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EFFECTS OF ISOMORPHOUS SUBSTITUTION IN HYDROTHERMALLY-SYNTHESIZED TOBERMORITE

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ABSTRACT

A series of tobermorites and substituted tobermorites was prepared in attempts to incorporate various contents of aluminum, iron and magnesium into the tobermorite structure. Earlier observations of Kalousek on the effects of aluminum substitution were largely confirmed. The presumed location of aluminum in tetrahedral sites was confirmed by *x*-ray fluorescence spectroscopy. Surface area measurements indicated that only a very modest decrease in particle size accompanied substitution. A strong high-temperature exothermic response characteristic of aluminum-bearing tobermorite can perhaps be attributed to formation of a very poorly crystalline aluminum-silicon spinel accompanying conversion of dehydrated tobermorite to wollastonite. The main Si-O lattice vibration did not shift as a result of substitution but bands at 1207 and 745 cm^{-1} were observed to shift to lower frequencies as a result of aluminum substitution. Successful incorporation of iron and magnesium into the tobermorite lattice appeared to be attained, but interpretation was complicated by the apparent formation of a small amount of xonotlite along with the tobermorite and by difficulties in securing reproducible syntheses.

INTRODUCTION

Tobermorite, a rare calcium silicate hydrate mineral described originally by Heddle (1880), has been found to be of considerable technical importance. It is produced on autoclaving concrete or sand-lime masonry blocks, and apparently serves as the principal binding agent in these building materials (Kalousek, 1954). Furthermore, there are several poorly-crystalline calcium silicate hydrates that seem to be closely related to tobermorite, the most notable among which is tobermorite gel, the basic cementing compound produced by the normal hydration of portland cement (Brunauer, 1962).

The crystal structure of tobermorite as determined by Megaw and Kelsey (1956) involves a combination of layer and chain silicate structural features of considerable complexity. The basic unit consists of a central sheet comprising a double layer of calcium and oxygen ions, coupled with rows of $SiO_2(OH)_2$ tetrahedra that are linked into chains running parallel to the *b*-axis direction. The chains occur on either side of the central sheet. The structural unit has been compared to a piece of double-sided corrugated cardboard, with the central sheet reinforced on each surface by the longitudinal ridges. Two of these structural units pack together with their ridges superposed vertically, *i.e.*, not nested. This leaves channels parallel to the *b*-axis that are presumed to contain additional calcium not located by the structural determination. On heating tobermorite to several hundred degrees there is a loss of water accompanied by a reduction in the basal spacing from about 11.2 Å to about 9.5 Å; this has been interpreted as indicating the close approach of the structural units into intimate contact. (Taylor, 1953; McConnell, 1954). Further heating to temperatures of 800–900° C. produces a phase change to wollastonite (β-$CaSiO_3$).

Little information exists on the range of isomorphous substitution possible in tobermorite. The subject is of interest since tobermorite arising in technical products may have considerable opportunity to incorporate foreign ions, notably iron and aluminum. Kalousek (1957) studied the incorporation of aluminum into synthetic tobermorite and noted changes in the *x*-ray diffraction and differential thermal analysis characteristics of the substituted phases. The present work confirms and extends these earlier observations on aluminum-bearing tobermorite and reports the results of attempts at similar incorporation of iron and magnesium into the tobermorite lattice.

Method of Synthesis

Well-crystallized tobermorite is readily synthesized from calcium hydroxide and quartz at comparatively low temperatures under hydrothermal conditions. The method used in this study was based on that of Kalousek (1957). The quartz was "Special Silica" (Ottawa Silica Co.), that passed the No. 325 sieve. The calcium hydroxide was derived from reagent-grade calcium carbonate that was calcined at 1050° C. for four hours. Eight grams of the resulting calcium oxide were weighed out analytically, suspended in 32 ml of freshly-boiled distilled water, and stirred for three minutes. The newly-formed calcium hydroxide was transferred to a malted milk mixer with an additional 40 ml of water. A 10.3 gram portion of oven-dried quartz was then added to the material and the resulting mixture was stirred at high speed for five minutes. The mixture, now of the consistency of heavy cream, was then transferred to hydrothermal vessels, sealed, and placed in an oven at 175° C. The reaction was allowed to proceed for 19 hours, after which the product was cooled, the bomb opened, and the sample immediately bottled.

The substituted tobermorites studied in this work were prepared in an identical manner except that an admixture bearing the substituting ions was mixed with the quartz in the dry state prior to the addition of the latter to the freshly-slaked lime.

Following Kalousek, a series of "Al-tobermorites" was prepared using kaolinite as the source of the aluminum. The kaolinite used was the "Hydrite 10" grade supplied by the Georgia Kaolin Co. On the assumption that Al substitutes for Si in the tobermorite (Kalousek, 1957), the kaolinite was added in amounts calculated to supply aluminum to substitute for 3, 5, 10, and 15% of the silicon ions in the resulting tobermorite product. The amount of quartz used was reduced by the calculated SiO_2 content of the added kaolinite. Two additional Al-tobermorites were prepared using reagent grade $Al(OH)_3$ (synthetic gibbsite) as the source of the aluminum. The amounts of silicon replaced in these preparations were calculated at 10 and 15%, respectively.

PROPERTIES OF Al-SUBSTITUTED TOBERMORITE

X-Ray Diffraction. X-ray diffractometer traces were secured from randomly-oriented powder mounts of unsubstituted tobermorite and the variously-substituted varieties. A General Electric XRD-5A instrument using nickel-filtered copper radiation was used. The unsubstituted tobermorite yielded a pattern in excellent agreement with published diffractometer traces of Kalousek (1957) and camera data of Heller and Taylor (1956). The aluminum-bearing products gave patterns substantially identical with that of the aluminum-free product except as described below. With one exception, mentioned later, the products obtained using kaolinite as the aluminum source gave patterns identical with those of the products of the same aluminum content prepared using gibbsite. In general, the results substantiate the earlier findings of Kalousek (1957) on the effects of aluminum substitution.

Kalousek reported an increase in basal spacing from 11.1 to 11.7 Å for samples containing aluminum contents in excess of 4% Al_2O_3. The present samples were examined repeatedly by low speed (0.2 degrees two-θ per minute) scanning through the region of the basal peak, which permitted evaluation of the apparent spacing to within about 0.02 Å. It was found that even in the lower range of aluminum substitution represented here, there is a direct linear relationship between the spacing and the degree of substitution, as shown in Fig. 1. The best value for the basal spacing of the synthetic unsubstituted tobermorite was 11.18 Å; that of the 15% Al-tobermorite was 11.45 Å.

A gradual decrease of the intensity of the (400) reflection at 2.81 Å with increasing aluminum content was noted. In the present work the intensity of this peak relative to that of the strongest tobermorite peak at 3.07 Å in each case was 55, 52, 44, 39, and 33% for samples containing zero, 3, 5, 10, and 15% replacement, respectively.

Kalousek noted the appearance of hydrogarnet in samples having compositions corresponding to substitutions greater than about 11 per cent. In the present investigation hydrogarnet was not detected in any of the products made using kaolinite, but the product with nominal 15%

Al-substitution made using gibbsite showed a distinct peak at 5.07 Å attributable to this phase.

Infrared Absorption Spectra. Spectra of the tobermorite samples were secured with a Perkin-Elmer 421 dual-grating spectrometer. The specimens consisted of thin films of the tobermorites deposited on potassium bromide plates. The dried tobermorite was suspended in spectral-grade carbon tetrachloride; then several drops of the suspension were pipetted so as to cover the surface of the previously oven-dried plates, which were retained in the drying oven. Immediate evaporation of the carbon tetrachloride left an incomplete but satisfactory deposit of the tobermorite on the plate surface. Each specimen was quickly transferred to the instrument and its spectrum obtained. These precautions were taken with a view toward minimizing any possible effects of adsorbed water.

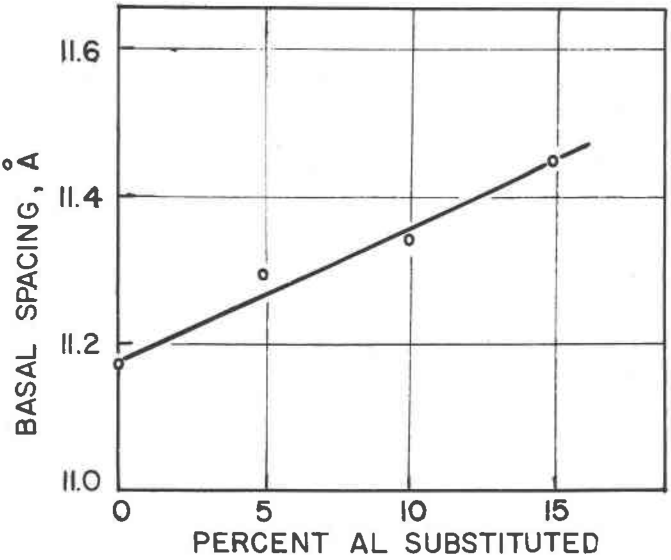

Fig. 1. Relation between basal spacing and degree of replacement of silicon by aluminum in Al-tobermorites.

The spectra as recorded show only very weak, broad absorption bands in the region characteristic of the stretching vibration of hydroxyl groups, in this case between 3000 and 3400 cm^{-1}. Other workers (Kalousek and Roy, 1957; Hunt, 1962) using the common potassium bromide pellet technique, have recorded spectra for tobermorite showing much more distinct bands of the hydroxyl stretching vibration. The weakness of the bands in the present case can probably be attributed to scattering resulting from the method of sample preparation (Farmer, 1964).

Spectra for unsubstituted tobermorite and the 10% Al-tobermorite are given in Fig. 2 for the region from 1800 to 600 cm^{-1}. The scale expansion feature of the instrument was used to enhance the definition of the various bands. There are several features which can be easily allocated, including the band at 1610–1620 cm^{-1} attributable to the bending vibration of water, the bands at 1450 cm^{-1} and 890 cm^{-1} which are attributable to carbonate derived from atmospheric carbonation in preparation and handling of the samples, and the main Si-O band of the tobermorite at about 965 cm^{-1}.

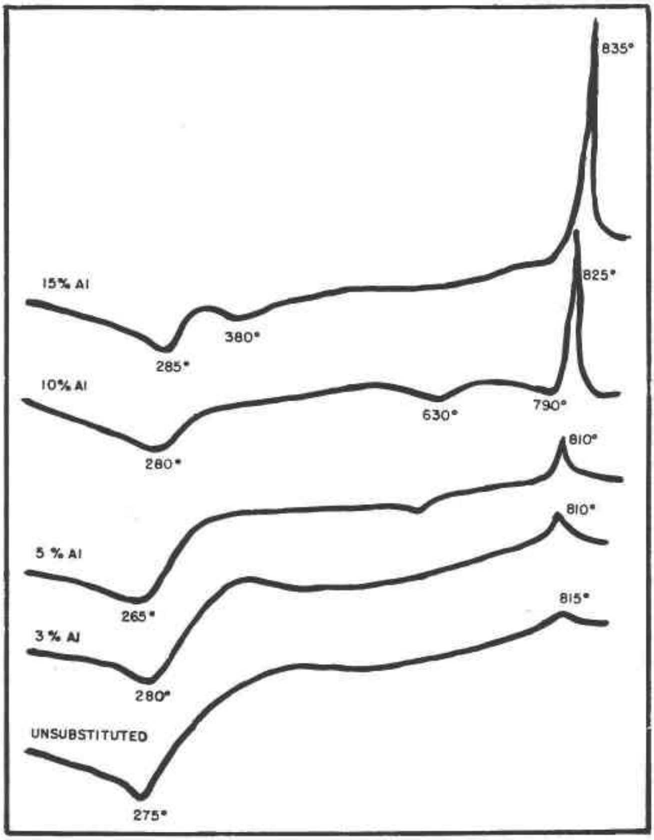

FIG. 2. DTA results for tobermorite and Al-tobermorites.

The effect of aluminum substitution on the spectrum of tobermorite does not appear to be a profound one. The sharpness of the bands is not affected, and the position of the main Si-O lattice vibration at 965–970 cm^{-1} is not altered significantly. There is an observable shift in the small band which appears at about 1205 cm^{-1} in unsubstituted specimens. As the aluminum content increases, the absorption weakens and the position of the center of the band shifts proportionately to lower frequencies. This phenomenon is illustrated in Fig. 3. Farmer (1964) called attention to a sharp band at 1200 cm^{-1} said to be characteristic of xonotlite. It is possible that a trace of this phase may be present in the unsubstituted tobermorite, although no evidence of its presence is apparent by *x*-ray diffraction. Nevertheless, it is felt that the regularity of the shift illustrated in Fig. 3 must be an indication of the effect of aluminum substitution on a particular vibration in tobermorite. The exact vibrational

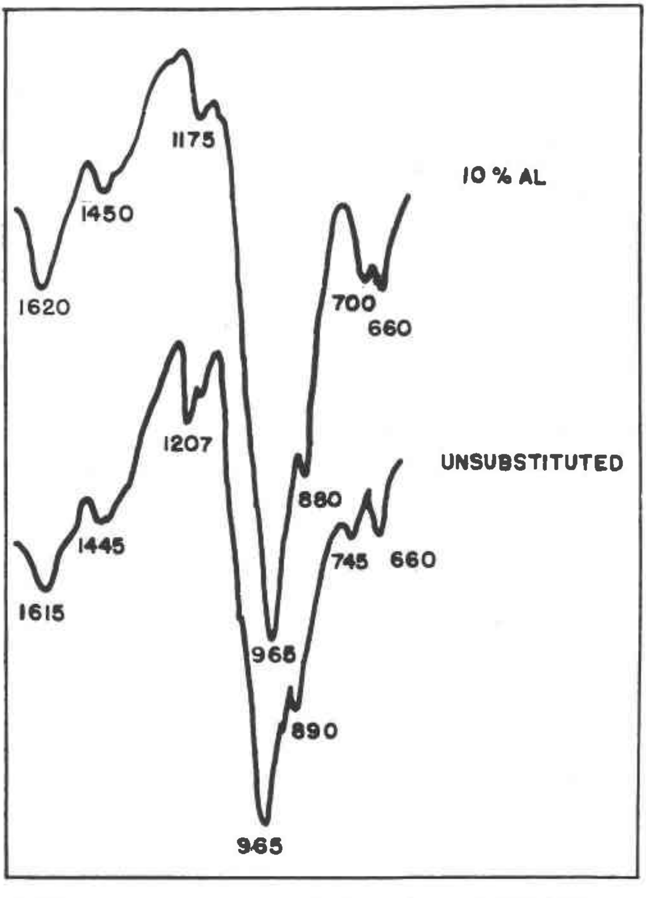

FIG. 3. Infrared absorption spectra of tobermorite and 10% Al-tobermorite.

mode involved is not known. Another shift of unknown significance involves the small band at 745 cm^{-1}, which shifts to about 720 cm^{-1} in the 3% Al-tobermorite, and further toward the low-frequency end with additional aluminum substitution. While CO_3^{2-} ions have a band in this region (the ν_4 vibration, which occurs at about 715 cm^{-1} for calcite), it is not reasonable to suppose that a carbonate vibration should shift as a result of aluminum substitution in the host tobermorite, particularly since the other carbonate bands at 1440–1450 cm^{-1} and 880–890 cm^{-1} do not shift. The assignment of this band to tobermorite is reinforced by reference to published spectra of tobermorite by Hunt (1962) and by Kalousek and Roy (1957), both of which show a very diffuse band in this region in the absence of any pronounced absorption at the position of the main carbonate band at 1450 cm^{-1}.

Particle Morphology. While no extended electron microscopic study was undertaken, observations of the particle morphology of a few of the samples were made using an R.C.A. EMU-3A instrument operated at 50 kv. All of the samples examined appeared to be composed of particles showing a thin, platy morphology, in agreement with results previously reported by others. Particles of both the unsubstituted tobermorite and of the Al-tobermorites showed a slight tendency toward elongation. Many of the particles had unusually acute terminations, and some were triangular in outline; one might associate such a morphology with pieces broken from large thin sheets. Some of the particles seemed to contain small inclusions, but the nature of these could not be determined.

Coordination of Substituted Aluminum. It has been demonstrated by various workers (White *et al.*, 1959; Brindley and McKinstry, 1961; Day, 1963) that the wavelength of the K-α x-ray emission peak of aluminum is affected significantly by the coordination of the aluminum ion, and that the coordination can be unequivocally determined by observation of the angular displacement of the position of the peak for a specimen compared to that from metallic aluminum. The measurement is readily made on a diffractometer equipped with a flow proportional counter and a helium or vacuum path to minimize absorption of the long-wavelength emitted radiation. The displacement range using an ethylene diamine ditartrate crystal is 0.04–0.06 degrees two-θ for tetrahedrally coordinated aluminum ions (coordinated to oxygen) and 0.08–0.12 degrees two-θ for octahedrally coordinated aluminum ions.

The angular displacement for the 15% Al-tobermorite specimen was measured using a suitably-equipped General Electric XRD-3 diffractometer. The goniometer was set successively at fixed angular settings at close intervals around the position of the aluminum Kα peak (142.45

degrees two-θ), and the intensity of emitted *x*-rays determined at each position by direct counting. A plot of the resulting intensity *vs.* angular setting gave a profile of the peak, from which the center was determined to within 0.01 degree. A similar measurement of the position of the peak from aluminum metal was made, and the displacement was calculated as the angular difference between the centers of the two peaks.

The displacement recorded for the 15% Al-tobermorite was 0.05 degrees two-θ; the same result was recorded in repeated trials on successive days. This result affords definitive evidence for the four-fold coordination of aluminum in Al-tobermorite, thus confirming Kalousek's assumption that the aluminum substitutes for silicon in the tetrahedral chains.

TABLE 1. SURFACE AREAS OF SYNTHETIC TOBERMORITES

Sample	Original Source of Aluminum	Surface Area, m^2/g
Unsubstituted tobermorite	—	78
3% Al-tobermorite	kaolinite	74
5% Al-tobermorite	kaolinite	117
10% Al-tobermorite	kaolinite	107
15% Al-tobermorite	kaolinite	103
10% Al-tobermorite	gibbsite	97

Surface Area. Surface areas of these materials were determined by water vapor adsorption, which is the procedure recommended by Brunauer and Greenberg (1960) for calcium silicate hydrates. Samples were initially oven-dried, then outgassed under moderate vacuum over P_2O_5 for four days. After weighing, they were allowed to equilibrate over sulfuric acid solutions in evacuated dessicators for a period of four days at 21° C., after which they were again weighed, and the concentration of the acid solutions determined by titration. The partial pressure of water vapor at equilibrium was determined from the concentration of the acid by application of the Gibbs-Duhem equation. The adsorption data were plotted according to the BET procedure (Brunauer *et al.* 1938), and yielded good straight lines from which the parameter "V_m" was evaluated by least squares. The surface area was calculated from V_m using an assigned area per water molecule of 11.4A^2 (Brunauer, Kantro, and Copeland, 1958). The results are given in Table 1.

The surface area of the unsubstituted tobermorite was 78 m^2/g, well within the range previously recorded for surface areas of well-crystallized tobermorites (Greenberg, 1954; Kalousek, 1954; Gaze and Robertson, 1956). The effect of aluminum substitution was to increase the surface area, but the amount of increase was much less than was anticipated.

Kalousek (1957) observed that the particle size of synthetic tobermorite "decreased markedly" with increasing aluminum content. The present data indicate that there is no proportional effect of aluminum substitution on surface area, the effect recorded varying irregularly from a slight decrease to a maximum increase of about 50%, as compared with similarly-synthesized tobermorite without substitution.

Differential Thermal Analysis. Synthetic tobermorite is known to yield only a broad, low-temperature endotherm at about 260° C., and a weak and indefinite high-temperature exothermic response at about 850° C. (Kalousek, 1954a). The endotherm reflects a loss of water and a reduction of the *c*-axis spacing to about 9.5 Å; the exotherm marks a recrystallization to wollastonite.

The samples were examined by DTA using a portable unit (Eberbach Co., Ann Arbor, Michigan) that was modified by replacing the insulating assembly supplied with the unit with a close-fitting sleeve of commercial pipe insulation. The apparatus so modified had a linear heating rate of 58° C. per minute from room temperature to about 600° C., after which the rate fell gradually to about 5° per minute at about 1000° C. This equipment consequently yields low-temperature peaks at slightly higher temperatures and high-temperature peaks at slightly lower temperatures than units capable of maintaining a constant rate of temperature increase, but the differences are not large and the peak shapes appear to be well-preserved.

DTA patterns for unsubstituted tobermorite and the series of Al-tobermorites made using kaolinite are shown in Fig. 4. It is obvious that, within this range of substitution, increases in the aluminum content led to increasing sharpness and intensity of the high-temperature exotherm, and also to increasing peak temperature. These effects have been observed by Kalousek (1957), who did not, however, attempt to explain them. Kalousek also noted a decrease in intensity of the exotherm for samples with still higher aluminum contents, which he attributed to dilution of the Al-tobermorite by increasing amounts of hydrogarnet formed as a companion phase.

On heating samples through the temperature range involved in the exotherm, it was found that at about 775° C. the Al-tobermorite samples started to undergo a remarkable shrinkage that was completed by about 800° C. The resulting product was at least partially fused; it was quite hard after cooling and could be removed from the sample well of the DTA unit only with considerable difficulty. In contrast, unsubstituted tobermorite did not undergo this response and was recovered as a friable powder after completion of the DTA run. The shrinkage is definitely not associated with delayed conversion of the 11Å tobermorite to the 9.5 Å dehydrated state: *x*-ray examination of a series of samples treated to various intermediate temperatures indicated that the latter conversion is complete by about 350° C. for all of the samples.

X-ray diffraction of all samples after the DTA runs showed only wollastonite as a crystalline phase, and the pattern for fused converted Al-tobermorite was indistinguishable from that of the unsubstituted product. We feel that both the exothermic response and the shrinkage observed for Al-tobermorites may be associated with the formation of a quasi-amorphous aluminosilicate compound, possibly an Al-Si spinel. As pointed out by Taylor (1959), the wollastonite produced on heating tobermorite probably has the normal Ca:Si ratio of 1.0. Because this ratio in the parent tobermorite is only 0.83, excess silica must also be produced along with the wollastonite. In the product from normal tobermorite samples this silica is presumed to be present in an amorphous state not detectable by *x*-ray methods. This free silica might readily react with some or all of the aluminum in the decomposed Al-tobermorite to produce an aluminosilicate of such poor crystallinity that it also escapes detection. Formation of such a quasi-amorphous compound, an Al-Si spinel, is held to be responsible for the similar strong DTA exotherm of kaolinite at about 980° C. (Brindley and Nakahira, 1959).

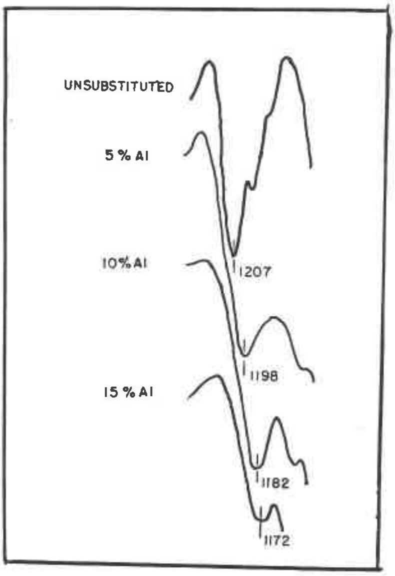

FIG. 4. Shift of adsorption band at 1207 cm^{-1} with increasing aluminum substitution.

It should be noted that the poorly-crystalline phase known as calcium silicate hydrate (I) also displays a strong high-temperature exothermic response, in this case in the absence of aluminum. However, this appears to be due to a different cause, since no fusion occurs and samples remain friable after the DTA run.

IRON- AND MAGNESIUM-SUBSTITUTED TOBERMORITES

A number of attempts were made to prepare synthetic tobermorites incorporating iron and magnesium, using the same technique used in the preparation of the aluminum substituted samples. The results of these attempts were somewhat less satisfactory than those described above, although it is felt that incorporation of both these elements into the tobermorite structure has been attained.

Samples were prepared incorporating iron in the form of hematite in amounts calculated to yield 5 per cent and 10 per cent replacement of silicon by iron. *X*-ray diffraction of the resulting products indicated that residual hematite was present, as was also obvious from the red color of the hydrothermal products. After firing these products to wollastonite (a compound whose *x*-ray peaks do not seriously overlap the main peaks of hematite) it was possible to estimate the amount of hematite remaining. Comparison of the peak heights for the main hematite peak with those for standards prepared by mixing hematite with a wollastonite produced by firing pure unsubstituted tobermorite suggested that practically all of the iron originally present was now present as hematite. It is possible that some of the iron could have entered the tobermorite structure and then been rejected on conversion of the tobermorite to wollastonite, and thus reappeared as hematite. However, in the light of subsequent observations reported below, this appears unlikely, and we were forced to conclude that little if any iron had entered the tobermorite structure.

Trials made using goethite as the source of iron were more successful. Goethite added in an amount calculated to replace 10 per cent of the silica in the resulting tobermorite produced an almost white product whose *x*-ray pattern showed no trace of goethite (main peak at 4.18 Å completely absent). Tobermorite was not the only silicate phase formed, however; the *x*-ray pattern revealed certain changes in the relative intensities of a few of the tobermorite peaks and several small additional peaks that could be interpreted as reflecting the formation of a small amount of xonotlite along with the tobermorite. Nor was all of the added iron incorporated in the silicate structures, despite the *x*-ray evidence. DTA of the product yielded a barely-detectable endotherm attributable to goethite, the size of which was very much less than that characteristic for the amount of goethite in the original mixture. Firing the product turned it a faint pink; *x*-ray examination of the fired product showed the presence of wollastonite and a small but definite main peak for hematite. It appeared that most of the goethite had entered the silicate structure, and only the small residual amount of goethite transformed to hematite on firing.

It was quite difficult to assess the residual goethite in the hydrothermal product, since the amount present was less than the limit of detectability by *x*-ray diffraction (goethite being a relatively poorly crystalline phase), and since the DTA endotherm was also weak and ill-defined. However, the hematite *x*-ray diffraction peak produced on firing the hydrothermal product was susceptible to measurement. Comparison of the size of this peak with those of the hematite-wollastonite standards previously mentioned suggested that hematite equivalent to about twenty per cent of the original amount of goethite used had been formed, implying that about eighty per cent had been incorporated into the silicate lattice. Neither the presence of unincorporated goethite nor the formation of a small amount of xonotlite seemed to affect the other observed properties of the tobermorite very significantly, the DTA, surface areas, and infrared spectra of this product being very similar to those of unsubstituted tobermorite. In particular, no enhanced DTA exotherm was produced as occurs in the case of aluminum substitution.

The attempt to incorporate magnesium added as MgO (synthetic periclase) was also at least partially successful; but the available evidence indicated that about 30% of the added MgO was not incorporated into the silicate product but was converted to brucite on hydrothermal treatment. Again, xonotlite was probably formed along with the tobermorite, and again no significant changes due either to magnesium substitution or to xonotlite contamination were manifest.

These experiments were carried out at Purdue University in 1963. More recently a number of attempts were made to duplicate these syntheses of iron- and magnesium-bearing tobermorites in the laboratory of the Bureau of Public Roads, using a Morey bomb and necessarily different batches of starting materials. Here, repeated attempts to incorporate iron added to the charge as goethite were unsuccessful, essentially all of the admixture remaining as a separate phase. In parallel experiments with magnesium added as MgO, however, most of the magnesium was incorporated into the tobermorite lattice. In these runs there was no indication of the formation of any xonotlite. Thus it appears that incorporation of iron and magnesium into the tobermorite lattice has been attained, but there appear to be some difficulties to be surmounted before reproducible syntheses can be secured and the effects of the incorporation of these foreign ions assessed unambiguously.

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