Thermal Decomposition of 14 Å Tobermorite From Crestmore

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The thermal decomposition of 14 Å tobermorite from Crestmore has been studied using weight and CO_2 loss curves, X-ray fiber rotation photographs, and infrared absorption spectra. The initial mineral has the approximate composition $5\,CaO \cdot 6\,SiO_2 \cdot 9\,H_2O$ with small amounts of CO_2 and B_2O_3. Part of the water is present in molecular form, and SiOH groups may also be present; this is compatible with the idealized constitutional formula $Ca_5Si_6O_{18}H_2 \cdot 8\,H_2O$. At 55 C, there is a sharp change to 11.3 Å tobermorite, $Ca_5Si_6O_{18}H_2 \cdot 4\,H_2O$. The 11.3 Å tobermorite loses most of its water gradually, at 55 to 200 C, apparently without undergoing fundamental change in structure. At 200 to 450 C, a 9.35 Å tobermorite is formed; this has the approximate composition $Ca_5Si_6O_{18}H_2$. At 450 to 650 C, most of the remaining water is lost, as well as the CO_2. This process appears to be a gradual one, in which some essential features of the structure are retained; the layer thickness increases to 9.7 Å. The process may occur through condensation between adjacent SiOH groups, as suggested previously (2). At 730 to 775 C a wollastonite-like intermediate phase is formed, which at 850 to 900 C gives place to wollastonite itself. Infrared absorption spectra are given for each of the main stages. The thermal behavior of the Crestmore tobermorite seems to be essentially similar to that of the Ballycraigy and some synthetic specimens, but the crystallization of wollastonite is more gradual. This is perhaps due to the presence of borate in the Crestmore mineral.

•MANY OF the studies made by T. C. Powers have been concerned with the role of water in cement pastes. Some of this water is present in capillary pores or other intercrystalline spaces. Part, however, is chemically combined in the gel particles themselves; this corresponds approximately to the "nonevaporable water." As is well known, the gel particles are believed to have a structure related to that of the crystalline tobermorite minerals, which can therefore in some degree be used as models for studying their properties.

The various naturally occurring and synthetic forms of 11.3 Å tobermorite do not all behave in the same way on heating. The natural mineral from Ballycraigy (N. Ireland) undergoes water loss and lattice shrinkage to the 9.3 Å form at 180-240 C; the latter changes to wollastonite at 750-780 C (1, 2). No intermediate phases other than the 9.3 Å tobermorite were detected. The mineral from Loch Eynort (Scotland), in contrast, loses its water without undergoing lattice shrinkage; the X-ray pattern is substantially unchanged up to 750 C, above which temperature wollastonite is formed (3). Some synthetic preparations behave like the Ballycraigy material (4), but others appear to behave like that from Loch Eynort (5). Detailed studies of the mineral from Crestmore (California) have until recently not been possible because the only known specimens were intergrowths known as crestmoreite, which contain several different

forms of tobermorite together with an apatite mineral (6, 7). The tobermorite in these intergrowths appears to behave in much the same way as the Ballycraigy mineral, but some evidence was obtained of an additional intermediate product formed during the conversion of the 9.3 Å tobermorite into wollastonite (8). The reason for these differences in thermal behavior between the various specimens is not known. Isomorphous replacement could possibly be responsible in the case of the natural minerals.

In 1961, Murdoch (9) described a crystalline 14 Å tobermorite from Crestmore which was free from other tobermorites and apatite minerals. It contained small amounts of B_2O_3 and CO_2, which, however, did not appear to affect the X-ray powder pattern. Prof. A. B. Carpenter made a specimen of this mineral available to us. It was decided to investigate its dehydration behavior using weight- and CO_2-loss curves, X-ray fiber rotation photographs, and infrared absorption spectra. The results might be expected to provide additional information bearing on the structures of the tobermorite minerals and, indirectly, on the way in which the nonevaporable water is present in cement pastes.

EXPERIMENTAL METHODS AND RESULTS

Material

The 14 Å tobermorite occurred as veins and linings of cavities in a hard rock, as described by Murdoch (9). The linings were often encrusted with scawtite. When chipped out, the material disintegrated to give mainly fibrous aggregates of crystals, though true single crystals could also be found. A sample of the 14 Å tobermorite was picked out, fiber by fiber, under the petrographic microscope. It appeared to be substantially free from scawtite, calcite and other impurities.

X-ray fiber rotation photographs gave results agreeing with those reported by Heller and Taylor (7) on the basis of studies of crestmoreite intergrowths. The geometrically orthorhombic cell for the present sample had a = 11.28, b = 7.32, c = 28.06 Å (V = 2317 Å^3). The fibers had length b, positive elongation, low birefringence, and mean refractive index 1.542 in sodium light. The specific gravity, determined by suspension, was 2.20. Together with the unit cell volume given above, this gives a cell formula weight of 3071. The pseudocell with a = 5.64, b = 3.66, c = 28.06 Å thus has a formula weight of 768.

Thermal Weight Loss Curves

A silica tube furnace was used; the sample was placed in a platinum microboat and was heated to constant weight at successively higher temperatures. A complete curve took several weeks to obtain. Figure 1A gives the results of two runs, which were obtained using slightly differing techniques. For run A, heating was carried out in a steady stream of dry, CO_2-free air. An unweighed sample was placed beside the weighed one, and, at various points on the curve, portions were removed from it for X-ray examination. For run B, the furnace was filled with dry, CO_2-free N_2 before each heating period. During each heating period, one end was closed and the other was connected to two absorption tubes containing standard $Ba(OH)_2$ solution. After each heating period, the gas in the furnace was swept through the absorption tubes with dry, CO_2-free N_2. The $Ba(OH)_2$ solutions were then titrated with acid, the furnace opened, and the boat weighed. It was assumed that any acid gas absorbed by the $Ba(OH)_2$ solution was CO_2; in this way, the curve in Figure 1B was obtained.

The results of the two runs represented in Figure 1A agreed well with each other and a mean curve was drawn. By subtracting the curve for CO_2 loss given in Figure 1B, a curve for water loss was obtained. The data from this curve were recalculated to give the number of water molecules retained per pseudocell (assumed to be of formula weight 768). The heavy curve in Figure 1D gives the results thus obtained. It will be termed the dehydration curve.

X-Ray Investigation

Samples heated as described above were examined by making X-ray fiber rotation photographs. Largely by comparing these with standard photographs of reference

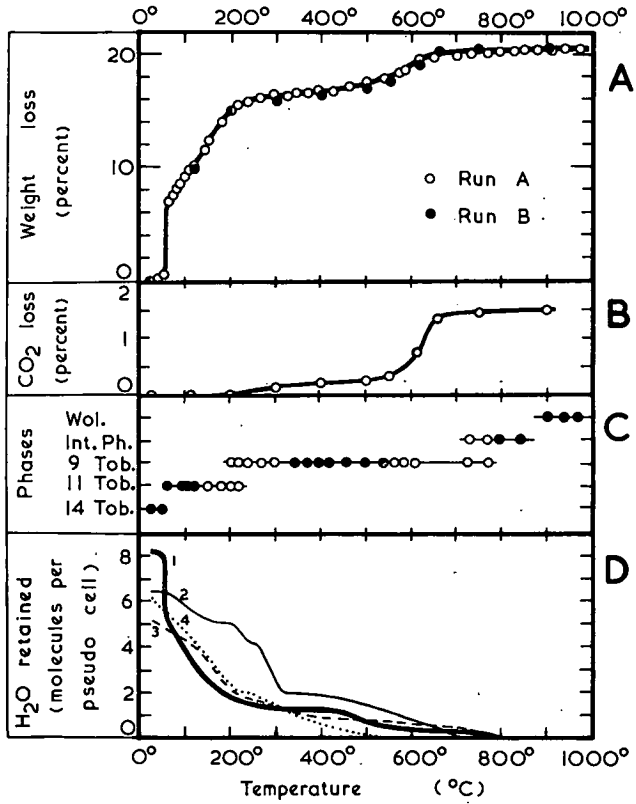

Figure 1. Thermal weight and CO_2 loss curves and phases detected by X-rays. A, Thermal weight loss curve; B, CO_2 loss curve. C, Phases detected by X-rays: 14 Tob. = 14 Å tobermorite; 11 Tob. = 11.3 Å tobermorite; 9 Tob. = 9.3-9.7 Å tobermorite; Int. Ph. = wollastonite-like intermediate phase; Wol. = wollastonite; full circles denote highly crystalline phases giving strong X-ray patterns, open circles denote poorly crystalline phases giving weak X-ray patterns. D, Dehydration curves: heavy curve 1, for the 14 Å tobermorite from Crestmore, is calculated from the weight and CO_2 loss curves given in A and B; curve 2 is for a mixed 14 Å-11 Å tobermorite from Ballycraigy (1); curve 3 is for the 11.3 Å tobermorite from Loch Eynort (3); curve 4 is for a synthetic 11.3 Å tobermorite (8); curves 2-4 are recalculated from data in the original papers.

substances, the phases present were determined. The main results are given in Figure 1C. The 11.3 Å tobermorite gave a normal pattern, similar to those reported previously (7). The 9.3 Å tobermorite, when formed below about 600 C, also gave a normal pattern closely similar to that reported for the corresponding product obtained from the Ballycraigy material (2); the exact value of the basal spacing (obtained by measurement of the 008 reflection) was 9.35 ± 0.05 Å. The patterns given by the products formed at 600 to 800 C require individual description. The 610 C sample gave a weak pattern which was generally similar to that of the 9.3 Å tobermorite formed at lower temperatures, but there was evidence of stacking disorder, and the basal spacing had risen to 9.5 Å. The 730 C sample gave a similar but still weaker pattern, with a basal spacing of 9.7 Å; some reflections attributable to the wollastonite-like intermediate phase were also present. The 770 C sample gave a pattern attributable mainly to this intermediate phase but with the addition of a 9.7 Å reflection attributable to the previous one.

Table 1 gives fiber rotation data for the wollastonite-like intermediate phase formed around 800 C. For comparison, corresponding data for the wollastonite formed at 940 C are included; these agree closely with those of natural wollastonite (7).

TABLE 1

X-RAY FIBER ROTATION DATA FOR SAMPLES HEATED AT 800 C AND 940 C

800 C Sample			940 C Sample			
Spacing (Å)	Relative Intensity	Layer Line	Spacing (Å)	Relative Intensity	Layer Line	Indexes
			7.7	m	0	200
4.4	w	0				
			3.83	s	0	400
			3.52	s	0	002
3.3	s	0	3.31	s	0	$20\bar{2}$
			3.09	s	0	202
2.97	vs	2	2.97	vs	2	320
2.80	w	0	2.80	vw	2	$32\bar{1}$
2.72	w	0	2.72	vw	0	$40\bar{2}$
			2.55	mw	0	600
2.47	m	0 & 2	2.47	ms	{0	402
					{2	122
			2.33	m	{0	003
					{2	520, $32\bar{2}$
2.27	m	0	2.29	m	0	601, $20\bar{3}$
2.18	m	2	2.18	m	2	322, 521
1.98	w	2	2.01	w	2	$52\bar{2}$
			1.98	w	0	602
			1.91	w	0	800
			1.86	vw	2	
1.83	ms	4	1.83	ms	4	040
			1.80	vw	0	
			1.75	m	0	
1.72	s	2	1.72	ms	2	

Layer line spacing 7.3 Å in both cases. Indexes relate to the monoclinic variety of wollastonite (parawollastonite) (7).

Infrared Investigation

Infrared absorption spectra were recorded for the unheated mineral and for samples heated at various temperatures. Figure 2 gives the most important results; those for samples heated at other temperatures are mentioned later. A double-beam instrument was used and was fitted with a NaCl prism, except for recording the 3000 cm^{-1} regions of the spectra given in Figures 2B-2F, for which a grating was substituted. Except in the case of the unheated mineral, the KBr disc technique was employed. Two different sample concentrations were used to obtain optimum conditions for different parts of the spectrum. For heating temperatures up to 250 C the sample was heated in the disc immediately before the spectrum was obtained. For higher temperatures, the sample was heated by itself, under conditions similar to those used in obtaining the weight loss curve; the disc was then prepared and was reheated at 100 C to drive off any moisture absorbed from the atmosphere immediately before the spectrum was recorded.

When the KBr disc method was used with the unheated mineral, a spectrum was obtained that was almost identical with that of the sample heated at 90 C. It was concluded that dehydration to the 11.3 Å form had occurred in preparing the disc, and a different method was therefore used: for frequencies above 1200 cm^{-1} a mull in C_2Cl_4 was used, and for lower frequencies the sample was deposited dry on a NaCl plate by allowing a suspension in CCl_4 to evaporate. As a check, this method was also used with a sample heated to 90 C; the resulting spectrum agreed with that obtained using KBr. The peaks marked X in the spectrum of the unheated mineral (Fig. 2A) are attributable to C_2Cl_4.

DISCUSSION

14 Å Tobermorite

The studies of McConnell (1) and of Megaw and Kelsey (10) showed that 11.3 Å tobermorite has the approximate composition $C_5S_6H_5$; this formula also represents the

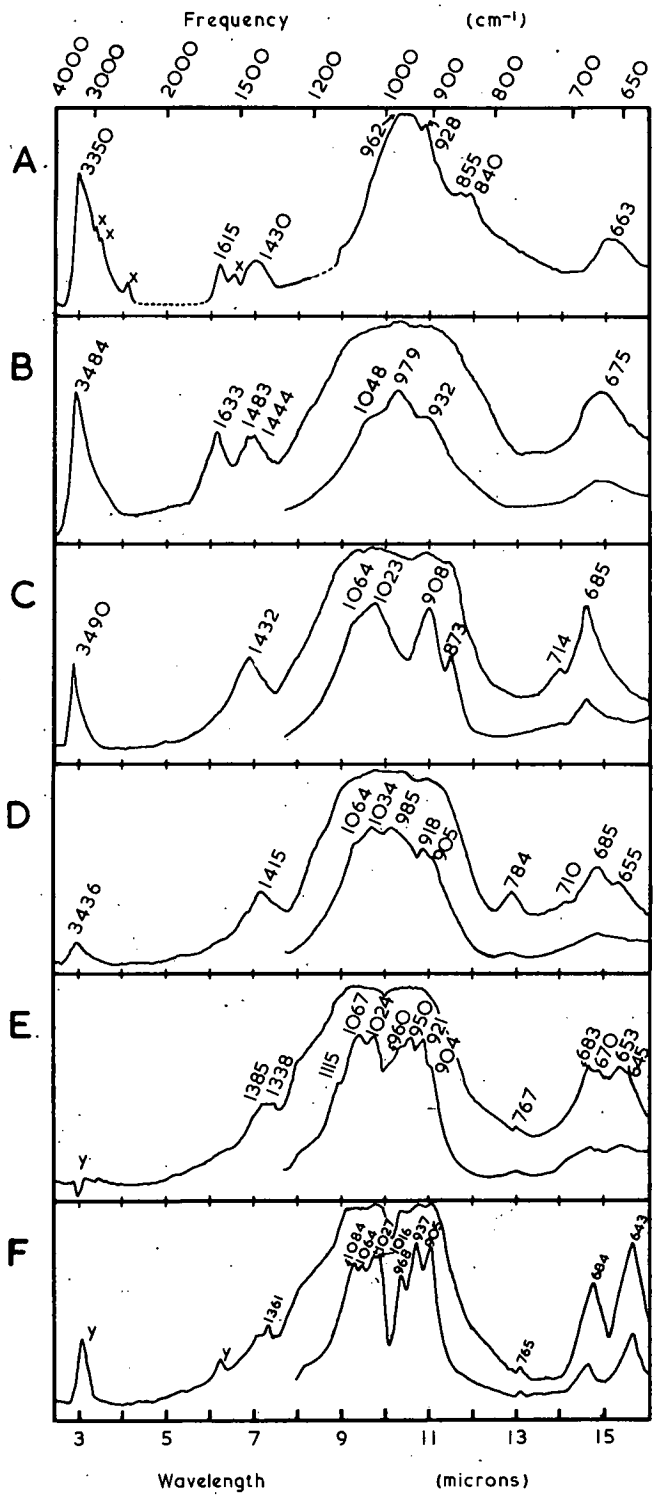

Figure 2. Infrared absorption spectra. A, Unheated mineral (14 Å tobermorite). B, Sample heated at 90 C (11.3 Å tobermorite). C, Sample heated at 520 C (9.3 Å tobermorite). D, Sample heated at 710 C (9.7 Å tobermorite). E, Sample heated at 800 C (wollastonite-like intermediate phase). F, Sample heated at 940 C (wollastonite). Peaks marked X and Y are attributable to C_2Cl_4 and water reabsorbed from the atmosphere respectively. Where two curves are shown, these are for different sample concentrations (0.33 and 2.0 mg in a 170-mg KBr disc).

atomic contents of the pseudocell. From packing considerations one might expect the pseudocell of 14 Å tobermorite to contain four water molecules more than that of the 11.3 Å form, thus making its formula $C_5S_6H_9$. The dehydration curve (Fig. 1D) indicates that there are in fact 8.2 molecules of water per pseudocell. The agreement between observed and predicted values may be considered satisfactory in view of the possible experimental errors and complications arising from isomorphous replacement. Further discussion of the composition and atomic cell contents would not be justified in the absence of a full chemical analysis.

The infrared spectrum of the unheated mineral (Fig. 2A) is similar to that reported for a synthetic 14 Å tobermorite by Kalousek and Roy (4). It includes a band at 3350 cm^{-1}, which could be due to molecular water or SiOH or both, and one at 1615 cm^{-1}, which could be due to molecular water but not to SiOH. There is no evidence of ionic hydroxyl. These results are compatible with the constitutional formula $Ca_5Si_6O_{18}H_2 \cdot 8\,H_2O$, in which there are two SiOH groups and eight water molecules.

The band at 1430 cm^{-1} could be due to CO_3^{2-} or BO_3^{3-} or both; since CO_3^{2-} is known to be present in the unheated mineral, and since a band remains in this region of the spectrum after it has been expelled, it is likely that both groups contribute to it. The absence of bands at 877 and 714 cm^{-1} suggests that little, if any, of the CO_3^{2-} is present as calcite. These results are compatible with Murdoch's (9) view that the CO_3^{2-} and BO_3^{3-} are present in the tobermorite itself. Gaze and Robertson (11) also considered that the tobermorite structure could accommodate a certain amount of carbonate ion.

The weight loss (Fig. 1A) and X-ray (Fig. 1C) results show that dehydration to the 11.3 Å form occurs sharply, at 55 ± 5 C.

11.3 Å Tobermorite

The dehydration curve (Fig. 1D) shows that, when formed at 55 C, this phase contains 5 molecules of water per pseudocell; this is compatible with the accepted formula $C_5S_6H_5$. The infrared spectrum of the 90 C sample (Fig. 2B) is in general agreement with those reported for 11.3 Å tobermorites by Kalousek and Roy (4), Berkovich et al. (12), Hunt (13), and Midgley (14). Hunt examined a natural specimen from Loch Eynort; the other investigators studied synthetic preparations. The Crestmore, Loch Eynort, and synthetic specimens of 11.3 Å tobermorite thus give infrared spectra that agree closely with each other. It would probably be necessary to re-examine all the specimens using an identical experimental technique to determine whether the small differences between the published spectra are significant. The broad complex of Si-O stretching bands centered around 980 cm^{-1} is distinctly different in form from that observed with the 14 Å tobermorite. This suggests that the silicate anions undergo changes, in configuration at least, when the mineral is dehydrated to the 11.3 Å form.

The bands attributed to water, SiOH, CO_3^{2-} and BO_3^{3-} are present in the spectrum of the 11.3 Å tobermorite. These results are compatible with the constitutional formula $Ca_5Si_6O_{18}H_2 \cdot 4\,H_2O$.

The change from the 14 Å to the 11.3 Å form took place sharply; in contrast, the change from the 11.3 Å to the 9.3 Å form is very gradual. The dehydration curve (Fig. 1D) shows a gradual loss of water which begins as soon as the 11.3 Å form appears (at 55 C) and continues up to its final disappearance at 200-250 C; by this time the number of molecules per pseudocell has fallen to 1.5. The X-ray photographs (Fig. 1C) showed strong, sharp patterns of 11.3 Å tobermorite up to about 120 C. With further increase in temperature the patterns became progressively more weak and diffuse; at 200-220 C there were indications that both 11.3 Å and 9.3 Å tobermorites were present. At 240 C and above the reflections of 11.3 Å tobermorite were no longer detected. Infrared spectra were obtained for samples heated at 150 and 200 C. The 150 C sample gave a spectrum similar to that of the 90 C sample, but there were some slight but distinct differences. Further changes could be seen in the spectrum of the 200 C sample which could be attributed to partial conversion to 9.3 Å tobermorite. These results could be explained either by postulating the existence of an intermediate phase not detected by X-rays or, perhaps more probably, by assuming that the 11.3 Å tobermorite can lose part of its water before collapse to the 9.3 Å

form takes place. This second explanation could account for the gradual nature of the water loss, the diffuseness of the X-ray patterns, and the various changes observed in the infrared spectrum.

9.3 Å Tobermorite

As stated, formation of this phase begins at about 200 C. Infrared spectra were recorded for samples heated at 250, 300, 350 and 520 C; all were essentially similar, but that of the 520 C sample was sharper than the others, and is shown in Figure 2C. Together with the X-ray evidence (Fig. 1C) this suggests that the 9.3 Å tobermorite formed at 400-550 C is more highly crystalline than that formed at lower temperatures. Samples formed at 300-450 C had a nearly constant water content of just over one molecule per pseudocell (Fig. 1D). They retained most of the CO_2 originally present (Fig. 1B). In the infrared spectrum (Fig. 2C), the band at about 1630 cm^{-1} is absent, but that at 3490 cm^{-1} is present, though somewhat weaker than in the spectra of the 14 Å and 11.3 Å tobermorites. This indicates that molecular water is absent but that SiOH is present. The band at about 1430 cm^{-1}, attributed to CO_3^{2-} and BO_3^{3-}, is present; the silicate absorption bands show marked changes. These results are compatible with the idealized formula C_5S_6H, or $Ca_5Si_6O_{18}H_2$; formulas given previously (1, 2, 7), which indicate higher water contents, would appear to be in error, at any rate for the product obtained from the Crestmore mineral. The present results do not support the conclusion of Kalousek and Roy (4) that 9.3 Å tobermorite contains water in molecular form.

The dehydration and CO_2 loss curves (Fig. 1B and 1D) show that the remaining water and CO_2 are lost mainly at 450-650 C. The X-ray evidence suggests that the loss of water does not lead to the immediate production of another phase, but that the structure of the 9.3 Å tobermorite persists without fundamental change, though with some deterioration in crystallinity. A similar conclusion was reached in the case of the Ballycraigy mineral (2); it was suggested that condensation occurred between SiOH groups of adjacent layers, which thus became joined by new Si-O-Si linkages. The present results show that, with the Crestmore mineral at least, dehydration causes an increase in layer thickness to about 9.7 Å. The transition is probably gradual, since the basal spacing varies continuously; multiple basal reflections were not observed.

Figure 2D gives the infrared absorption spectrum of a sample heated at 710 C. It is distinctly different from those of the products obtained at either lower or higher temperatures (Fig. 2C and 2E) and is closely similar as regards its Si-O bands to one reported by Kalousek and Roy (4) for a synthetic preparation heated at 650 C, which had been shown by X-rays to be a 9.5 Å tobermorite. The spectrum in Figure 2D can probably be regarded as that of the near-anhydrous 9.7 Å tobermorite. The considerable differences that exist between this spectrum and that of the hydrous 9.3 Å tobermorite (Fig. 2C) suggest that marked changes have occurred in the silicate anions. This provides some support for the view, mentioned previously, that additional Si-O-Si links are formed on dehydration.

The band at 1415 cm^{-1}, attributed in the spectra of samples heated at lower temperatures to CO_3^{2-} and BO_3^{3-}, is still present in those of the samples heated at 710 C and above, although it has shifted to slightly lower frequencies. This can be attributed to loss of the carbonate groups (Fig. 1B), the residual absorption thus being due to borate. The presence of a band in this region in samples from which the CO_2 has been removed shows that the boron is in threefold coordination; tetrahedrally coordinated boron would not absorb here, but in the region of 1000 cm^{-1}.

Transition to Wollastonite

The X-ray evidence (Fig. 1C) shows that the 9.7 Å tobermorite changes to a wollastonite-like intermediate phase at 730-770 C, and that the latter changes to wollastonite itself at 850-900 C. The X-ray fiber rotation pattern of the intermediate phase (Table 1) is similar to that of wollastonite, but there are distinct differences. Some of the strongest reflections of wollastonite are absent, at least one additional reflection is present, and some other reflections are altered in spacing. Perhaps the most

striking feature is the increased intensity of the $20\bar{2}$ reflection relative to 400 and 002. It has been shown with the Ballycraigy tobermorite that the wollastonite ($10\bar{1}$) plane is formed nearly parallel to tobermorite (001); a possible mechanism for the reaction was suggested (2). The strength of the $20\bar{2}$ reflection in the intermediate phase in the present case suggests that this phase can be regarded as an imperfectly crystalline wollastonite in which the layer structure of the tobermorite has persisted to some extent. The atoms are relatively well ordered into layers parallel to wollastonite ($10\bar{1}$), but within these layers the development of the wollastonite structure is not yet complete.

Figure 2E gives the infrared spectrum of the 800 C sample; a sample heated at 780 C gave an essentially similar spectrum. This spectrum can be attributed to the intermediate phase. It is similar to, but not identical with, that of wollastonite formed at 940 C (Fig. 2F). This supports the conclusions given earlier.

The X-ray results (Fig. 1C and Table 1) show that the crystallization of wollastonite is completed at 850-900 C. The infrared absorption spectrum of a sample heated at 940 C is given in Figure 2F. For comparison, a spectrum was also recorded for a specimen of natural wollastonite. It was similar to that of the 940 C sample, except that the bands at 1361 and 765 cm^{-1} were absent. These bands can be attributed to the presence of borate (15) in the Crestmore mineral. The shift in frequency of the 1361 cm^{-1} band that occurs between 710 and 800 C must be attributed to a change in the environment of the borate group.

Comparison with Tobermorites From Other Sources

In Figure 1D, the dehydration curve obtained in the present investigation is compared with those obtained for Loch Eynort, Ballycraigy and synthetic specimens. Agreement is close except for the Ballycraigy specimen, despite the fact that the Loch Eynort tobermorite does not pass through a 9.35 Å stage on dehydration. The very different results reported for the Ballycraigy tobermorite can perhaps be explained by a difference in experimental technique.

The X-ray and infrared results obtained in the present investigation indicate that the thermal behavior of the Crestmore tobermorite is in general similar to that of the Ballycraigy mineral and of the synthetic preparation studied by Kalousek and Roy (4). The crystallization of wollastonite seems to take place more gradually than with the Ballycraigy mineral. This can perhaps be attributed to the presence of the borate ions, which might well impede the formation of wollastonite.

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