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# THE SYNTHESIS AND STABILITY OF TILLEYITE, $Ca_5Si_2O_7(CO_3)_2$

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ABSTRACT. At 5,000 lbs/in.$^2$ of $CO_2$ tilleyite is stable between 930 and 970°C and at 3,000 lbs/in.$^2$ of $CO_2$ between 870 and 930°C. The conditions of its stability are defined, on a $P_{CO_2}$-T diagram, by a narrow band lying between the more carbonated calcite + wollastonite assemblage and the less carbonated spurrite.

Under the conditions of the experiments it was found that traces of alumina and fluoride were necessary to effect the synthesis of tilleyite. A consideration of natural mineral assemblages currently supports the evidence that the presence of these two components is very effective in promoting the formation of tilleyite. With sufficient alumina the formation of gehlenite can be detected in apparent equilibrium with calcite + wollastonite, tilleyite or spurrite.

## INTRODUCTION

Tilleyite, $Ca_5Si_2O_7(CO_3)_2$. was discovered in 1933 at Crestmore (Larsen and Dunham, 1933; Dunham, 1933) and has since been described from other contact altered limestones in four different localities. These are New Mexico (Glass, Jahns and Stevens, 1944), Carlingford (Nockolds, 1947) Camus Mor (Tilley, 1947) and Camasumary (Wyatt, 1953). It is clearly a rarer mineral than spurrite, $5CaO.2SiO_2.CO_2$, which is also characteristic of certain contact altered limestones.

Tilleyite was incorporated into Bowen's (1940) decarbonation series by Nockolds (1947) and with Tilley's (1942) discovery of rankinite the progressive contact metamorphism of a limestone, with some siliceous impurity, or into which some silica was introduced metasomatically, is now represented by the following steps:

(1) Calcite + Quartz $\rightleftarrows$ Wollastonite + $CO_2$
(2) Calcite + Wollastonite $\rightleftarrows$ Tilleyite + $CO_2$
(3) Tilleyite $\rightleftarrows$ Spurrite + $CO_2$
(4) Wollastonite + Spurrite $\rightleftarrows$ Rankinite + $CO_2$
(5) Rankinite + Spurrite $\rightleftarrows$ Larnite + $CO_2$ (Tilley, 1951)

## EXPERIMENTATION AND RESULTS

*Previous work.*—Using Tuttle cold-seal pressure vessels it was found possible to investigate reaction (1) in the laboratory and to obtain equilibrium $P_{CO_2}$-T data for it (Harker and Tuttle, 1956). Attempts to study reactions (2) and (3) were thwarted by the failure of tilleyite to form in any of the experiments. A $P_{CO_2}$-T curve was obtained, however, for the reaction: Calcite + Wollastonite $\rightleftarrows$ Spurrite + $CO_2$ (Tuttle and Harker, 1957) and it appeared that this represented a true equilibrium because the reaction was reversible. The reason for the failure of a tilleyite + $CO_2$ assemblage to appear over a temperature range between that covered by the calcite + wollastonite and the spurrite + $CO_2$ assemblages was unknown.

*The synthesis of tilleyite.*—Through the kind cooperation of Professor Tilley and Dr. Nockolds, an analyzed sample of natural tilleyite from Ireland was made available for further experiments. J. Scoon's analysis gave $SiO_2$ = 24.39, $Al_2O_3$ = 0.23, $Fe_2O_3$ = 0.08, MgO = 0.21, CaO = 57.01, $CO_2$ = 17.23, $H_2O$ (+) = 0.62, percent. The results of some of these experiments are shown in table 1 (runs 1 to 31). After 30, 172, 242 and 329 hours at 930°C and 4,000 to 4,200 lbs/in.$^2$ of $CO_2$ the natural material was unchanged. At somewhat higher temperatures tilleyite broke down to spurrite and at somewhat lower temperatures to calcite + wollastonite in approximately 40 hours. This suggested that tilleyite might well have a field of stability on the low temperature side of the previously determined spurrite + $CO_2$ stability field.

However in the region in which the natural tilleyite appeared unchanged even after long runs, calcite and silica in the ratio of 5:2 always yielded calcite + wollastonite + $CO_2$. Attempts to produce tilleyite by changing the CaO:$SiO_2$ ratio by up to 5 percent to values on either side of 5:2 and by adding 4 percent ferrous oxalate were of no avail and efforts to flux the reaction with a trace of water, by using a hydrated silica, were also useless. Tilleyite was finally crystallized, however, both from calcite + wollastonite and from spurrite + $CO_2$ when these starting materials themselves had been formed by the controlled breakdown of natural tilleyite, (runs 29, 30 and 32).

It was noted that tilleyite-bearing rocks invariably contain some alumina bearing mineral and Professor Tilley (personal communication) has observed that fluorine, in fluorite, cuspidine or idocrase, is commonly present where

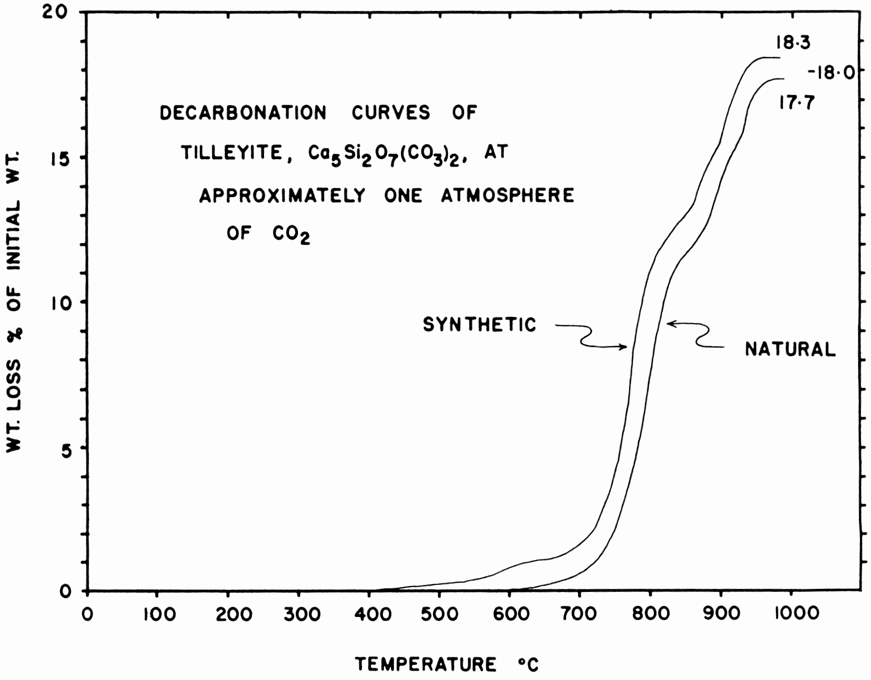

Fig. 1. Thermal dissociation curves of Natural Tilleyite from Carlingford, Ireland, (Material provided by Professor C. E. Tilley), and of Synthetic Tilleyite, (from run 65, see Table 1). The runs were carried out at one atmosphere in a continuously recording thermobalance. Tilleyite ideally contains 18.0% $CO_2$.

tilleyite develops (see table 2). At his suggestion runs were made with varying percentages of calcium fluoride included in aluminous starting materials. As a result tilleyite could be produced reliably from a variety of starting materials including calcite + quartz, calcite + amorphous silica and oxide mixes, within the stability range indicated by the behavior of the natural tilleyite. Experiments in this range using starting materials containing up to 8.6 percent $Al_2O_3$ with no $CaF_2$ resulted in the formation of gehlenite, with calcite + wollastonite. Starting materials with fluoride additive, but no alumina, produced no tilleyite but with sufficient fluoride an unidentified phase made its appearance.

The optical properties of a synthetic tilleyite made from a calcite + quartz mixture with 8.95 percent $Al_2O_3$ and 2.25 percent $CaF_2$ are as follows: $\alpha = 1.604 \pm .003$, $\beta = 1.630 \pm .004$ and $\gamma = 1.653 \pm .003$. Similar measurements on the material from Carlingford gave $\alpha = 1.599$, $\beta = 1.632$ and $\gamma = 1.656$. Figure 1 shows the thermal decarbonation curves of the natural and synthetic tilleyites at atmospheric pressure in a covered crucible and at a heating rate of approximately 8°C/min. The x-ray powder diffraction patterns of natural and synthetic tilleyites can be compared in figure 2.

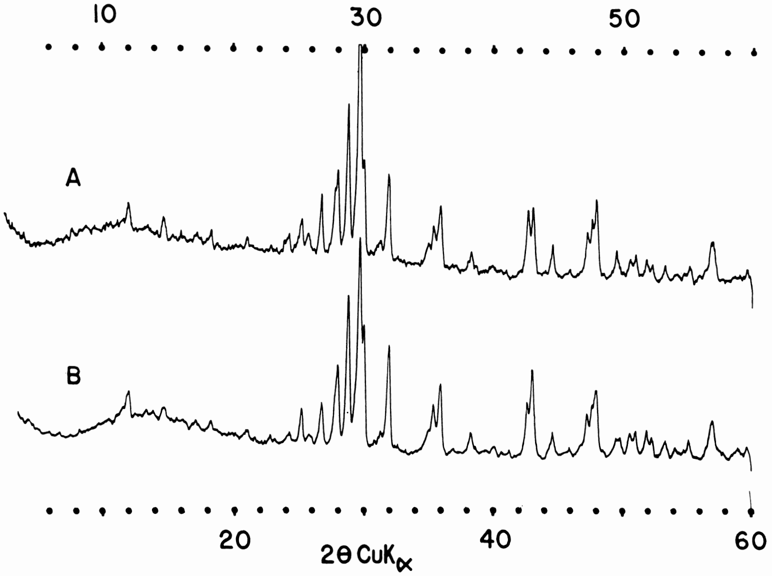

Fig. 2. X-ray powder diffraction patterns of
(A) Natural Tilleyite from Carlingford, Ireland. (Material provided by Professor C. E. Tilley).
(B) Synthetic Tilleyite, (from run 65, see Table 1).

*Stability of tilleyite in the presence of excess $CO_2$.*—The experiments from which it has been possible to outline the stability field of tilleyite are listed in table 1 and the results plotted in figure 3. The starting materials "CAS gel" indicate those made by gelling, drying and carefully igniting ethanolic mixtures of ethyl orthosilicate, calcium nitrate and aluminum nitrate solutions, (after Roy, 1956). The lime:silica ratio was always 5:2 but the alumina content was varied as indicated under "Starting Materials". The final compositions of the samples derived from these gels were spot checked analytically. Calcium fluoride was added subsequently. The products were identified by x-ray powder diffraction and/or optical examination.

In all but selected runs the pressure vessels were raised to operating conditions as quickly as possible by preheating the furnaces. In order to supress the development of calcite + wollastonite or spurrite with rising temperature the $CO_2$ pressure was raised with the temperature to maintain conditions about 30°C on what is believed to be the low temperature side of the spurrite stability field. By a rough extrapolation of the tilleyite $\rightleftarrows$ spurrite + $CO_2$ curve (assuming ideality for the $CO_2$ and plotting log p against l/T) the equilibrium $CO_2$ pressure at about 700°C is probably only a few hundred lbs/in.$^2$. The P-T conditions of the pressure vessels even during initial heating were thus probably always in or close to the tilleyite field, at least above 700°C.

In a few selected runs, the pressure vessels were brought up to temperature and pressure purposely through stability fields other than those in which they were finally run. In runs 49 to 52 inclusive the temperature was raised before the pressure. It is felt that the trace of tilleyite found in 51 must be left over from material formed as the P-T conditions passed through the tilleyite field. In runs 53 to 56, the pressure was raised before the temperature, and the P-T conditions were held at 4,000 lbs/in.$^2$ $CO_2$ and 907°C for 72 hours before being raised into the tilleyite field.

Altogether thirty-seven separate starting materials were made up of various kinds and with varying amounts of alumina and fluoride. Most of these were of the gelled type because in such the alumina appeared to be in a more active state than when it was mixed separately as an oxide powder. This is illustrated by some of the runs in which a *mixture* of calcite and quartz was used as the basic starting material with various amounts of alumina and calcium fluoride admixed mechanically. Runs 63 and 78 failed to produce tilleyite but *gelled* starting material with no more of the additives succeeded.

It appears that the stability of tilleyite is not appreciably changed by varying the amounts of these two additives above about 0.2 percent of each. It may be observed, however that with only these small amounts complete conversion to tilleyite was effected in only one run, (number 65) close to the center of the tilleyite field. This same starting material was only converted partially to tilleyite in runs 45 and 73 when starting materials containing a slightly higher percentage of the additives were converted largely to tilleyite under the same conditions. In runs 53, 54, and 55 some tilleyite was produced by those starting materials with the greater amounts of additives whereas 56 with only 0.2 percent of each failed to produce any detectable amounts of tilleyite. On the basis of these few runs it is very tentatively suggested that the minimum amounts of alumina and fluorine necessary for tilleyite formation, in the P-T range covered by these experiments, are 0.2 and 0.1 percent respectively.

The $P_{CO_2}$-T curve for the reaction tilleyite $\rightleftarrows$ spurrite + $CO_2$ plotted in figure 3 is at somewhat lower temperatures at 5,000 lbs/in.$^2$ of $CO_2$ than the published curve for the reaction calcite + wollastonite $\rightleftarrows$ spurrite + $CO_2$

(Tuttle and Harker, 1957, fig. 1). However some doubt has been cast on the exact location of the upper part of the previously published curve as runs 4 and 5 of the present work are not in agreement with it. In view of conflicting evidence it is concluded that the lower limit of stability of spurrite at 5,000 lbs/in.$^2$ of $CO_2$ is approximately 970°C. Within the limits of error, therefore, it appears that the lower limit of stability of spurrite coincides with the upper limit of stability of tilleyite.

*Role of alumina and fluoride additives.*—The introduction of the two components $Al_2O_3$ and $CaF_2$ into the system $CaO$—$SiO_2$—$CO_2$ could complicate the equilibria under consideration in two ways. First, with the introduction of fluorine at such high temperatures there is the possibility of creating a heterogeneous volatile phase (Brisi, 1957). With larger amounts of fluorine this might be the case. However in the runs significant to the stability of tilleyite the amounts were very small. Considering the size of the samples and the volume of the heated pressure chamber $F_2$:$CO_2$ was approximately 1:400, by weight. At higher ratios, up to 1:20, producing appreciable amounts of the "X" phase, the results of runs of variable duration did not change the apparent stability of the carbonate phases as would be expected had this been an important factor, (see Harker, 1958).

Second, the addition of alumina and fluorine theoretically changes the variancy of the $P_{CO_2}$-T curves of figure 3. However it appears that only very small amounts of $Al_2O_3$ and $F_2$ are necessary for the formation of tilleyite. As little as 0.2 percent of $Al_2O_3$ and 0.1 percent $F_2$ suffice. Moreover under the conditions of these experiments tilleyite does not show any evidence of accepting major amounts of these components into its structure. With more than 2 percent of each, extra phases, gehlenite and "X", are evident in appreciable

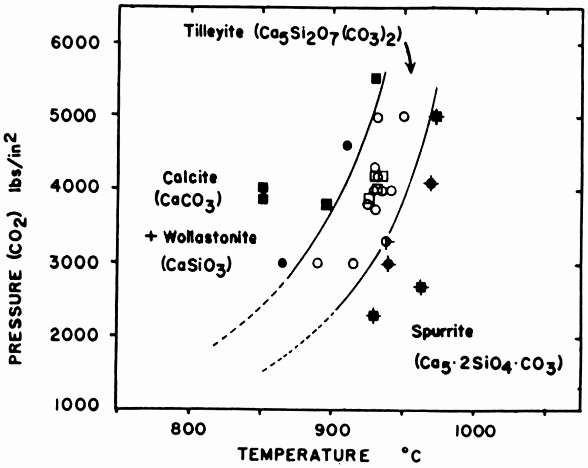

Fig. 3. $P_{CO_2}$-T curves outlining the field in which Tilleyite + $CO_2$ assemblages are stable.

Square symbols indicate experiments carried out using Natural Tilleyite. Circular symbols indicate experiments carried out using Analytical Reagents.

amounts. Furthermore no significant difference in lattice spacings could be found between the natural specimen with 0.2 percent $Al_2O_3$, and a synthetic tilleyite grown from a starting material with 0.2 percent $Al_2O_3$ and 0.2 percent $CaF_2$, and a synthetic tilleyite grown from a starting material with 8.18 percent $Al_2O_3$ and 4.75 percent $CaF_2$ (see table 3). It can be assumed therefore that within the limits of experimental error the $P_{CO_2}$-T curves are univariant.

It is of interest to note that throughout the range of these experiments alumina always appeared as gehlenite. Grossularite was not expected as the runs were all above 850°C (Roy and Roy, 1957). Compared with Yoder's (1950) decarbonation series in an argillaceous limestone it is evident that between 3,000 and 5,000 lbs/in.[2] of $CO_2$, a wollastonite-calcite-gehlenite assemblage is formed before the development of tilleyite. At lower $CO_2$ pressures tilleyite might be expected to form at lower temperatures, over longer periods and in the presence of appreciable water, because of its occasional association with grossularite.

## CONCLUSIONS AND PETROLOGIC CONSIDERATIONS

The one analysis of natural tilleyite shows 0.2 percent $Al_2O_3$ and no fluorine. It may be that fluorine is only acting as a mineralizer. Its mineralizing action is well illustrated by a comparison of run 34, in which 8.6 percent $Al_2O_3$ was present, with some of the subsequent shorter runs with less alumina but some fluoride, e.g. 36, 61, 62, 70, etc. In these later runs the gehlenite is well crystallized and easily seen under the microscope and in the x-ray patterns of the products. In 34 it is very poorly crystallized. It is thus more difficult to imagine the alumina purely as a catalyst and it is suggested that the trace that was needed for the tilleyite synthesis could hold an important place in the structure by substituting for an occasional silicon atom while a fluorine atom takes the place of an oxygen. However the amounts involved are very small and it would be difficult to prove this.

Whether or not the alumina or fluorine enter the tilleyite structure to any extent it is clearly evident that the influence of these two components in very small amounts is extremely favorable to the formation of tilleyite. Some petrographic evidence in support of this is found at Scawt Hill where spurrite occurs but where tilleyite and fluorine bearing minerals are apparently absent. (Professor Tilley, personal communication). It will be interesting to see if tilleyite and fluorine bearing minerals are present together or absent together in the spurrite bearing rocks (1) of the Tres Hermanas Mountains, New Mexico, presently being studied by Homme and Rosenzweig (1958), and (2) of the metamorphosed Onerahi limestone near Tokatoka, New Zealand (Mason, 1957).

There are at least two localities where tilleyite might be expected although its occurrence has not yet been reported. These are in the contact altered limestones some 250 km from the mouth of the Nishanaya Tunguska River in Russia. (Sobolev, 1935) and in the skarns in the central part of the Christmas Mountains, Texas (Clabaugh, 1953). In both these localities the metamorphic grade must at least have been high enough to produce tilleyite in the aureole, for spurrite occurs in the contact rocks. Furthermore both alumina and fluorine bearing minerals are present.

The position of tilleyite in the decarbonation series is where it would be expected from its $CO_2$ content relative to the calcite + wollastonite and spurrite assemblages. The tilleyite facies lies only one step beyond the wollastonite-calcite facies. However, this step is a large one, about 330°C at 5,000 lbs/in.$^2$ of $CO_2$ and if the formation, or preservation, of tilleyite depends on the presence of specific foreign components, its rarity in nature is readily understood. Moreover the tilleyite stability field is narrow on a $P_{CO_2}$-T diagram and in nature is likely to be confined to relatively narrow metamorphic zones. Unlike spurrite which may be stable with higher index minerals, such as rankinite and larnite, the stability of tilleyite (+ $CO_2$), per se, is limited to the field indicated in figure 3. It may well be regarded as the most sensitive of all single index minerals in the decarbonation series.

The absence of tilleyite at granite-limestone contacts is as significant as the absence of spurrite, as far as $CO_2$ pressures are concerned, (Tuttle and Harker, 1957, p. 232). It appears likely that even at high total pressures the *effective* partial pressure of $CO_2$ will be lowered in proportion to the $H_2O:CO_2$ ratio by weight in the fluid phase (Harker, 1958). This means that at granite-limestone contacts a relatively high $CO_2$ pressure is normally maintained preventing the formation of tilleyite, and higher grade minerals, which, at very low $CO_2$ pressures should be able to form, with sufficient time and mineralizers, at much lower temperatures.[1] There is apparently insufficient water emanating from the granites to flush out the $CO_2$ in the country rocks. Such evidence is difficult to reconcile with concepts involving the metasomatic enplacement of granites in which hydrous fluids (ichors) allegedly sweep through large volumes of country rock.

## ACKNOWLEDGMENTS

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[1] Since this work was completed McConnell (1958) has synthesized tilleyite from calcite + afwillite at temperatures of the order of 550°C and water pressures of 22,500 lbs/in.$^2$.

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### Table 1
### Runs Made to Determine the Stability of Tilleyite

| Run | Starting Materials | $CO_2$ Pressure lbs/in.$^2$ | Temp °C | Duration Hrs | Products |
|---|---|---|---|---|---|
| 1 | Cc+SH | 5,500 | 930 | 144 | Cc+Wo |
| 2 | Ty (natural) | " | " | " | Ty (+Cc+Wo) |
| 3 | Ty (natural) | 5,000 | 970 | 43 | Sp |
| 4 | Cc+Wo | " | " | " | Sp |
| 5 | Sp | " | " | " | Sp |
| 6 | Ty (natural) | 4,200 | 935 | 171 | Ty |
| 7 | Cc+SH (10% extra Cc) | " | " | " | Cc+Wo |
| 8 | Cc+SH $\left\{\begin{matrix}\text{10\% extra Cc}\\ +4\%\ Fe(COO)_2.2H_2O\end{matrix}\right\}$ | " | " | " | Cc+Wo |
| 9 | Ty (natural) | 4,000 | 930 | 30 | Ty |
| 10 | Cc+Wo | " | " | " | Cc+Wo(+Sp) |
| 11 | Sp | " | " | " | Cc+Wo |
| 12 | Ty (natural) | 4,000 | 880 | 39 | Ty(+Cc+Wo) |
| 13 | Cc+Wo | " | " | " | Cc+Wo |
| 14 | Sp | " | " | " | Cc+Wo |
| 15 | Ty (natural) | 4,000 | 850 | 33 | Cc+Wo |
| 16 | Ty (natural) | 3,900 | 927 | 312 | Ty |
| 17 | Cc+Wo | " | " | " | Cc+Wo |
| 18 | Sp | " | " | " | Cc+Wo |
| 19 | Ty (natural) | 3,900 | 850 | 312 | Cc+Wo |
| 20 | Cc+Wo | " | " | " | Cc+Wo |

TABLE 1 (Continued)

| Run | Starting Materials | $CO_2$ Pressure lbs/in.$^2$ | Temp °C | Duration Hrs | Products |
|---|---|---|---|---|---|
| 21 | Sp | " | " | " | Cc+Wo |
| 22 | Ty (natural) | 3,800 | 895 | 285 | Ty+Cc+Wo |
| 23 | Cc+SH (10% extra Cc) | " | " | " | Cc+Wo |
| 24 | Cc+SH {10% extra Cc+<br>4% $Fe(COO)_2.2H_2O$} | " | " | " | Cc+Wo |
| 25 | Ty (natural) | 2,700 | 963 | 152 | Sp |
| 26 | Ty (natural) | 2,300 | 930 | 146 | Ty+Sp |
| 27 | Cc+SH | " | " | " | Sp |
| 28 | Tv (natural) | 4,200 | 932 | 329 | Ty |
| 29 | Ty+Sp (from run 26) | " | " | " | Ty alone |
| 30 | Ty+Cc+Wo(from run 22) | 4,150 | 937 | 172 | Ty alone |
| 31 | Ty (natural) | 4,000 | 930 | 242 | Ty |
| 32 | Ty+Cc+Wo(from run 22) | " | " | " | Ty alone |
| 33 | Cc+SH+16.3% $CaF_2$ | 4,150 | 937 | 172 | Cc+X |
| 34 | CAS gel (8.6% $Al_2O_3$) | 4,200 | 932 | 329 | Cc+Wo (+Ge) |
| 35 | CAS gel {(8.18% $Al_2O_3$) +Ty<br>(4.75% $CaF_2$) seed} | 4,150 | 937 | 172 | Ty+X+Ge+Cc |
| 36 | As above but no seed | 4,000 | 930 | 242 | Ty+X+Ge+Cc |
| 37 | Ty (from run 74) | 7,700 | 915 | 64½ | Cc+Wo |
| 38 | CAS gel {0.2% $Al_2O_3$<br>0.2% $CaF_2$} | " | " | " | Cc+Wo |
| 39 | CAS gel {8.5% $Al_2O_3$<br>1.77% $CaF_2$} | " | " | " | Cc+Wo+Ge |
| 40 | CAS gel (1.96% $Al_2O_3$) | " | " | " | Cc+Wo |
| 41 | CAS gel (1.96% $Al_2O_3$) | 5,000 | 930 | 185 | Cc+Wo |
| 42 | CAS gel {0.2% $Al_2O_3$<br>0.2% $CaF_2$} | " | " | " | Cc+Wo(+Ty) |
| 43 | CAS gel {1.96% $Al_2O_3$<br>0.27% $CaF_2$} | " | " | " | Cc+Wo+Ty |
| 44 | Ty(+Cc) (from run 68) | " | " | " | Ty |
| 45 | CAS gel {0.2% $Al_2O_3$<br>0.2% $CaF_2$} | 5,000 | 950 | 144 | Ty+Cc+Wo |
| 46 | CAS gel {1.96% $Al_2O_3$<br>0.27% $CaF_2$} | " | " | " | Ty(+Cc+Ge) |
| 47 | CAS gel {1.93% $Al_2O_3$<br>1.83% $CaF_2$} | " | " | " | Ty (+Ge) |
| 48 | Ty (from run 75) | " | " | " | Ty |
| 49 | CAS gel {0.2% $Al_2O_3$<br>0.2% $CaF_2$} | 4,600 | 910 | 240 | Cc+Wo |
| 50 | CAS gel {8.18% $Al_2O_3$<br>4.75% $CaF_2$} | " | " | " | Cc+Ge+Wo+X |
| 51 | CAS gel {1.93% $Al_2O_3$<br>1.83% $CaF_2$} | " | " | " | Cc+Wo(+Ge+Ty) |
| 52 | Ty (+Ge) (from run 47) | " | " | " | Cc+Wo(+Ge) |
| 53 | CAS gel {3.7% $Al_2O_3$<br>1.4% $CaF_2$} | 4,300 | 930 | 216 | Ty+Cc+Wo+Ge(+X) |

TABLE 1 (Continued)

| Run | Starting Materials | | $CO_2$ Pressure lbs/in.$^2$ | Temp °C | Duration Hrs | Products |
|---|---|---|---|---|---|---|
| 54 | CAS gel | 0.79% $Al_2O_3$<br>0.75% $CaF_2$ | " | " | " | Cc+Wo+Ty(+Ge) |
| 55 | CAS gel | 5.3% $Al_2O_3$<br>0.9% $CaF_2$ | " | " | " | Cc+Wo+Ty+Ge |
| 56 | CAS gel | 0.2% $Al_2O_3$<br>0.2% $CaF_2$ | " | " | " | Cc+Wo |
| 57 | CAS gel | 1.93% $Al_2O_3$<br>1.83% $CaF_2$ | 4,100 | 970 | 167 | Sp(+Ge+X) |
| 58 | CAS gel | 1.96% $Al_2O_3$<br>0.27% $CaF_2$ | " | " | " | Sp(+Ge) |
| 59 | CAS gel | 0.2% $Al_2O_3$<br>0.2% $CaF_2$ | " | " | " | Sp |
| 60 | Ty (from run 75) | | " | " | " | Sp |
| 61 | CAS gel | 8.5% $Al_2O_3$<br>1.77% $CaF_2$ | 4,000 | 930 | 141 | Ty+Cc+Ge(?+X) |
| 62 | CAS gel | 8.18% $Al_2O_3$<br>4.75% $CaF_2$ | " | " | " | Ty+X+Ge+Cc |
| 63 | Cc+Qz | 0.84% $Al_2O_3$<br>0.21% $CaF_2$ | 4,000 | 930 | 172 | Cc+Wo |
| 64 | CAS gel | 0.2% $Al_2O_3$<br>2.0% $CaF_2$ | " | 935 | " | Ty |
| 65 | CAS gel | 0.2% $Al_2O_3$<br>0.2% $CaF_2$ | " | 940 | " | Ty |
| 66 | CAS gel | 1.96% $Al_2O_3$<br>0.27% $CaF_2$ | 3,800 | 925 | 164 | Ty(+Cc+Ge,?+Wo) |
| 67 | Cc+Qz | 1.85% $Al_2O_3$<br>1.91% $CaF_2$ | " | " | " | Ty(+Cc+Ge,?+Wo) |
| 68 | CAS gel | 0.98% $Al_2O_3$<br>1.94% $CaF_2$ | " | " | " | Ty(+Cc) |
| 69 | CAS gel | 1.93% $Al_2O_3$<br>1.83% $CaF_2$ | " | " | " | Ty(+Cc+Ge) |
| 70 | Cc+Qz | 8.95% $Al_2O_3$<br>2.25% $CaF_2$ | 3,750 | 930 | 240 | Ty+Cc+Ge+X |
| 71 | CAS gel | 1.93% $Al_2O_3$<br>1.83% $CaF_2$ | " | " | " | Ty+Cc(+Ge,?+X) |
| 72 | CAS gel | 8.5% $Al_2O_3$<br>1.77% $CaF_2$ | " | " | " | Ty+Cc+Ge(?+X) |
| 73 | CAS gel | 0.2% $Al_2O_3$<br>0.2% $CaF_2$ | 3,300 | 937 | 280 | Ty+Sp |
| 74 | CAS gel | 0.2% $Al_2O_3$<br>2.0% $CaF_2$ | " | " | " | Ty |
| 75 | CAS gel | 0.98% $Al_2O_3$<br>1.94% $CaF_2$ | " | " | " | Ty |
| 76 | CAS gel | 1.93% $Al_2O_3$<br>1.83% $CaF_2$ | 3,000 | 887 | 191 | Ty+Cc+Wo(?+Ge) |

TABLE 1 (Continued)

| Run | Starting Materials | $CO_2$ Pressure lbs/in.$^2$ | Temp °C | Duration Hrs | Products |
|---|---|---|---|---|---|
| 77 | CAS gel 3.7% $Al_2O_3$<br>1.4% $CaF_2$ | " | " | " | Cc+Wo+Ty(?+Ge) |
| 78 | Cc+Qz 8.95% $Al_2O_3$<br>2.25% $CaF_2$ | " | " | " | Cc+Wo+Ge+X |
| 79 | Ty (from run 64) | " | " | " | Ty |
| 80 | CAS gel 1.93% $Al_2O_3$<br>1.83% $CaF_2$ | 3,000 | 915 | 191 | Ty+Cc+Ge(+X, ?+Wo) |
| 81 | CAS gel 3.7% $Al_2O_3$<br>1.4% $CaF_2$ | " | " | " | Ty+Ge(?+X) |
| 82 | CAS gel 8.95% $Al_2O_3$<br>2.25% $CaF_2$ | " | " | " | Ty+Cc+Ge |
| 83 | Ty (from run 64) | " | " | " | Ty(+X) |
| 84 | CAS gel 0.2% $Al_2O_3$<br>0.2% $CaF_2$ | 3,000 | 940 | 459 | Sp |
| 85 | CAS gel 8.98% $Al_2O_3$<br>4.75% $CaF_2$ | " | " | " | Sp+Ge+X |
| 86 | CAS gel 1.93% $Al_2O_3$<br>1.83% $CaF_2$ | " | " | " | Sp(+Ge+X) |
| 87 | Ty(+Ge) (from run 47) | " | " | " | Ty+Sp |
| 88 | Ty(+Ge) (from run 47) | 3,000 | 865 | 650 | Cc+Wo(+X+Ge) |
| 89 | CAS gel 1.93% $Al_2O_3$<br>1.83% $CaF_2$ | " | " | " | Cc+Wo(+X+Ge) |
| 90 | CAS gel 8.98% $Al_2O_3$<br>4.75% $CaF_2$ | " | " | " | Cc+Wo+Ge+X |
| 91 | CAS gel 3.7% $Al_20_3$<br>1.4% $CaF_2$ | " | " | " | Cc+Wo(+Ge, ?+X) |

Table 1—Runs made with C:S ratios on or close to tilleyite (5CaO:2$SiO_2$).

CAS gel = Anhydrous oxide mixture prepared from gel (see text).

Cc = Calcite

Ty = Tilleyite

Wo = Wollastonite

Ge = Gehlenite

Sp = Spurrite

X = Unidentified phase

Qz = Quartz

SH = $SiO_2nH_2O$ (87.64% $SiO_2$).

( ) = Trace of material indicated.

TABLE 2

Natural Occurrences of Tilleyite and the Minerals Associated with it

| | |
|---|---|
| Crestmore<br>(Larsen and Dunham, 1933) | Tilleyite, Merwinite, Vesuvianite, Grossularite, Wollastonite, Spurrite, Gehlenite |
| New Mexico<br>(Glass, Jahns and Stevens, 1944) | Tilleyite, Vesuvianite, Andradite, Magnetite, Fluorite |
| Carlingford<br>(Nockolds, 1947) | Tilleyite, Melilite, Calcite<br>Vesuvianite, Spurrite, Melilite, Tilleyite |
| Camus Mor<br>(Tilley, 1947) | Spurrite, Tilleyite, Calcite, Grossularite<br>Gehlenite, Tilleyite, Calcite, Spurrite (Cuspidine) |
| Camasumary<br>(Wyatt, 1953) | Tilleyite, Spurrite, Wollastonite, Melilite (Cuspidine) |

TABLE 3

Observed (CuK$\alpha$) Spacings and Intensities for

1) Natural Tilleyite. 2) Synthetic Tilleyite (run 65, with 0.2% $Al_2O_3$ and 0.2% $CaF_2$) and 3) Synthetic Tilleyite (run 62, with 8.18% $Al_2O_3$ and 4.75% $CaF_2$; *peaks much weakened or suffering interference from the excess of gehlenite and the "X" phase have been omitted).

| 1) Natural Tilleyite | | 2) Synthetic Tilleyite | | 3) Synthetic Tilleyite | | |
|---|---|---|---|---|---|---|
| d spacings Å | Relative Intensity | d spacings Å | Relative Intensity | d spacings Å | Relative Intensity | Estimated Accuracy of d |
| 7.33 | 10 | 7.34 | 13 | 7.35 | 20 | ± 0.01 |
| 5.99 | 7 | 5.99 | 9 | * | | ± 0.01 |
| 4.21 | 3 | 4.22 | 7 | * | | ± 0.01 |
| 3.674 | 3 | 3.673 | 4 | * | | ± 0.01 |
| 3.534 | 13 | 3.534 | 23 | 3.532 | 20 | ± 0.004 |
| 3.453 | 5 | 3.452 | 7 | 3.450 | 8 | ± 0.004 |
| 3.335 | 22 | 3.333 | 29 | 3.331 | 24 | ± 0.003 |
| 3.214 | 20 | 3.210 | 19 | 3.214 | 14 | ± 0.003 |
| 3.190 | 32 | 3.191 | 47 | 3.192 | 40 | ± 0.003 |
| 3.099 | 61 | 3.101 | 91 | * | | ± 0.003 |
| 3.011 | 100 | 3.011 | 100 | 3.011 | 100 | ± 0.003 |
| 2.982 | 39 | 2.980 | 75 | 2.982 | 66 | ± 0.002 |
| 2.896 | 3 | | | | | ± 0.002 |
| 2.860 | 4 | 2.859 | 7 | * | | ± 0.003 |
| 2.803 | 39 | 2.803 | 56 | 2.803 | 46 | ± 0.002 |
| 2.566 | 8 | 2.566 | 7 | * | | ± 0.003 |
| 2.535 | 16 | 2.536 | 18 | 2.537 | 26 | ± 0.003 |
| 2.501 | 22 | 2.501 | 31 | * | | ± 0.002 |
| 2.350 | 8 | 2.351 | 10 | 2.354 | 14 | ± 0.002 |
| 2.248 | 3 | | | | | ± 0.004 |
| 2.119 | 19 | 2.119 | 22 | 2.119 | 20 | ± 0.002 |
| 2.100 | 38 | 2.100 | 43 | * | | ± 0.002 |
| 2.032 | 13 | 2.031 | 13 | * | | ± 0.002 |
| 1.942 | 3 | 1.942 | 4 | * | | ± 0.002 |
| 1.926 | 21 | 1.925 | 26 | * | | ± 0.002 |
| 1.910 | 22 | 1.910 | 22 | 1.911 | 30 | ± 0.002 |
| 1.896 | 44 | 1.897 | 39 | 1.895 | 40 | ± 0.002 |
| 1.840 | 8 | 1.841 | 10 | 1.840 | 12 | ± 0.001 |
| 1.831 | 5 | 1.831 | 9 | 1.831 | 20 | ± 0.003 |
| 1.804 | 12 | 1.805 | 16 | * | | ± 0.001 |