

Study on Genesis of Wollastonite*

Part I

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(With 2 Tables and 10 Text-figures)

Abstract

In view of that some modifications of calcium metasilicates are synthetically preparable in the CaO-SiO₂ system and there are also rooms to inspect whether the previous opinions concerning genesis of wollastonite or of allied minerals may be really valid or not, some kinds of experiments in laboratory as well as field surveying in several locations have been put in operation. As a result, it has been reasonably ascertained that wollastonite together with a part of other skarns might have been produced far more frequently in low-temperature veins than as so-called 'reaction skarn' derived thermometasomatically from solid reaction, and impregnated or diffused appearance of the mineral under consideration, though ordinarily adhered to pyrometasomatic process, are used to represent nothing other than aggregates or networks of veinlets originated at lower temperature.

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I. Introduction

Modifications of wollastonite grouped chemically into meta-silicate have so far been classified into the following:

(a) α -CaSiO₃: or pseudo-wollastonite: The crystals concerned, pseudo-hexagonal or more probably monoclinic in habit, are happenly found contained either in silica bricks mixed with unsuitable amount of lime or in slags and in reaction products of slags with

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fire bricks, although both their occurrence and even their pseudomorphs are discernible nowhere in Nature.

(b) β -CaSiO₃: They are stable at temperatures lower than 1180°C and used to appear as triclinic, and monoclinic wollastonite in Nature

Triclinic ones revealing transformation into α -modification at 1200°C are generally included in slags produced at lower temperature and also crystallized on devitrification of lime-silica glass, while they are ordinarily comprised in the contact zone of limestone and/or dolomite with certain intrusives.

Monoclinic ones named para-wollastonite occur rarely in Nature, though they have ever been found embraced merely in ejected blocks of limestone at Vesuvias, Santorin, and Monte Somma etc.

Of three modifications, triclinic wollastonite is most commonly observed associated with garnet, hedenbergite, vesuvianite, tremolite, actinolite and so forth in the contact of carbonate rocks with intrusives and similarly appear as skarns in contact, or pyrometasomatic deposits but not as minerals composing igneous rocks.

On the other hand, since GOLDSCHMIDT first pointed out an important role of wollastonite as indicator of P-T relation in lithologic metamorphism on the basis of thermodynamical interpretation for the reaction:



genesis of the mineral derived through this process seems to have become more significant in geological field.

In view of this, the CaO-SiO₂ system was experimentally scrutinized on ignition of law materials provided for cement by the present writer. The fact is however that such a low-temperature wollastonite as was expected has by no means been obtainable, but some noteworthy results other than those anticipated have been found. Thus it has become necessary to inspect whether or not these data might have been applicable similarly in Nature, and actual occurrence of wollastonite disposed at certain locations in western Japan has been carefully researched in detail.

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II. Previous works

There have been a number of morphological studies of wollastonite, as are mentioned in the following:

HAÜY (1822) regarded the mineral in question as an independent species grouped into

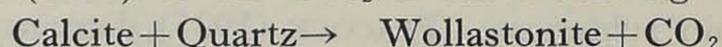
orthorhombic system on equality with amphiboles and pyroxenes. PHILLIPS (1823) indicated it to bear cleavage angle similar to that shown by tubular spar classified previously into triclinic system by himself. MOHS (1825) implied it synonymously with prismatic augite spar and considered to belong to triclinic or monoclinic system. BROOKE (1831) reported monoclinic symmetry as to the specimen from Vesuvias. VOM RATH (1869) investigated the well-defined Vesuvian crystal, suggesting a new orientation in the specimen concerned. HESSENBERG (1870) showed the specimens from Santorin and Cziklova to be in good accordance with the results given by VOM RATH. SCACCHI (1889) recognized twinning on orthopinacoid of Vesuvian crystal. GROSSER (1891) derived new elements into VOM RATH's idea concerning orientation on the basis of detailed measurements. ZAMBONINI (1910) failed in recognition of SCACCHI's twinning but reached confirmation for the preceding observation in many points. EAKLE (1917) noticed the specimen obtained from crystalline limestone at Crestomore, California to be of hemimorph bearing a not completely monoclinic symmetry or to be triclinic. KATAYAMA and NAKAMOTO (1935) justified the grouping of wollastonite not into monoclinic system but into triclinic one in the study of the specimen from Hokizawa, Kanagawa Pref. and pointed out the confusion caused by singular angle revealing 90° in α . BOWEN (1933) remarked both the simplification of indices by transformation of (140) into (010) and the extinction angle of 2° on the thin section parallel to the base concerning the specimen similar to that obtained from Crestomore by EAKLE. PEACOCK (1935) studied the mineral with assistance of some authors such as PALACHE, PABST, FOSHAG, WARREN, SCHROEDER and so on, reaching conclusion that the specimens from Crestomore are surely triclinic, and those from Monte Somma are regarded as aggregate composed of triclinic modification bearing property simpler than those from Crestomore as well as of monoclinic holohedry without no relation to twinning.

Crystal structures of wollastonite have also been röntgenometrically researched by many authors.

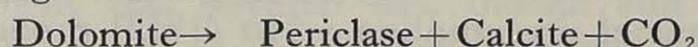
WARREN (1931) indicated wollastonite to be grouped more suitably into triclinic modification of quite different structure than into monoclinic one represented by pyroxene group on the basis of certain evidences. PEACOCK (1935) demonstrated the existence of monoclinic modification beside triclinic one and designated it para-wollastonite. M.B. BARNICK (1935) found out the tripple rings [of Si_3O_9] included in para-wollastonite structure in opposition to general presumption. ITO (1950) proposed an idea of proto-wollastonite derived from his theory concerning twinned lattices, illustrating the formation of respective modifications to be ascribable to different manners of twinning. K. DARNBERGER-SCHIFF, LIEBAU and THILO (1952) discovered the resemblance in x-ray patterns either in the pair of monoclinic wollastonite with $(\text{NaPO}_3)_x(\text{I})$ or in that of triclinic wollastonite with $(\text{NaAsO}_3)_x$, and supposed the chains of (SiO_3) differing in distortion from those of pyroxene structure in wollastonite instead of BARNICK's opinion. LIEBAU (1956) manifested röntgenographically the similarity of β -wollastonite to $(\text{NaAsO}_3)_x$, put the x-ray data of rhodonite and the fundamental structure of chain-silicate in order (1957) and then clarified the structure of pyroxmangite, when he demonstrated either the structures of β -wollastonite, rhodonite, and pyroxmangite bearing characteristic periodicity with repetition of three, five, and seven chains respectively or their difference from pyroxene structure composed of two chains. BALOW (1957) introduced six types of chain structures instead of two types proposed previously by BRAGG on which the classification of silicates has long been based, suggesting the periodicity with repetition of three chains in wollastonite and that of two chains in pyroxenes.

Noticeable is that bulk of works have concerned the synthetic study of wollastonite.

DAUBREE (1857) prepared quartz and wollastonite at 400°C in the steel tube but there remains uncertainty. GORGEU (1884) obtained $\text{CaCl}_2 \cdot \text{CaO}$ through passing humid air on red-heated CaCl_2 involved in the opened vessel, $\text{CaO} \cdot \text{SiO}_2$ through addition of precipitated silica to one equivalent of CaCl_2 , $2\text{CaO} \cdot \text{SiO}_2$ in the case of two equivalent of CaCl_2 , and chlorides, chlorosilicates, tridymite (?) and long-prismatic wollastonite on heating the mixture of 1g SiO_2 , 15g CaCl_2 and 3g NaCl in the current of moisture, and then (1887) wollastonite together with deliquescent Ca-chlorosilicates such as $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{CaCl}_2$ and $\text{CaO} \cdot \text{SiO}_2 \cdot \text{CaCl}_2$ through ignition of the mixture of 1g SiO_2 with 15-20g CaCl_2 under an ordinary pressure and passing air as well as steam. A. De Grammont (1891) succeeded the synthesis of wollastonite mixed with amorphous materials, pulverous crystallites and datolite on heating the mixture of 25g borax with 5g precipitated CaSiO_3 held in FRIEDEL's apparatus in presence of water at 400°C for 35 hours. Doelter (1906) synthesized wollastonite through heating the mixture of 11g $\text{Ca}(\text{HCO}_3)_2$, precipitated SiO_2 and 45c.c. H_2O at 400°~425°C. CHURIN (1916) produced apophyllite associated with wollastonite through immersing 25g pulverized calcite and 7.5g K_2SiO_3 in 22c.c. H_2O saturated with CO_2 gas and then heating the mixture held in the sealed glass-tube at 210°C for 226 hours, suggesting the reactivity between silicious and calcareous solution assumably contained in hydrated igneous solution. FONDA and FROELICH (1948) investigated the structure of CaSiO_3 synthesized from pure materials and reached such recognition that the products manufactured at 1150°C lower than transition point were α - CaSiO_3 , a high-temperature modification, showing no transformation from α to β on cooling but addition of MnO or MnO with PbO made it possible to prepare β - CaSiO_3 , a low-temperature modification, owing to that a sort of solid solution might have been produced between CaSiO_3 and MnSiO_3 while ascension of transition point might have been brought with contents of MnO . HARKER and TUTTLE (1956) ascertained experimentally the reaction: $\text{Calcite} + \text{Quartz} \rightleftharpoons \text{Wollastonite} + \text{CO}_2$ and brought to light either their results to be intervened between the respective P-T data given theoretically by GOLDSCHMIDT (1912) and DANIELSON (1950) or that P_{CO_2} -T curve relating to the reaction:



under less than 40,000 lbs/in² is situated on the side of lower temperature than in the case of curve connecting with the reaction:



Specific references regarding simply the synthesis of $\text{CaO} \cdot \text{SiO}_2$ appeared in the CaO-SiO_2 system are not exiguous.

ALLEN, WHITE and WRIGHT obtained wollastonite through heating CaSiO_2 glass at 800°-1000°C and pointed out that 1190° was regarded as the lowest temperature causing $\alpha \rightarrow \beta$ transformation and possibly descended to certain extent with heating for long duration whereas transformation of pseudo-wollastonite into low-temperature wollastonite was not realized even through slow cooling and either its change through heating at 900°-1100°C for 36 - 60 hours or its revival to low-temperature modification through heating with water holding temperature higher than critical point in the steel bomb for several days were not recognized at all. DAY and SHEPHERD (1906) and A.L. DAY, SHEPHERD and WRIGHT (1906) reported certain kinds of minerals belonging to CaO-SiO_2 series. RANKIN and WRIGHT (1915) developed the study of CaO-SiO_2 system. FERGUSON and MERWIN (1919) reported the experimental data related to solid solution appeared between various species of minerals in CaO-SiO_2 system. GREIG (1927) revised a part of the results concerning high-silica region. BOWEN, SCHAIRER and POSNJACK (1933) indicated

any solid solution with excess of SiO_2 or that of CaO to be not included in CaSiO_3 compound at all, and proposed that eutectic composition established between pseudowollastonite and tridymite was to be revised and transition from $\alpha\text{-CaSiO}_3$ to $\beta\text{-CaSiO}_3$ might be taken place at 1150° or at lower temperature, OSBORN and SCHAIRER (1941) estimated it more accurately as $1125^\circ \pm 10^\circ\text{C}$. Now it seems that studies on the genesis of metallic ore deposits accompanying skarn minerals are also to be alluded to in relation to occurrence of wollastonite in Nature.

BERNHARD VON COTTA (1865) was the first dealing with the theme in question as to Banat deposits. UMPLEBY (1914) emphasized an importance of the materials supplied from magmatic source in the Mackay copper deposit derived from contact of Cretaceous granite porphyry with Carboniferous limestone, wherein overlapping effects of the subsequent metasomatism on the preceding one were also observed. LINDGREN (1914) described positively the metasomatic effects on limestone. UMPLEBY (1916) reached the conclusion similar to that proposed by Lindgren concerning seven examples. T. KATO (1916) supported the same theory in the surroundings of Hana-no-yama deposits located in Yamaguchi Pref. SUZUKI (1932) ascertained the mobilized materials in the Ofuku deposit, Yamaguchi Pref. MUGNUSSON (1936) illustrated the formation of skarns in most of the iron deposits distributed in Central Sweden to be ascribed to reaction of the core body of ores formed earlier with surrounding dolomite on regional heating through later granite and designated them "reaction skarns" as was previously stated by LINDROTH. SCHMITT (1939) pointed out no variation in volume and the supply of a large amount of silica, iron and zinc on the basis of his study of Pewabic mine. GEJER (1939) believed it simply through metasomatism of granitic magma on limestone and dolomite, ascribing the formation of iron ore accompanying skarns in scarce amount to the reaction of ore beds. JAHNS (1944) alluded to addition of abundance of materials in the formation of tactite embraced in Iron Mountain beryllium deposit derived metasomatically from Paleozoic limestone through action of vapor and hydrothermal solution. HALSER (1950) recognized the supply of iron, a little amount of silica and magnesia subsequent to recrystallization together with isochemical metamorphism at the contact of limestone with granodiorite in Philipsburg. TILLEY (1951) investigated in detail on zonal distribution of skarns developed mainly in dolomite at its contact with Tertiary granite and divided the skarns into primary ones and those associated with boron-fluorine ores.

With special reference to the genesis of wollastonite are there some works to be mentioned.

GOLDSCHMIDT (1912) evaluated P-T condition suitable for genesis of wollastonite through metamorphism of silicious limestone from thermal data obtained on the basis of Nernst's approximation. NIGGLI (1916) concluded that, in his study of alkali-carbonate melts, equilibrium under a given pressure was established at a higher temperature in the pair of calcite-orthosilicate than in that of calcite-quartz or of calcite-wollastonite. ESKOLA (1922) was of opinion that (a) wollastonite is stable even at certain temperature lower than its transition point if under a condition in that SiO_2 came into contact with calcareous substances other than carbonate and free CO_2 was not present in the system, (b) the reaction shown by GOLDSCHMIDT becomes irreversible if CO_2 produced is transported away with gas or solution during the process of slow cooling and thus (c) wollastonite plays a role of geologic thermometer revealing the maximum temperature for its presence. Furthermore he divided the grade of metamorphism appeared on limestone into four types of paragenetic pair such as (1) quartz-limestone, (2) tremolite-limestone, (3) diopside-limestone and (4) wollastonite-limestone. WILLBOURN (1926) (1927) explained the band-

ing of wollastonite appeared along bedding planes of marble in Beatrice deposit to be connected merely with chemical action of tin-bearing pegmatite on the passage. LINDGREN (1924) observed an abundance of materials added to limestone occurred at Bingham and suggested the formation of wollastonite to be attributable to SiO_2 brought from any source other than the wall rocks. OSBORN (1931) assumed wollastonite as was derived from arenaceous layer intercalated in limestone at the contact of the latter with quartz-monzonite in Marulan district. TILLEY (1931) reported both the veinlets of wollastonite deposited from lime-rich solution passing through flint and its paragenesis with xonotlite in his research regarding the contact of dolerite with chalk at Scawt Hill. Moreover he disputed the formation of melilite rocks through reaction of magmatic solution with chalk and that of wollastonite in the related rocks to be confined along the margins of flint nodules appeared in endogeneous contact-zone. SCHEME (1932) illustrated a sort of contaminated igneous rocks including hedenbergite, andradite, and wollastonite to be concerned with the reaction of skarns with pegmatite representing the later stage of acid magma. KROGER and ILLNER (1939) also performed the experiments relating to P-T curve appeared in such reaction as was already dealt with by Goldschmidt. TOM, BARTH, CORRENS, and ESKOLA (1939) referred to the theory of metamorphism systematically. BOWEN (1940) expressed the CaCO_3 - SiO_2 system according to the phase rule but from particular point of view in that either univariant reaction in the system including CaO , SiO_2 , and CO_2 or effects of the components involved were pursued for inspection. PITCHER (1950) justified the genesis of wollastonite through reaction of limestone with SiO_2 derived from veins in his study of calc-silicate skarn veins embraced in limestone of Lough Anure. DANIELSON (1950) estimated the conditions suitable for the production of wollastonite according to the data recalculated thermodynamically for the reaction: $\text{CaCO}_3 + \text{SiO}_2 \rightleftharpoons \text{CaSiO}_3 + \text{CO}_2$ and found out the variation of free energy to be more convenient for the formation of wollastonite at certain temperature higher than 280°C under 1 atm-pressure of CO_2 . HARKER and TUTTLE (1956) compared the P_{CO_2} -T curve obtained experimentally in the reaction: $\text{Calcite} + \text{Quartz} \rightleftharpoons \text{Wollastonite} + \text{CO}_2$ with that calculated and emphasized the preparation of wollastonite to be very easy in presence of a slight amount of water. KENNEDY (1959) reported that thermal influence of Tertiary dolerite on the vein-like and nodulous cornstone enclosed in sandstone yielded a sort of reaction skarn in such process that calcium diffused out from cornstone might have reacted with quartz and produced wollastonite pseudomorph after the latter.

III. Synthetic experiments

(A) Reaction between CaCO_3 and SiO_2

(1) General remarks

As was cited already, some of opinions seem to have found connection of the genesis of wollastonite with reaction between calcite and quartz and others with that between limestone and magmatic solution or with the theories relating to thermal, or regional metamorphisms, through which both calcite and quartz were subjected to variation of temperature as well as of pressure.

The results obtained by COBB (1910) from heating manipulation of the mixture of CaCO_3 and SiO_2 at 500° - 1400° C indicate the beginning of the reaction in question at ca. 800°C . Those given by JANDER and HOFFMAN (1931) on the basis of formula suggested by JANDER (1927) makes either the velocity constant or activation energy of the reaction between BaCO_3 and SiO_2 clear to be calculated. TURNER's data (1932) reveal

that, in his heating experiments concerning calcite mixed with quartz or with sillimanite and pure gold in various ratios, thermal dissociation of the former is able to be more activated and CO_2 is expelled in more amount, with increasing contents of the mixed materials.

In the study related to ignition of raw materials for cement has however confirmed the writer the activation of thermal dissociation suggested by Turner, easier formation of larnite instead of wollastonite, and some of unexpected results.

(2) Volumetry of CO_2

The experiments have been put into operation by means of the apparatus and through the procedures according nearly to those given by JANDER and HOFFMANN.

(a) Arrangement

The apparatus provided for experiments is indicated in Fig. 1.

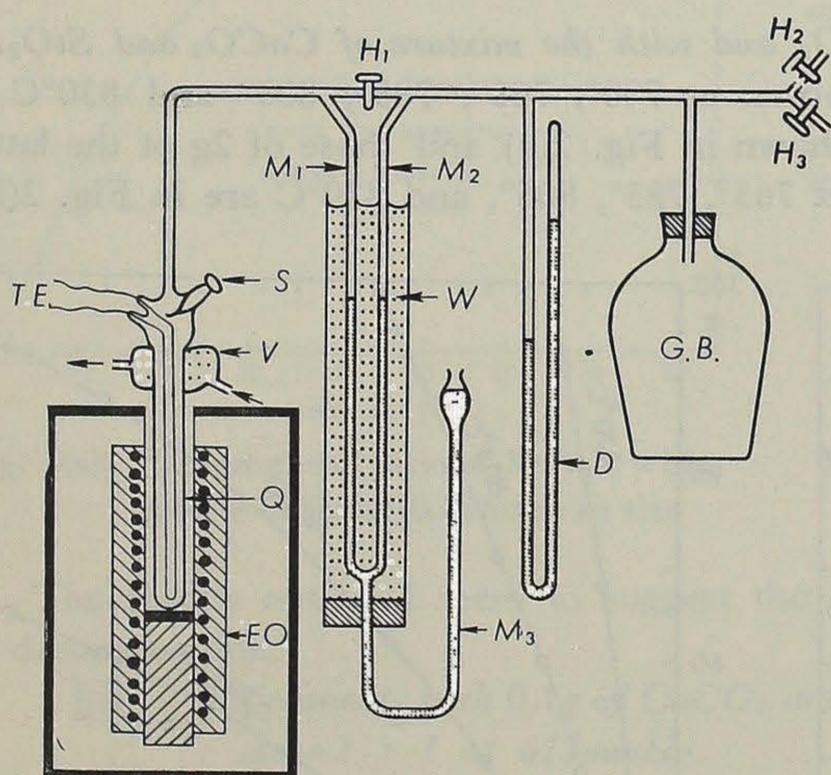


Fig. 1 Apparatus represented schematically

- E.O.: Electric furnace
- Q : Silica-glass tube
- T.E.: Thermocouple
- S : Glass cap
- G.B.: Glass bottle
- M_1, M_2 : Burette
- M_3 : Bottle including mercury
- W : Cooling water
- D : Manometer
- H_1, H_2, H_3 : Plug
- V : Pipe of cooling water

CaCO_3 and BaCO_3 manufactured by Merck and the purified quartz sand from Ottawa were provided for experiments, impurities of the latter being indicated in Table 1.

Grain-size of quartz was sorted through standard sieve of $0.044 \sim 0.088$ mm, all of the materials used were dried up in the oven at 120°C for two hours, and native gold, 99.9% in purity, was divided into two portions with respective grain-size of less than 44μ and 88μ for each experiment.

Measuring manipulation: The mixture composed of the materials in certain molecular ratio was mingled sufficiently with ethyl alcohol or with acetone and held in the electric oven so as to expel the volatiles. 0.1g or 0.2g of this mixed specimen placed in a platinum dish with inner diameter of 0.7cm and depth of 1.3cm is hung at the end of (S) in Fig. 1.

Pressure of CO_2 was controlled to be in suitable condition through regulation of its volume found in preliminary blank test. At the temperature kept constant, the specimen

Table 1. Impurities of quartz sand
(Wt. %, Analyst: M. TSURUMAKI)

Fe_2O_3	0.007 %
Al_2O_3	0.070
CaO	0.040
MgO	0.030
Na_2O	0.040
K_2O	0.021

was dropped from the dish into quartz tube (Q) by means of turning over (S). Volume of CO_2 produced in the reaction was measured on (M_1) in such a manner that, for reading its variation at constant pressure, the heads of mercury on (M_1) and (M_2) was regulated to be similar to each other through controlling (M_3) bottle, and was recalculated as that at standard state (0°C , 1 atm) both from its temperature measured indirectly through that of water (W) surrounding the passage and from its pressure read on the manometer (D).

(b) *Results obtained in experiments*

Variations in volume of CO_2 produced in the cases of variously mixed specimens at certain temperatures were indicated in terms of % representing the ratios to total CO_2 yielded theoretically from complete dissociation of carbonates, since CO_2 here obtained was ascribable not to the solid reaction appeared in the related system but mainly to mere dissociation of carbonates.

(i) *Experiments merely with CaCO_3 and with the mixture of CaCO_3 and SiO_2 .*

Decomposed ratios of 0.1g of the former at 700° , 765° , 785° , 805° and 830°C at 663mmHg with duration in minutes are shown in Fig. 2(a) and those of 2g of the latter revealing the ratio $\text{CaCO}_3:\text{SiO}_2=2:1$ at 765° , 785° , 805° , and 830°C are in Fig. 2(b).

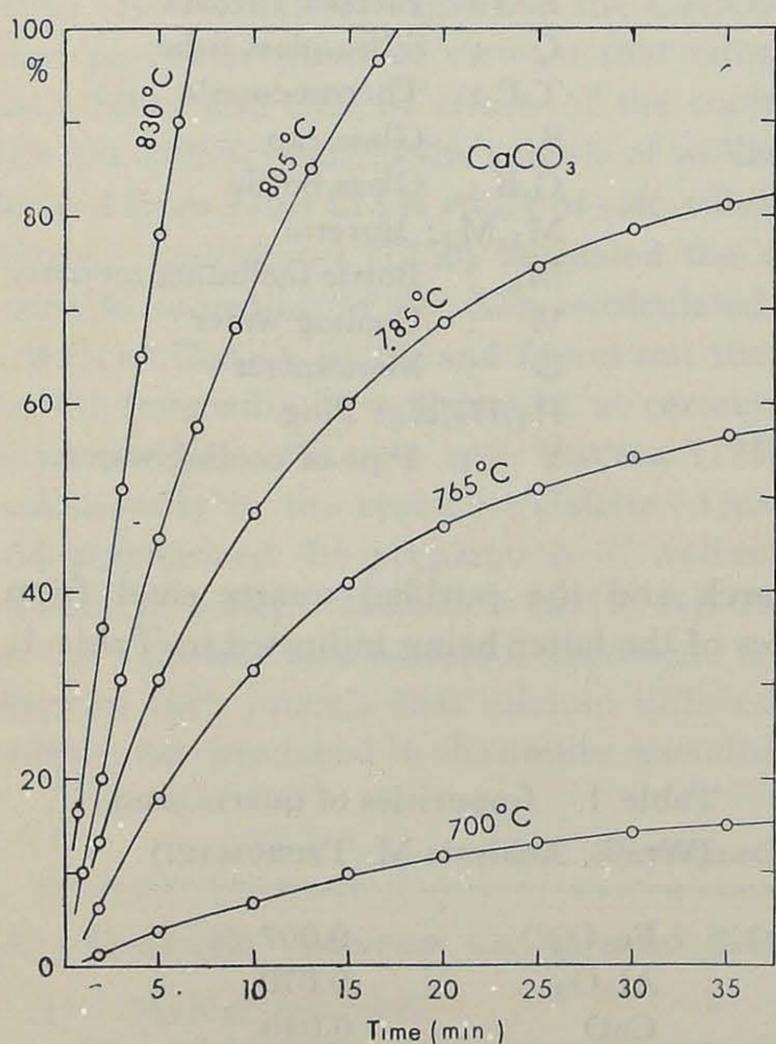


Fig. 2(a). Decomposed ratio of CaCO_3 .

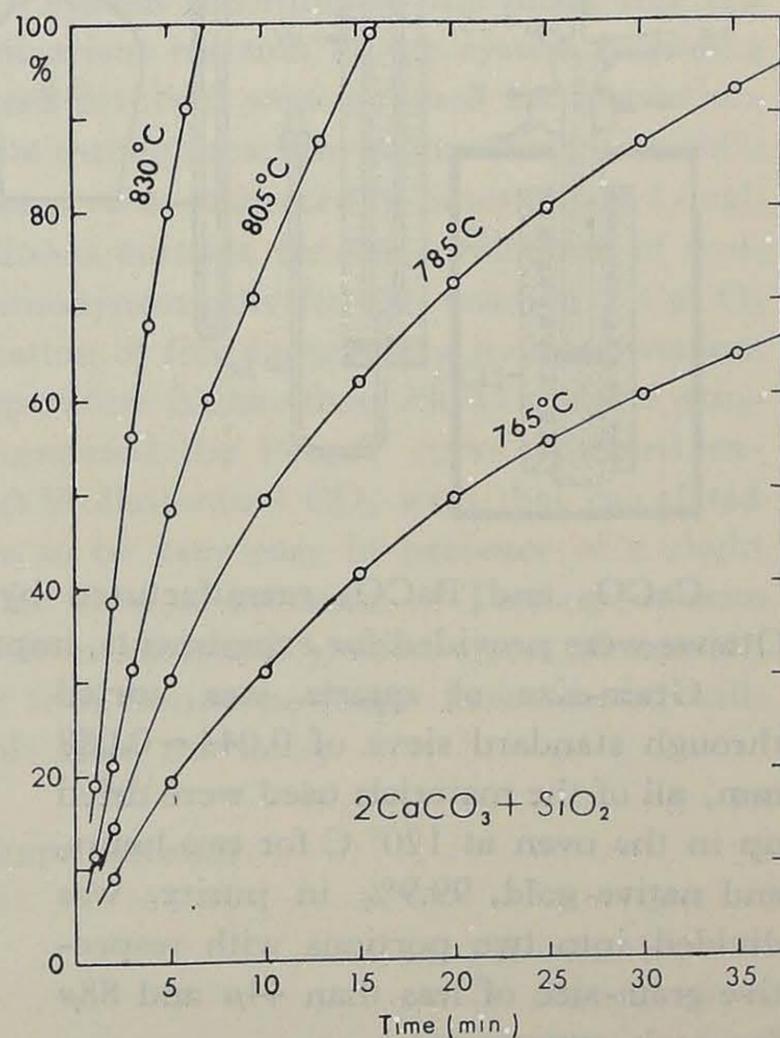


Fig. 2(b). Decomposed ratio of the mixture of CaCO_3 and SiO_2 .

The results obtained seem to suggest the remarkable effects of SiO_2 on decomposition not in the experiments at higher temperatures such as 805° and 830°C but in those at 765° and 785°C .

(ii) *Experiments with 0.2g of the mixtures of BaCO_3 and SiO_2 at 517mmHg.*

Decomposed ratios of BaCO_3 in the mixture representing the ratio $\text{BaCO}_3:\text{SiO}_2$ (0.044-0.088mm in size)=1:3 at 750° , 800° , and 900°C are shown in Fig. 3(a) and

those in the similar mixture with SiO_2 bearing grain-size of less than 0.025mm at 700°, 750°, and 800°C are in Fig. 3(b).

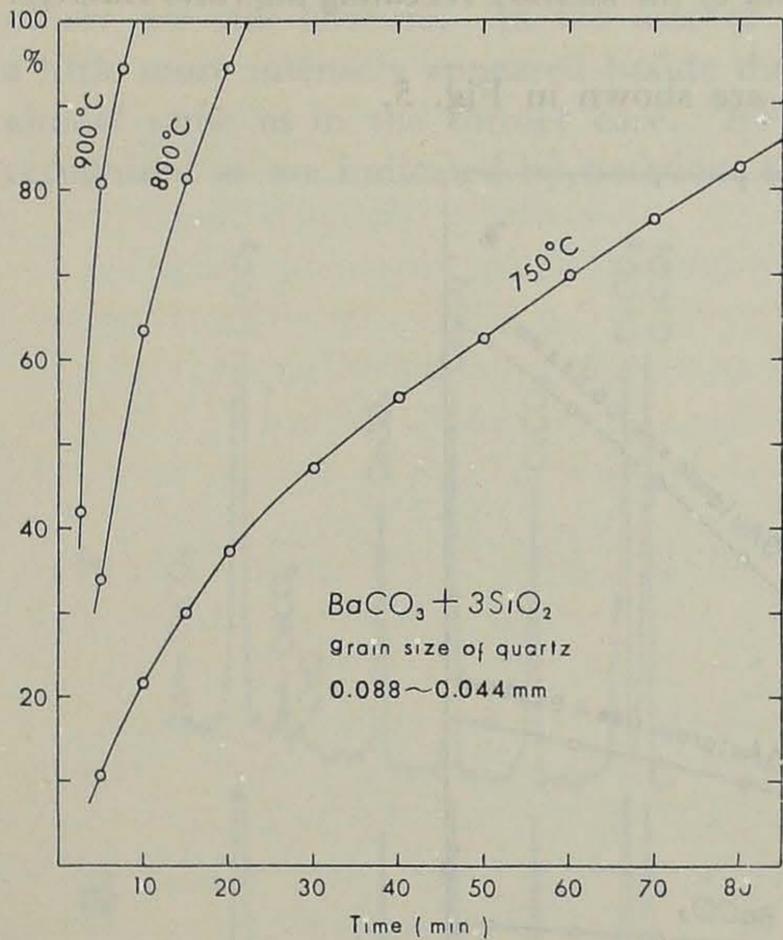


Fig. 3(a). Decomposed ratio of BaCO_3 with quartz of 0.044-0.088mm in size

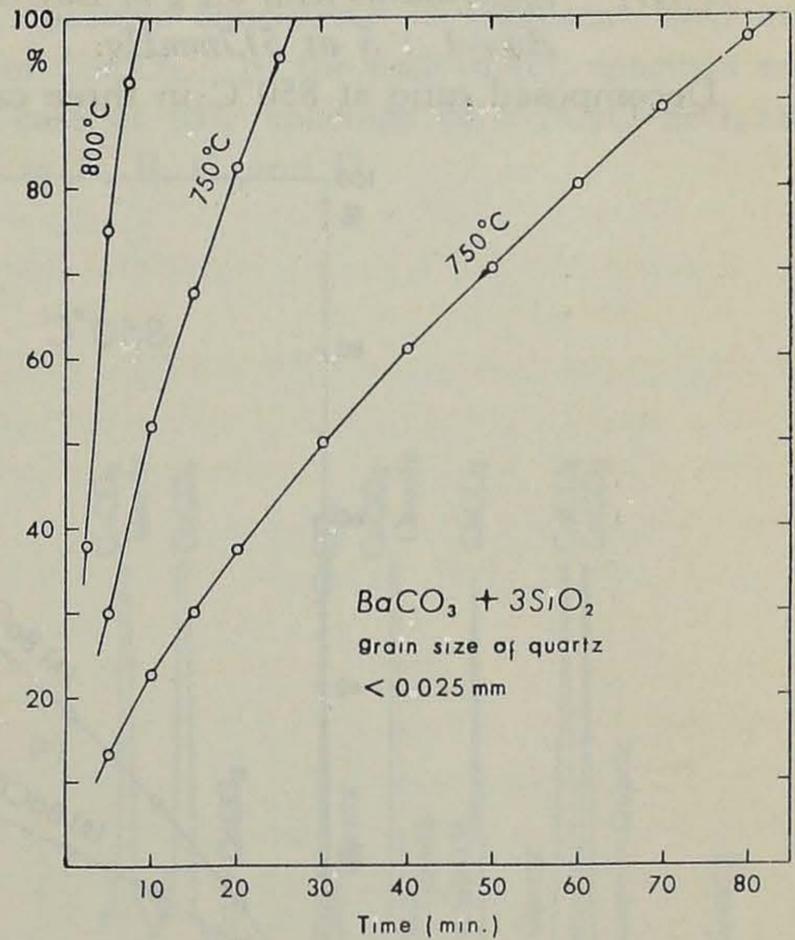


Fig. 3(b). Decomposed ratio of BaCO_3 with quartz of less than 0.025mm in size

The results obtained seem to suggest the noticeable effects of grain-size of quartz on decomposition.

(iii) Experiments with 0.1g of CaCO_3 and of the mixtures revealing the ratio $\text{CaCO}_3 : \text{Au} = 2 : 1$ at 613mmHg.

Decomposed ratios at 700° in either cases are shown in Fig. 4.

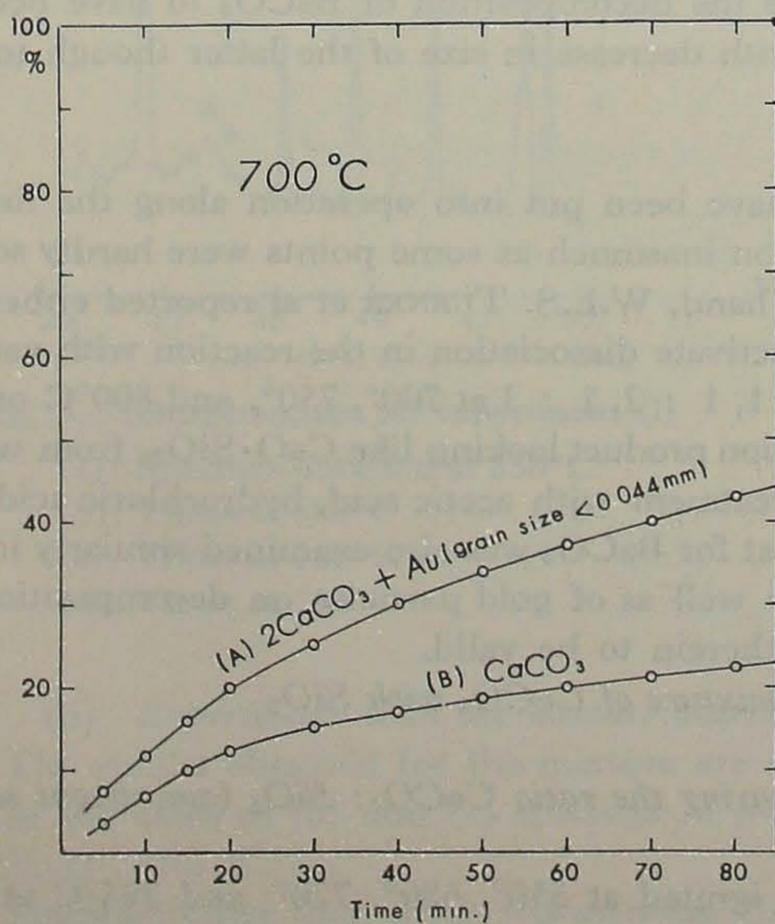


Fig. 4

(A) Decomposed ratio of CaCO_3 in presence of Au particles (less than 0.044mm in size)

(B) Decomposed ratio of CaCO_3 with nothing

The results seem to indicate the decomposition of CaCO_3 to have been really activated in presence of Au.

(iv) *Experiments with 0.2 g of BaCO_3 and of the mixture revealing the ratio BaCO_3 : $\text{Au}=1 : 3$ at 517mmHg.*

Decomposed ratio at 850°C in three cases are shown in Fig. 5.

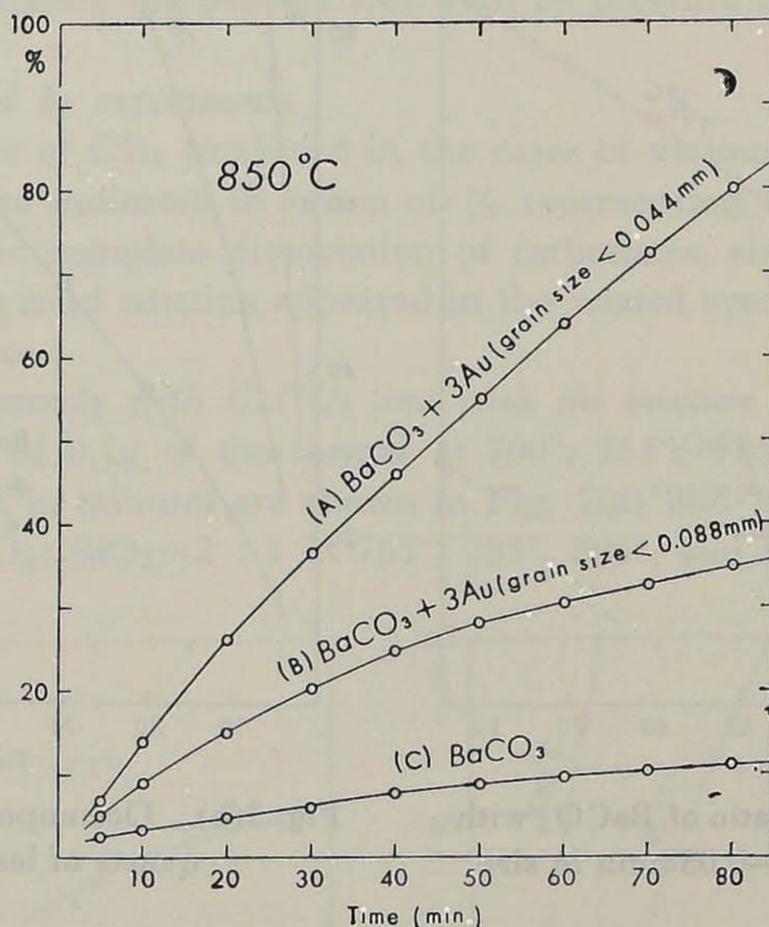


Fig. 5.

- (A) Decomposed ratio of BaCO_3 in presence of Au particles (less than 0.44mm in size)
 (B) Decomposed ratio of BaCO_3 in presence of Au particles (0.044-0.88mm in size)
 (C) Decomposed ratio of BaCO_3 with nothing

The results obtained seem to indicate the decomposition of BaCO_3 to have become easier with addition of Au particles and with decrease in size of the latter though to less extent than in the case of SiO_2 added.

(c) *Scrutiny of the data*

The reality is that the experiments have been put into operation along the line to inspect inconsistency with JANDER's equation inasmuch as some points were hardly solved only according to his view. On the other hand, W.E.S. TURNER et al reported either the catalytic role of SiO_2 and Au particles to activate dissociation in the reaction with various ratios of CaCO_3 to the formers such as 1 : 1, 1 : 2, 1 : 3 at 700° , 750° , and 800°C or the genesis of microscopically fine-grained reaction product looking like $\text{CaO}\cdot\text{SiO}_3$, from which silica was dissolved in solution through treatment with acetic acid, hydrochloric acid and sodium carbonate. In view of this the test for BaCO_3 was also examined similarly in the case of CaCO_3 and the effects of silica as well as of gold particles on decomposition of the carbonate concerned were confirmed therein to be valid.

(3) *Reaction products on ignition of the mixture of CaCO_3 with SiO_2*

(a) *Röntgenometric inspection*

(i) *Experiments with the mixture bearing the ratio CaCO_3 : SiO_2 (amorphous silica) = 2 : 1*

The results obtained for the mixture ignited at 550° , 680° , 720° , and 785°C at 663

mmHg for thirty minutes are shown in Fig. 6.

In the case of (a), spacing of CaCO_3 merely are most conspicuous while those of others are still obscure. In the case of (b), spacings considered to represent CaO are a little more intensely appeared beside those of CaCO_3 . In the case of (c), spacings are almost same as in the former case. In the case of (d), spacings of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_3$ are recognized as are indicated by notations such as A, B, C, and D.

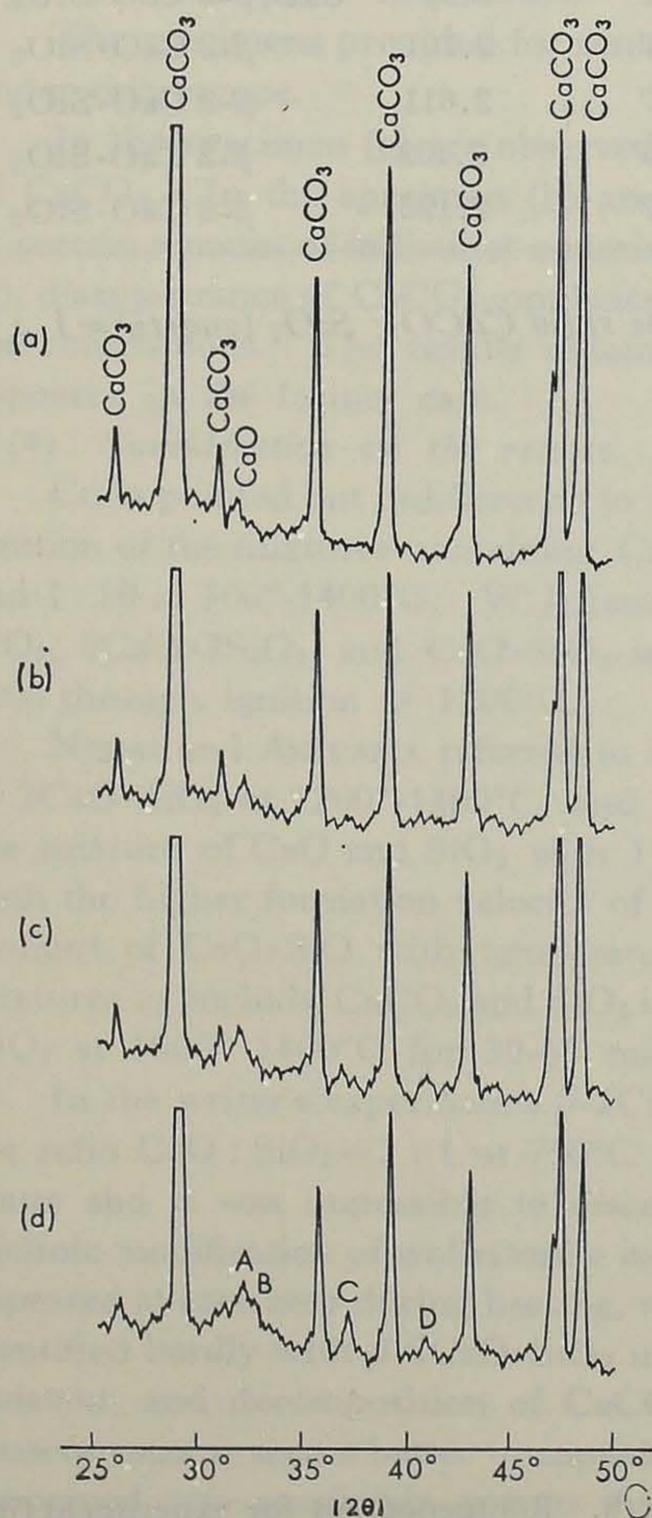


Fig. 6. Röntgenogram for experiment (i)

- (a): Spacings obtained at 550°C
- (b): Those at 680°C
- (c): Those at 720°C
- (d): Those at 785°C

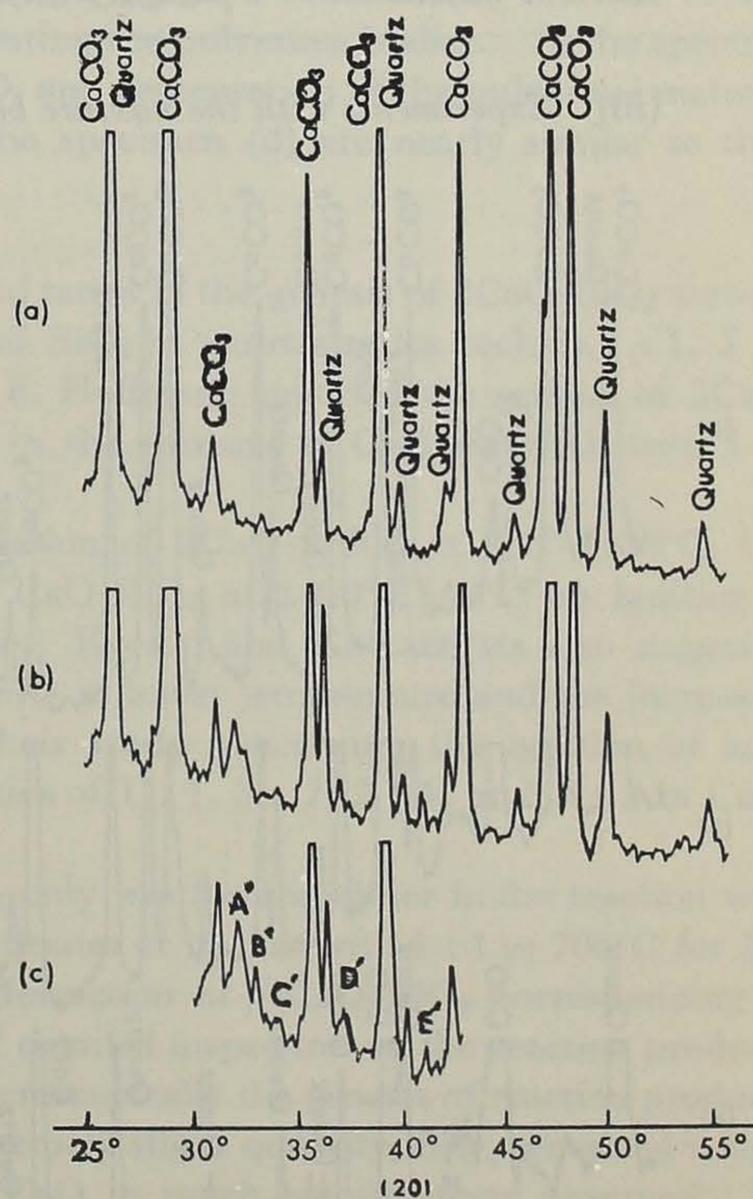


Fig. 7. The röntgenogram for experiment (ii)

- (a): Spacings obtained prior to ignition
- (b): Those obtained for the mixture ignited at 750°C at 663 mmHg for 60 minutes
- (c): Those obtained similarly in the former case but in different condition of x-ray

(ii) Experiments with the mixture bearing the ratio $\text{CaCO}_3 : \text{SiO}_2$ (quartz) = 2 : 1

The results obtained for the mixture are shown in Fig. 7.

In the cases of (b) and (c) spacings of $\beta\text{-}2\text{CaO}\cdot\text{SiO}_3$ appear as are denoted by A', B', C', D', and E'.

Spacings other than those representing CaCO_3 and SiO_2 in experiments (i) and (ii)

are indicated in Table 2, showing formation of CaO and β -2CaO·SiO₂.

Table 2. Röntgenometrical data obtained in experiments

Experiment (i)			Experiment (ii)		
Peak	d(Å)	Composition	Peak	d(Å)	Composition
A	2.77	CaO, β -2 CaO·SiO ₂	A'	2.77	CaO, β -2 CaO·SiO ₂
B	2.717	β -2 CaO·SiO ₂	B'	2.701	β -2 CaO·SiO ₂
C	2.411	CaO, β -2 CaO·SiO ₂	C'	2.611	β -2 CaO·SiO ₂
D	2.199	β -2 CaO·SiO ₂	D'	2.409	β -2 CaO·SiO ₂
			E'	2.196	β -2 CaO·SiO ₂

(iii) Experiments with the mixture bearing the ratio CaCO₃: SiO₂ (quartz)=1 : 1.

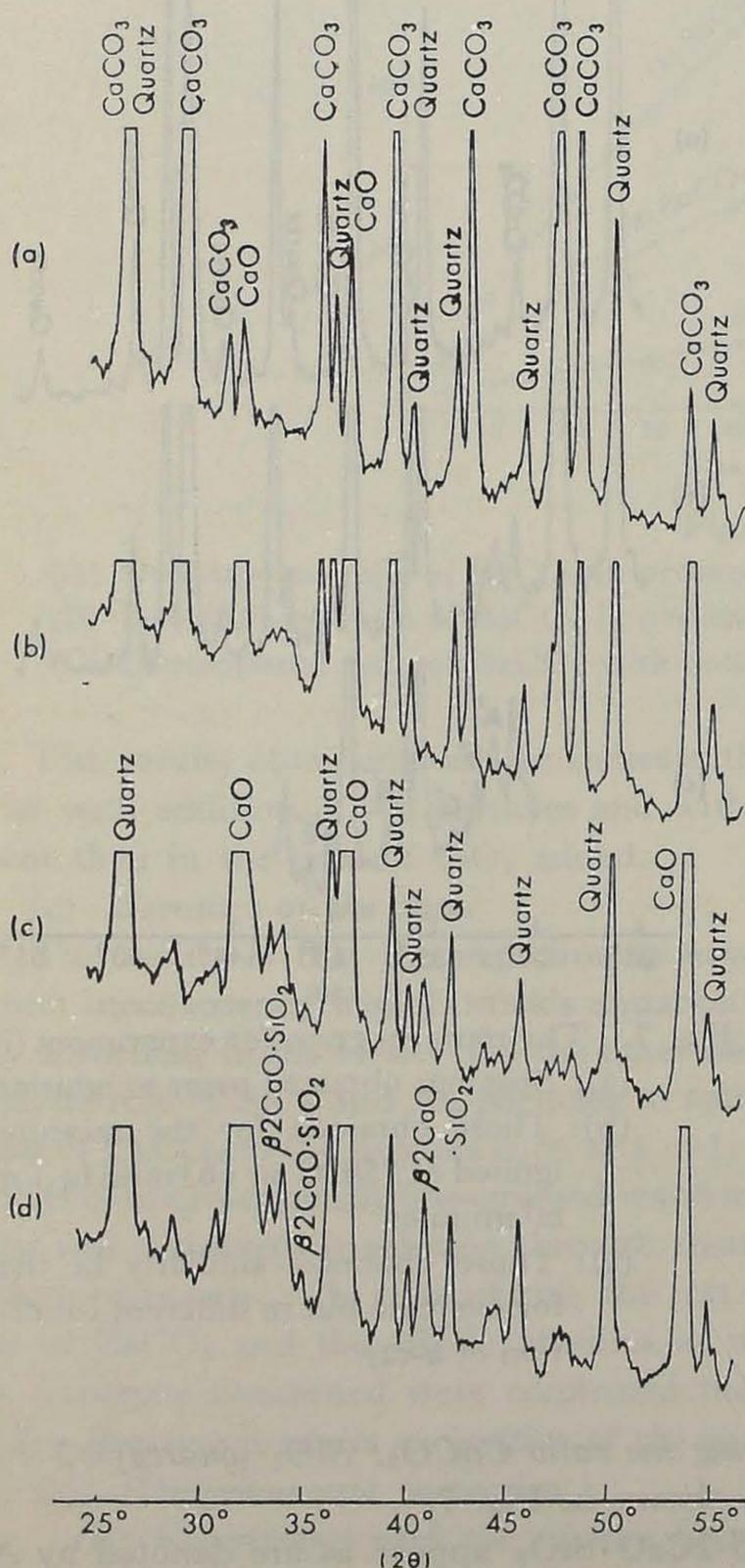


Fig. 8. Röntgenogram for experiment (iii)
 (a): The spacings obtained for 0.5 hour
 (b): Those for 5 hours
 (c): Those for 146 hours
 (d): Those for 242 hours

The mixtures held at $700^\circ \pm 10^\circ\text{C}$ in air in the siliconite oven for 0.1, 1, 2, 5, 11, 23,

47, 71, 95, 119, 146, 170, 218, and 242 hours were examined and the results obtained for four specimens held for 0.5, 5, 146, and 242 hours are shown in Fig. 8.

In the case of (a) spacings of CaO together with those of CaCO₃ and SiO₂ appear. Those of β -2CaO·SiO₂ are found accompanying the formers in the case of (b), become more intense in the case of (c), and seem to suggest the crystallization of β -2CaO·SiO₂ in the case of (d).

(b) *Microscopic examination*

The specimens provided for röntgenometric inspection were, as they were, scrutinized under microscope.

In the specimen (a) are observed a little amount of CaO derived from decomposition of CaCO₃. In the specimen (b) are recognizable either a considerable increase of CaO or certain amount of indistinct materials cementing the pulverous bodies. In the specimen (c), disappearance of CaCO₃, opulence of CaO, and cementation of the pulverous materials are conspicuous. The results obtained in the specimen (d) are nearly similar to those appeared in the former case.

(4) *Consideration on the results*

COBB pointed out indifference to the mixed ratios in the genesis of 2CaO·SiO₂ through ignition of the mixtures containing CaCO₃ and SiO₂ in various ratios such as 1 : 1, 3 : 1, and 1 : 10 at 500°-1400°C. W. J. Jander and E. Hoffmann reported the genesis of 2CaO·SiO₂, 3CaO·2SiO₂, and CaO·SiO₂ in order in the mixture of CaO and SiO₂ with 1 : 1 ratio through ignition at 1200°C.

NAGAI and AKIYAMA referred to the formation of 3CaO·2SiO₂ at 900°-1100°C, that of 2CaO·SiO₂ at 1200°-1400°C, and that of CaO·SiO₂ at 1450°-1540°C on ignition of the mixture of CaO and SiO₂ with 1 : 1 ratio. KONDO and KAWASHIMA also suggested both the higher formation velocity of 2CaO·SiO at lower temperature and the increasing amount of CaO·SiO with temperature in their study concerning the ignition of such mixtures as include CaCO₃ and SiO₂ in the ratios of 1 : 1, 3 : 2, 2 : 1, and 3 : 1 in CaO : SiO₂ at 1000°-1400°C for 30-60 minutes.

In the writer's experiments β -2CaO·SiO₂ only was formed either in the reaction with the ratio CaO : SiO₂=2 : 1 at 750°C for 60 minutes or in that with 1 : 1 at 700°C for 242 hours and it was impossible to discern the formation of β -CaO·SiO₂ corresponding to triclinic modification of wollastonite in spite of detailed inspection on the reaction products appeared at each step during heating, while microscopically the genesis of reaction products identified hardly with β -2CaO·SiO₂ in an extremely slight quantity, SiO₂ remained nearly constant, and decomposition of CaCO₃ into CaO in much amount were observed. In consequence, it seems better to consider that CO₂ gas derived from heating of the mixture concerned was ascribable not to that produced contemporaneously with formation of wollastonite as a result of solid reaction but merely to that originated mainly through thermal dissociation of CaCO₃.

(B) **Reaction between CaO and SiO₂**

(1) *General remarks*

Since the data pointing directly to the mechanism of solid reaction were not obtainable in the case of the mixtures dealt with at certain temperatures lower than 900°C, manners of diffusion in the solid reactions were cautiously scrutinized concerning the planer contacts of pulverous CaO prepared through ignition of CaCO₃ at 900° - 1,000°C for about 30 minutes with powders of SiO₂ (quartz) and, furthermore, behaviors of BeO, MgO, and BaO instead of CaO were inspected in conditions similar to those applied in

the reaction with CaO.

(2) Experiments

Quartz sands provided for the experiments were the same as those used in the preceding and sorted similarly through standard sieve of $44\sim 88\mu$. CaO was prepared through decomposition of CaCO_3 manufactured by Merck. Other chemicals such as BeO, MgO, and BaO were of a special sort.

Powders of quartz was placed at the lower half of Pt crucible with diameter of about 3cm and depth of about 4cm, hardened with definite pressure so as to be flat on the surface, then covered with powders of BeO, MgO, and BaO, and again hardened. The content thus prepared was heated in the siliconite furnace at 1300°C , and 1500°C for an hour and at 1500°C for 1, 2, and 3 hours respectively. The experiments were put into operation similarly in opposite arrangement of SiO_2 and others, in that the former was placed covering the latter.

The reaction layer appeared at the contact of one with the other was divided into three parts and röntgenometrically scrutinized, while, at the same time, thin sections of the content were examined under polarizing microscope.

(3) Results obtained

Although the reaction layer produced at 1300°C and 1400°C was too thin to be separated one from another, that formed through heating at 1500°C for an hour were estimated about 4mm in thickness, that for 2 hours about 6mm, and that for 3 hours about 8mm. The reaction layer sampled for röntgenometric procedures was divided into for parts such as (a) near CaO, (b) in the center, (c) near SiO_2 , and (d) in SiO_2 . The röntgenograms obtained from each part are shown in Fig. 9.

X-ray data indicate both the formation of $\alpha\text{-CaO}\cdot\text{SiO}_2$ corresponding to pseudowollastonite as a sort of reaction product and the variation of most parts of SiO_2 remained to react into β -cristobalite associating a little amount of β -quartz remained. Difference, and variation of diffractive intensity appeared in respective parts concerning specific spacing of each component are represented in Fig. 10, wherein the spacing of 2.48\AA for β -cristobalite, that of 3.34\AA for β -quartz, and that of 3.23\AA for $\alpha\text{-CaO}\cdot\text{SiO}_2$ are particularly selected for comparison. As is clear in the diagram (Fig. 10). part of β -quartz not reacted with CaO are more abundant and its spacing is more intensely appeared with approaching to SiO_2 side. Whereas remarkable variation in β -cristobalite and $\alpha\text{-CaO}\cdot\text{SiO}_2$ is not observed throughout the reaction layer. In another specimens, formation of $\beta\text{-2CaO}\cdot\text{SiO}_2$ has also been confirmed near CaO side.

On ignition of SiO_2 with other materials at 1500°C for 3 hours, width of reaction layer was estimated $0.2\sim 0.3\text{mm}$ in the case with BeO, about 0.1mm in the case with MgO, and about 10mm in the case with BaO.

Microscopic examination of the reaction layer with crossed nicols reveals that sparkling fine grains of β -quartz or β -cristobalite are embraced in $\alpha\text{-CaO}\cdot\text{SiO}_2$ with lower index and their grain-size are more larger with approaching to SiO_2 side and vice versa on the opposite side, while $\alpha\text{-CaO}\cdot\text{SiO}_2$ is found displaying here and there a sort of flow texture with crossed nicols and lower magnification. Photomicrograph of reaction layer is given in Photo 1.

(4) Consideration on the results obtained

According to the schematic diagram given by W. JANDER and E. HOFFMANN for the contact produced through reaction between SiO_2 and CaO at $1000^\circ\sim 1200^\circ\text{C}$, it seems that (1) growth of $2\text{CaO}\cdot\text{SiO}_2$ is the first, (2) productions of $3\text{CaO}\cdot 2\text{SiO}_2$ and $3\text{CaO}\cdot 2\text{SiO}_2$ associated with $2\text{CaO}\cdot\text{SiO}_2$ are subsequent to the former, (3) disappearance of $3\text{CaO}\cdot$

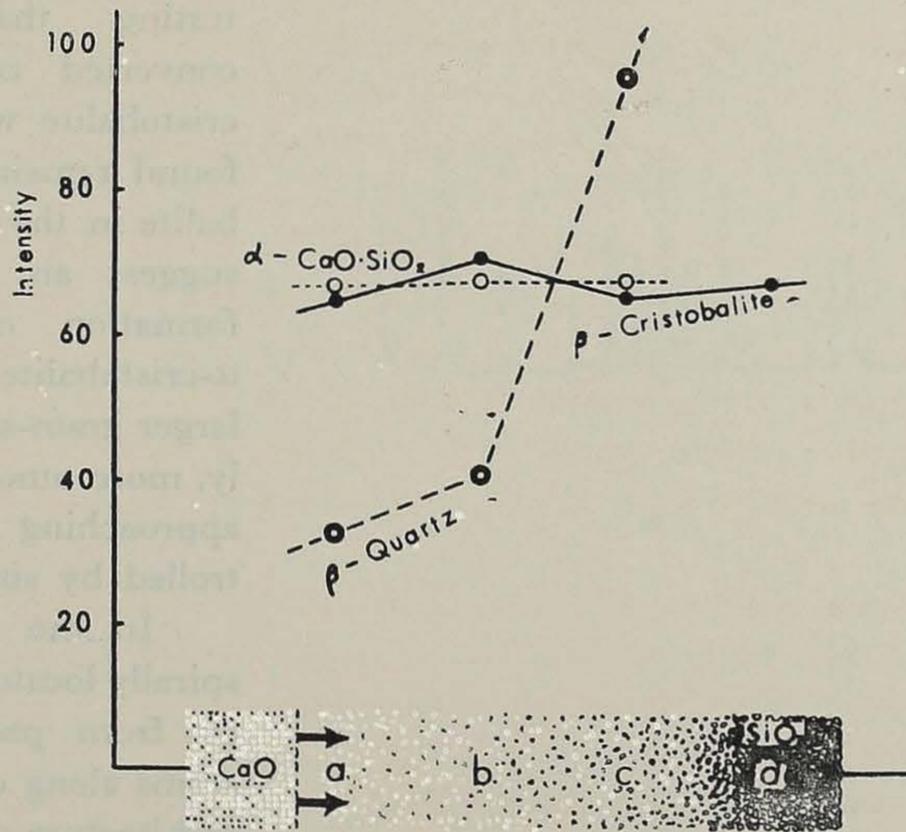


Fig. 9. Röntgenograms for each part
 CuK α , 15mA, 35KV, Scale factor:
 4-1-8,
 Scanning speed: 1°/min,
 Chart speed: 1cm/min,
 Slit: 1°-1°-0.1mm.

SiO₂ and appearance of CaO·SiO₂ follow, (4) mobilization of CaO from 2CaO·SiO₂ after entering into composition results in formation of CaO·SiO₂ in larger size, and (5) diffusion velocity of CaO is more rapid than that of SiO₂. As for the mechanism relating to formation of reaction layer, the results obtained in the writer's experiments make it clear that pulverous bodies of SiO₂ and CaO might have initially constructed the reaction layer and then CaO·SiO₂ might have migrated in fluidal condition at 1500°C nearly its melting point, accompanying easier diffusion of CaO and SiO₂ in the reaction zone of a little fluidity. On the other hand, scrutiny of the ignition product composing the layer may suggest such a difference as is regarded not as mutual diffusion between CaO and SiO₂ but as an isolated one of the former.

As was enlightened in the preceding, low quartz is more predominant both in amount and in intensity on SiO₂ side in spite of homogeneous disposition of β -cristobalite in the layer concerned. This is probably due to that, in general, β -quartz is to transform into α -quartz and then into β -cristobalite in an ideal condition but, in his case, α -cristobalite converted directly into β -modification not through high quartz because of incomplete transformation of α -quartz, if in larger grain-size, into α -cristobalite and of rapid cooling from considerably higher temperature, while the parts remained still as α -quartz also came back into β -quartz. As regards this, two parts of pulverous quartz, 5~20 μ and 44~76 μ in respective grain-size, were heated in separate Pt-crucibles at 1500° for 3 hours and cooled rapidly in air.

