amounts of calcium and boron. It is possible that the wollastonite found at 870 °C begins to crystallize from this material, but there is no definitive evidence for or against this.

Such a mechanism involves the movement of calcium, a relative large cation, in addition to movement of the small cations present, through a relatively close-packed oxygen structure. Furthermore, datolite dehydroxylates at the same temperature as do the calcium silicate hydrates xonotlite and foshagite, and Dent and Taylor (1956) and Gard and Taylor (1958) have shown that only silicon and hydrogen ions move in these reactions. The calcium ions are in six-fold coordination in both these structures and appear not to move. Taylor (1955) and Nicol (1971), however, have shown that calcium ions can undergo migration during a dehydration reaction, provided that loss of water molecules from the hydrated structure leaves empty channels through which the calciums can move. In datolite there are no water molecules as such; however, the calcium ions in datolite are in approximately eight-fold coordination, and they enter similar eight-fold coordination in the melilite structure. Now oxygens in eight-fold coordination will be further apart than corresponding oxygens in an octahedral arrangement, and so, at high temperatures, it is conceivable that the increased thermal vibrations of the oxygens may increase their separations to a point where channels are formed in the oxygen lattice that are large enough to allow the calcium ions to move by a process similar to the 'filled–empty tetrahedron' mechanism suggested by Taylor (1960) for silicon migration.

Datolite and its product, boron-melilite, are both fairly compact structures with oxygen densities near 570 oxygens per 10^{-26} m^3 compared with oxygen densities of only about 460 in the calcium silicates afwillite and xonotlite. Migration of large calcium atoms through this compact oxygen lattice in datolite is likely to be energetically very demanding, and may account for the large activation energy of the reaction. Alternatively, it is to be noted that the transformation of datolite to boron-melilite involves silicon migration whereby two silicons are removed from each unit cell of datolite, or, effectively, one mole of silica from every mole of datolite, $2CaO.\ B_2O_3.2SiO_2.H_2O$. This requires simultaneous breakage of two Si–O bonds. The energy of the Si–O bond is of the order of 100 kcal, and values of the activation energy for viscous flow of pure silica, which also involves simultaneous disruption of two Si–O bonds, are in excess of 170 kcal $mole^{-1}$ (Hetherington *et al.*, 1964). It may or may not be a coincidence that the activation energy for the datolite dehydroxylation reaction is of this magnitude. While we are confident that the high activation energy for datolite breakdown is connected with one or both of the above factors, apportionment of relative importance cannot be made until comparable kinetic and thermal data on other hydrated calcium silicates is available. Whatever the reason for the high activation energy it is evident from the high value for the pre-exponential constant or 'frequency factor' that the reaction is able to proceed very quickly once the energy is available, and that there are no real obstacles to the progress of the reaction interface. This must reflect the basic similarities between datolite and melilite-type structures, a point already emphasized by Bakakin *et al.* (1970).

Conclusions. This study of datolite dehydroxylation emphasizes the basic similarities between the datolite and melilite structures and demonstrates that a boron variety of melilite exists, although apparently a metastable one. When datolite transforms to boron-melilite topotactically the new product forms in such a way as to cause minimum movement of the large oxygen and calcium atoms. Nevertheless, although only minor rearrangement of the oxygens is required to produce the two orientations of the melilite phase, substantial movements of silicon and boron and to a smaller extent calcium must take place. Silicon and boron probably migrate through the tetrahedral layer by the 'filled–empty tetrahedron' mechanism. Movement of calcium in a similar manner from one eight-fold coordinated site to another is possible as the tetrahedral layer rearranges itself. This is probably easier to accomplish than in structures where calcium is in six-fold coordination with oxygen. The reaction mechanism is thus inhomogeneous, with migration of calcium and boron into the new phase domains and counterwise migration of protons and some silicon so that effectively silica and water are removed from domains of the new melilite phase. The high activation energy for the reaction reflects the energy required to force the large calciums through the relatively close-packed datolite structure, or the energy required to strip silica from the melilite domains, or both. On the other hand, the large value for the pre-exponential constant indicates that the transformation is easily accomplished once the energy is available. In another sense this confirms the basic similarities between the datolite and melilite structures.

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Note added in proof. Dr. M. H. Hey has drawn our attention to a paper by Von H. Bauer (*Neues Jahrb. Mineral. Monatsh.* 1962, 127–40) on diadochy between boron and aluminium in gehlenite. Bauer synthesized members of the $Ca_2Al_2SiO_7$–$Ca_2B_2SiO_7$ series from pure oxide and carbonate starting materials and found complete solid solution up to 60 % of the boron end-member. More boron-rich members only appeared as stable phases in the sub-solidus region, while those near pure $Ca_2B_2SiO_7$ were markedly metastable and could not be obtained free from other phases. The cell dimensions of Bauer's boron-rich product were given as *a* 7·115 Å, *c* 4·812 Å. These values compare well with those quoted here for the tetragonal dehydroxylated datolite product when allowance is made for impurities and the poorly crystalline nature of the samples, although there is no certainty that boron and silicon are distributed between available sites in the same way in both phases. Bauer referred to his boron-rich end-member as 'Borgehlenit'. In a later reference to the same work, Černý (*Canad. Min.* **10**, 638) used the anglicized term 'boron-gehlenite'.