ART. VI. — *On Wollastonite and Psuedo-Wollastonite. — Polymorphic Forms of Calcium Metasilicate;* by E. T. ALLEN and W. P. WHITE, with optical study by FRED. EUGENE WRIGHT.

[By permission of the Director of the U. S. Geological Survey.]*

Introductory.†—Wollastonite is said to occur in massive rocks as an original constituent, but is perhaps confined to nepheline syenite such as is described from Alnö by Törnebohm, who found it as inclusions in feldspar, in nepheline and in ægirine. Similar rocks have been described by Mügge and others. It is also not uncommon in the crystalline schists. In some such cases, like that described by Cross from Brittany, the wollastonite is a secondary product and forms pseudomorphs after plagioclase. Among the crystalline limestones of the ancient schist series it is abundant, and it is found also in related rocks of the same series, such as garnetite and calcareous slates. Heinrich Wulf‡ has also described it as an original constituent of the crystalline schists in Hereroland in Southwest Africa, and one of his rocks consists of nearly equal parts of wollastonite and diopside.

Wollastonite is most abundant in and most characteristic of contact metamorphic limestones, either along the periphery of massives or in fragments included in a variety of eruptive rocks. It is thus usually classed as a contact mineral. It often forms well-shaped crystals of visible size, but no pseudo-wollastonite

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† For the introductory paragraphs upon the natural occurrence of wollastonite, the authors are indebted to Dr. George F. Becker.

‡ Min. Petr. Mitth., viii, 230, 1887.

is known in nature nor any paramorph of wollastonite after pseudo-wollastonite. On the other hand, pseudo-wollastonite in crystals no less than a centimeter in width has been observed in artificial slags by Vogt and others.

Had the schists containing wollastonite crystallized at temperatures above 1180°, it would seem from the following investigation that the calcium silicate must have separated out as pseudo-wollastonite, and that even had it afterwards gone over by paramorphism into wollastonite, the original form must have left its traces. Such, too, must have been the case had the contact metamorphosis of limestones taken place at a higher temperature or had the fragments of limestones, often very small, which are included in effusive rocks, been heated above this critical temperature. Such included fragments are often sharply angular, and there is no probability that they were ever melted. Of course, the character of a melt is greatly modified by the constituents present, so that the admixture of other substances than calcium silicate must be taken into account; but it would appear that other substances, such as iron compounds, could only reduce the melting temperature of the mixture, making it safe to conclude that wollastonite can under no circumstances have formed above 1180°. The effect of pressure is probably without influence upon this conclusion in view of the very low vapor tension of the mineral at its inversion temperature. The present investigation therefore adds a very considerable amount of exactness to our knowledge of the temperatures at which the metamorphism of limestone has gone on. If the wollastonite of the nepheline syenite is primitive, at least one family of deep-seated intrusives has also been injected at temperatures lower than 1180°.

Messrs. Day and Shepherd have shown that wollastonite is very generally stable, and apt to make its appearance under a wide range of circumstances from melts of very different compositions. This, too, is in entire accord with the geological evidence afforded by contacts along which the chemical conditions vary greatly and rapidly, while wollastonite, through its frequency, exhibits, in nature as well as in the laboratory, a strong tendency to form under varying conditions.

Preparation of Wollastonite.—Attempts to synthesize the mineral wollastonite ($CaSiO_3$) generally result in the formation of a substance, apparently uniaxial, which has never been found in nature. Even when the natural wollastonite is fused and cooled again, it is almost invariably the uniaxial form which crystallizes. The genuine wollastonite has been observed as an accidental product of slow cooling in glasses, and crystals of it, in a few instances,* have been obtained by intention from artifical magmas, usually without any clear insight into the causes of its formation. Hussak† obtained it as one of the products from a mixture of silicates and borates of calcium and sodium; Doelter‡ from a magma made of lime and silica with fluorides of calcium and sodium. Methods of this kind will evidently yield mixtures more or less complex of which wollastonite is only one constituent and in which the experimenter is confined entirely to optical methods for the examination and identification of the mineral.

In connection with an extended study of the pyroxenes, it was our purpose to prepare wollastonite, determine its properties, and discover, if possible, its relation to the artificial form.

Suspecting that temperature was the determining factor,§ we first prepared a glass of the composition $CaSiO_3$, and by heating this at a temperature of 800° to 1000° succeeded in getting true wollastonite in pure condition and in portions of 50 grams at a time. The glass, to be sure, is a little difficult to prepare on account of the strong tendency of the liquid to crystallize. Although once we obtained 100 grams of it by simply cooling in the furnace where it was melted, it almost always crystallizes prematurely when thus treated. The safest way is to melt smaller portions and then chill suddenly in cold water.

For the preparation of the glass, we used the purest quartz and calcium carbonate obtainable. The latter contained only a few hundredths of a per cent of alkali and magnesium, the quartz, about two-tenths of one per cent of total impurities, chiefly oxide of iron. The ingredients were weighed in exact proportions and melted in a platinum crucible. It requires over 1500° to melt this mixture, a temperature readily reached by a Fletcher gas furnace.‖ When the contents of this crucible are quite fluid, the crucible is seized with tongs and plunged into cold water, care being taken not to agitate the liquid silicate. In this way, one obtains a brilliant colorless glass. Frequently a portion will crystallize in spite of the efforts of the operator, but if the quantity is small and not too much scattered, it can be separated mechanically from the glass with little trouble. The glass needs now only to be heated in a platinum crucible over the flame of a Bunsen burner, when it crystallizes directly and quite rapidly to wollastonite.

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* Morozewicz, N. Jahrb. f. Min. 1894, ii, 223. Vogt, Die Silikatschmelzlösungen i, p. 45.

† Hussak, Zeitschr. für Kryst. und Min., xvii, 101.

‡ Doelter, Tschermak's Mitt. Petr. Mitth., x, 83, 1888.

§ Doelter has also expressed this view. N. Jahrb. f. Min. Referate, 1886, i, 123.

‖ 4la—Buffalo Dental Mfg. Co.

Properties.—The pure mineral is white in the mass and shows when prepared by the process just described the fibrous structure which is commonly characteristic of the natural mineral. A perfectly transparent variety in beautifully formed crystals of short prismatic habit was obtained later in an entirely different manner, which will be described subsequently. A detailed microscopic study of both varieties by Mr. Wright accompanies this paper.

The density of the fibrous material varies considerably, being dependent on the temperature of crystallization, and perhaps upon other conditions. The variation is satisfactorily accounted for by the presence of bubbles, or more probably vacuous spaces, which the microscope shows are generally present in the crystalline mass. They are probably the residual spaces which are left by the condensation of substance about the crystal nuclei. In one of the preparations, Prep. IV, which in crystallizing almost reached the inversion point, these bubbles were not found, and the crystalline fibers were much coarser. The following determinations were made by the method of Day and Allen:[*]

Specific Gravity of Fibrous Wollastonite, prepared by the devitrication of the glass. Determinations were made at 25° and compared with water at 25°.

Prep. I.	Heated about 3 days at a maximum temperature of 860°.	2·907 2·907
Prep. II.	Heated 17 hours at a maximum temperature of 950°.	2·876 2·876
Prep. III.	Heated 22 hours at a maximum temperature of 980°.	2·896 2·896
Prep. IV.	Formed from an under-cooled mass which began to crystallize at 1030° and rose in the process to a temperature of 1127°. The microscope showed a coarsely fibrous mass without the bubbles which appeared in I, II and III.	2·9145 2·9156 —— 2·915

The density of the glass from which the wollastonite is prepared is here given for purposes of comparison. The glass is perfectly free from bubbles and hence shows a practically constant density, which differs but little from that of wollastonite, being a trifle lighter than the densest preparation.

Specific Gravity of Glass of the Composition $CaSiO_3$, determined at 25°, compared with water at 25°.

Prep. *a.*	Prep. *b.*	Prep. *c.*
2·901	2·905	2·905
2·902	2·905	2·903

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[*] Isomorphism and Thermal Properties of the Feldspars, this Journal, xix, 125, 1905. Publication No. 31, Carnegie Institution of Washington, p. 55.

The Inversion of Wollastonite to Pseudo-Wollastonite.—It is sufficiently well known that the polymorphic forms of solid crystalline bodies are divided into two well-marked classes, the monotropic and the enantiotropic. Substances which, like phosphorus, belong to the first class, possess one form which is more stable than the other at all temperatures below the melting point. The unstable form may therefore change directly into the other over a considerable range of temperature, but the change in the opposite direction cannot be brought about. In substances of the second class, the enantiotropic bodies, the transformation from one to the other takes place at a characteristic temperature point, known as the inversion point, and is reversible. Each form of a monotropic substance possesses its own melting point, while in enantiotropic substances only one form melts in the region of its stable existence, viz: that form which is stable at the higher temperature.*

In calcium silicate we have unquestionably a case of enantiotropy, for one form changes to the other at a definite temperature, and the change is, under proper conditions, reversible.

When wollastonite, either natural or artificial, is heated to about 1180°, it passes entirely into the hexagonal form. This change of state occurs without melting, for, in every case, the coarsely-powdered mineral which we employed in experiment was found, after the inversion, to have shrunk away from the walls of the crucible, forming a sintered cake, which, of course, a liquid could never have done. Moreover, the separate grains of the substance always preserved their sharp edges.

Brun† states that natural wollastonite from Auerbach melts at about 1350° and then quickly solidifies. There is, of course, the possibility that a rapidly heated charge might pass the inversion point without change and melt in the metastable region, as sulphur is known to do. A special effort was made to test this possibility in the following manner: a 50 gram charge of the purest natural wollastonite obtainable (from Diana, N. Y.) was heated in the electric furnace past the inversion point at the fastest rate consistent with the safety of the heating coil, i. e., about 16° per minute. To hinder inversion as much as possible, we selected rather large fragments of the mineral with comparatively little surface. At 1260° a perceptible absorption of heat was observed, immediately after which the temperature was lowered and the charge examined. Some fragments had undergone a slight local vitrification which gave the effect of glazing, but the original form of each

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* Roozeboom, Heterogene Gleichgewichte, vol. i, pp. 109, 110. Findlay, The Phase Rule, 1904, p. 42.

† Archives des Sciences phys. et nat., série 4^e, tome 18, p. 551.

was preserved down to the corners and edges, which remained as sharp as ever, and the microscope proved that all had been converted into pseudo-wollastonite. We were therefore unable to reproduce Brun's results or to explain them.

To locate the inversion point, we experimented in two different ways. On the one hand, we established a point below which inversion would not occur, by heating powdered wollastonite in contact with the hexagonal form at measured temperatures for more or less protracted intervals. At a temperature of 1100° there was no sign of inversion after a period of 60 hours. We relied upon microscopic evidence for our conclusion.*

A charge made up in the same way and held at 1170° for an hour likewise showed no indication of change, but the same charge returned to the furnace and kept at 1190° for another hour showed that the transformation had begun. The change revealed itself in the formation of small grains and patches of pseudo-wollastonite, embedded in the original wollastonite, which were plainly visible between crossed nicols. 1190° is therefore the lowest temperature at which we can certainly say that inversion takes place. Changes in the solid state are well known to be very sluggish, and this one, as will appear farther on, is a rather extreme case. It may therefore well be that if experiments were continued for very long periods, the true inversion temperature would be found to fall somewhat lower down.

By the use of Frankenheim's method,† in which the temperature is observed at regular intervals as heat is continually supplied to the mass, we were able to detect a small absorption of heat corresponding to the physical change revealed by the microscope.

A departure from previous practice was made in the use of a control element. The heating of a furnace can not be made perfectly regular even with storage batteries of large capacity, but the temperature rises with continual slight fluctuations, which, of course, are shared by the charge in the crucible, where they are indistinguishable in their effect on a thermo-element from slight evolutions or absorptions of heat in the charge itself. The control element, which gives the temperature of the furnace, enables a correction to be applied for the furnace fluctuations. It is read alternately with the element in the charge. In general, it is not easy to tell exactly what effect upon the charge is produced by a given fluctuation in

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* For the examination of these mixtures the authors are indebted to Mr. W. Lindgren of the U. S. Geological Survey.

† Day and Allen, Isomorphism and Thermal Properties of the Feldspars, this Journal, xix, 93, 1905; Publication No. 31, Carnegie Institution of Washington.

the furnace, but the average difference of temperature between the two elements measures the rate at which heat is passing into the crucible, and any change in this difference shows an absorption or evolution of heat, provided that no great change in the average rate of heating has occurred.

INVERSION OF WOLLASTONITE.

Rate of heating in degrees per minute.	Inversion temperature.	
8·8	1232	
3·6	1225	(See curve 1, Table I.)
1·0	1198	
1·1	1197	(See Table II.) Mixed with inverted form.
1·0	1211	Mixed with inverted form.

These results indicate, in harmony with the microscopic evidence, that the presence of the inverted form has, under the given conditions, little or no effect on the inversion. That the inversion temperature should seem to be higher as the rate of heating increases, was to be expected. The last sample was carried as far as 1245°, and on cooling was found to be inverted only in part.

The Reversion of Pseudo-Wollastonite.—When pure pseudo-wollastonite was cooled, even very slowly, it did not revert to wollastonite. Our first efforts to overcome this inertia were along the usual lines. We added to the mass a small quantity of the more stable phase (wollastonite) and allowed plenty of time for equilibrium to assert itself. The two forms, mixed in about equal proportions, were spread in a thin layer at the bottom of a platinum crucible, and on this was placed a deeper layer of the pseudo-wollastonite. Experiments lasting from 36 to nearly 60 hours at temperatures ranging from 900° to 1100° were without effect; the optical method of identification always showed both substances and indicated no change whatever. We next tried the effect of the solvent action of water. The two forms, mixed as we have described above, were heated for several days in a steel bomb with water above its critical temperature. The bomb held tight, but there was no indication of change in the crystals. We will not therefore describe the apparatus and the conditions of experiment in detail. Both crystalline forms were proved by the microscope to be practically unchanged by this treatment, and chemical tests showed little hydrolysis. This is somewhat surprising in view of the fact that these silicates impart an alkaline reaction to water on standing in the cold. It should be remarked that the quantity of water used was very small, only 3 to 4 cc. to 2 gr. of substance. On the glass

Table I.

Inversion.

Curve I.

Control.	Rise in 2 min.	Crucible.	Rise in 2 min.	Diff.
11481				
	92	11360		167
573			92	
	93	452		167
666			93	
	94	545		168
760			94	
	90	639		166
850			91	
	92	730		166
942			90	
	98	820		171
12040			92	
	96	912		176
136			99	
	91	12011		170
227			90	
	89	101		170
316			82	
	90	175		188
406			59	
	96	**232**		222
502			79	
	98	311		240
600			124	
	95	435		213
695			121	
	96	556		189
791			114	
	97	670		170
888			105	
	97	775		162
985			101	
	84	876		151
13079			98	
	92	974		151
171			96	
	97	13070		150
268				

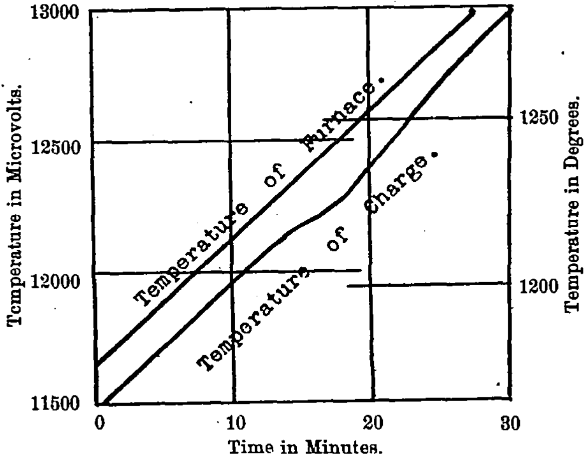
Table II.

Inversion.

20 per cent of the inverted form was mixed with the charge so as to start the action at the lowest possible temperature.

Control.	Rise in 2 min.	Crucible.	Rise in 2 min.	Diff.
11795				
	62	11662		133
857			62	
	59	724		133
916			58	
	57	782		134
944			54	
	56	836		134
12000			55	
	60	**891**		137
060			59	
	56	950		139
116			56	
	54	12006		136
170			55	
	54	061		137
224			53	
	51	114		136
275			50	
	49	164		134
324			52	
	51	216		132
375			54	
		270		128

Curve I.—Inversion of Wollastonite.
Inversion Temperature, 1225°.
Rate of Heating, 3·6° per minute.



there were signs of some action. The grains were cemented tightly together, while the microscope disclosed what appeared to be an incipient crystallization.

From water we turned to the solvent action of a fused salt.* The necessary properties in a salt which should answer our purpose are evidently the possession of an ion common to calcium silicate, so that metathesis may not result; sufficient fusibility, and sufficient solubility, in order that the excess may be removed after the process is complete.

These requirements are fulfilled by calcium vanadate, $Ca(VO_3)_2$, which is prepared by heating calcium carbonate with the proper proportion of vanadic acid. In the first trial, we heated one gram of vanadate with several grams of pseudo-wollastonite at a temperature of 800° to 900° for a number of days. The solvent was then partially extracted by hot water, after which the residue, so far as possible, was removed by very dilute hydrochloric acid. The product was all changed into wollastonite. In later experiments, we tried larger quantities of vanadate and heated for different periods. One gram of vanadate readily transforms 5 grams of silicate and is removed when the change is accomplished with less trouble than a

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* Calcium chloride forms chloro-silicates. Gorgeu, Bull. Soc. Min., x, 271. In our experiments we did not get a pure product, though the majority of it, when a large excess of calcium chloride was used, crystallized in transparent lath-like crystals of orthorhombic (?) symmetry. The ratio of chlorine to silica in the product was in accord with the formula $2CaSiO_3.CaCl_2$.

larger quantity. The mass thus formed is scarcely pasty at the highest temperature of an ordinary Bunsen burner, yet the yellow color shows that the silicate is completely permeated by the vanadate. If one desires as large crystals as possible, it is well to take more vanadate and heat for a longer time. To get the silicate in pure condition, it is best to break up the fused mass in a mortar, with a little water, cover it with, say, 50 to 100 cc. cold water, and then add a few drops of dilute hydrochloric acid, stirring thoroughly. After a few minutes, pour off the water and repeat the treatment until the water is no longer colored yellow. In this way the calcium vanadate is decomposed and removed more readily than with water alone, while if one keeps the acid cold and very dilute, the silicate is not decomposed to any extent, and the microscope shows the product to be unmixed with foreign matter. It consists, as stated above, entirely of wollastonite in beautiful transparent crystals of short prismatic habit, with sharp edges and well developed faces. The largest were about 0·2 mm long.

This formation of wollastonite could hardly be anything else than a true reversion. It is well known that such transformations in solid bodies may be facilitated by the use of solvents which probably overcome resistance to molecular movement. In this case, at the temperature of 800 to 900°, wollastonite should be the more stable polymorph, possessing a lower vapor pressure and a lower solubility. Given a nucleus of this form, therefore, the other should pass into solution and continually precipitate in the form of wollastonite. That this is really what happens, we proved by stopping the transformation before it was complete (5 grams silicate to 1 gram vanadate heated three hours). Large grains of pseudo-wollastonite remained unchanged except for a rounding of corners and edges, and side by side with them appeared small well-formed crystals of wollastonite.

As these crystals, on account of their freedom from bubbles or pores, seemed especially adapted for the determination of density, two separate preparations were made for this purpose.

	PREP. I. Sp. gr. 2·914. Analysis.	PREP. II. Sp. gr. 2·912. Analysis.	Cal. for $CaSiO_3$
SiO_2	51·94	52·00	51·86
CaO	47·69	47·46	48·14
Fe_2O_3 etc.	·19	·18	----
V_2O_4*	·38	·49	----

* Both preparations had a pale blue tint, which led us to suspect that the vanadium had been reduced in the process of heating over the gas flame to the blue oxide V_2O_4.

These numbers show very satisfactory agreement with the specific gravity 2·915 of the wollastonite which crystallized from an under-cooled melt, and may be regarded as the true specific gravity of pure wollastonite.

Some further light has been thrown on the formation of wollastonite by the unpublished work of Messrs. Day and Shepherd of this laboratory. They have examined the entire series of lime-silica mixtures and have obtained wollastonite easily in a variety of mixtures. There appears to be little difficulty in obtaining true wollastonite as soon as an excess of either component is present in the charge. The metasilicate first crystallizes in the hexagonal form, but the inversion to wollastonite occurs during cooling with little or none of the difficulty which we encountered in pure $CaSiO_3$ preparations. True wollastonite can, in fact, be obtained more readily out of concentrations with a slight excess of CaO than by the use of vanadic acid, but the crystals so formed are not large enough for convenient microscopic study, and cannot be readily separated.

In accord with nearly all of our laboratory experiments, both crystallization and inversion go on more slowly in the presence of an excess of silica, due probably to mechanical inertness or viscosity.

Pseudo-Wollastonite.—This form may be obtained by heating wollastonite above 1180°, or by crystallizing a melt above this temperature. It is only rarely that anything but pseudo-wollastonite is obtained on cooling a melt, but to insure its formation the melt needs only to be slightly agitated to overcome the instability. Pseudo-wollastonite has been described optically by Bourgeois.* It shows a basal cleavage, is optically positive, and very nearly uniaxial, though Bourgeois regards it as really monoclinic. Doelter† combats this view, but Mr. Wright in the microscopic part of this paper finds additional arguments in support of it. It crystallizes, under such conditions as have obtained in our experiments, in fibrous, fan-shaped aggregates. The density of the inverted but still unmelted crystals is variable, owing, no doubt, to the presence of bubbles, and not to be distinguished with certainty from the wollastonite, showing again that the volume change which accompanies the inversion is very small.

SPECIFIC GRAVITY OF WOLLASTONITE AT 25° COMPARED WITH WATER AT 25°.

1. Inverted but not melted.	2. Inverted but not melted.	3. Melted.
2·886	2·896	2·913
2·886	2·896	2·912

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* Bull. Soc. Min., v, 14–15.

† N. Jahrb. f. Min., 1886, i, 120 and 122.

Melting Point of Pseudo-Wollastonite.

This was determined in practically the same way as the inversion, except that some of the readings were made every half minute. The rates of heating varied between 2·1 and 2·7° per minute.

FIRST SAMPLE. FOUR MELTINGS.

	Microvolts.	Degrees.[*]
El H	16058	1511·0
	16065	1511·5
	16062	1511·3
	16073	1512·1

SECOND SAMPLE. ONE MELTING.

	Microvolts.	Degrees.	
El G	16053	1512·0	(curve 3.)
El L	16072	1512·1	

THIRD SAMPLE. ONE MELTING.

	Microvolts.	Degrees.
El G	16060	1512·7

FOURTH SAMPLE. TWO MELTINGS.

	Microvolts.	Degrees.
El F	16104	1513·5
	16104	1513·5

Melting point, 1512.

Summary and Conclusions.

1. Wollastonite and pseudo-wollastonite are enantiotropic forms of calcium metasilicate, showing an inversion point at about 1180°. The change $W_n \longrightarrow W_p$[†] is easily effected by heating above this temperature, while the reverse change has not been accomplished without the addition of other substances, owing to the sluggish nature of the silicate. Cases of suspended transformation are common enough, but a reversion which fails altogether even after heating for days in contact with the stable form is remarkable. We may compare it to the case of the glasses of the alkaline feldspars, which resist all attempts to make them crystallize by heating and sowing with nuclei. The fact very well illustrates one of the difficulties which the experimenter constantly encounters in the study of

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[*] Fractions of degrees are given in order to show the agreement obtainable in such determinations. The absolute value of the melting point is dependent upon the thermoelectric extrapolation of the gas scale, and is subject to correction whenever the latter shall be extended to this point.

[†] Let W_n represent the optically negative form, and W_p the positive.

TABLE III.*

Melting of Pseudo-Wollastonite. Curve 2.

Control.	Rise in 2 min.	Melt.	Rise in 2 min.	Risein ¼ min.	Control.	Rise in 2 min.	Melt.	Rise in 2 min.	Risein ¼ min.
15616					16109			33	8
							15993		8
	72	15604				66	16001		7
							008		7
688			70		175			27	6
							021		7
	72	674				70	028		6
							034		6
760			66		245			26	7
							047		7
	76	740				70	054		6
							060		7
836			66		315			28	7
							074		8
	77	806				65	082		10
							092		12
913			62		380			69	16
							126		25
	74	868				90	151		32
							183		
987			55		470			247	
	59	923				108	398		
			45		578				
16046	63	968		9					
		977		8					

the silicates. Molten calcium vanadate brings about the reversion at temperatures below the inversion point by the formation of a solution from which the more stable wollastonite crystallizes in well-formed prismatic crystals. Excess of lime or silica also facilitates the reversion.

Following the invariable rule, the change $W_n \longrightarrow W_p$ occurs with an absorption of heat. The volume change which accompanies this transformation is so slight that it is uncertain which form is the more dense.

The pseudo-wollastonite melts at 1512° to a comparatively thin liquid, which almost always crystallizes above 1200° on cooling down again. This explains why true wollastonite cannot generally be formed from a liquid of its own com-

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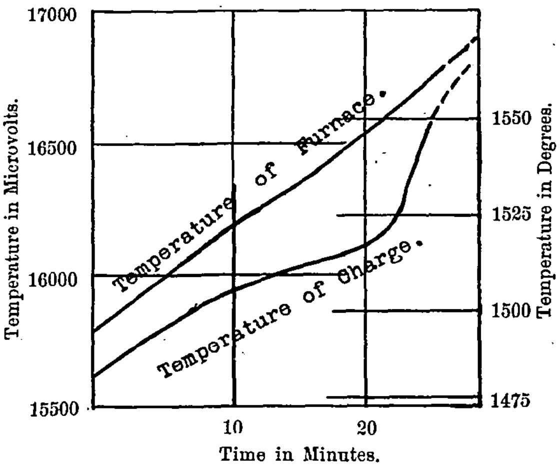
* All the numbers in this table are 7 microvolts too high, on account of a slight, unavoidable leakage current through the insulation of the hot furnace. Hence the true melting point is 16053 microvolts, as given in the previous table.

CURVE II.—Melting of Pseudo-Wollastonite.
Melting Point, 1512°.
Rate of Heating, 2·7° per minute.



position. We have already shown that the liquid can be undercooled to a glass; it follows naturally that by a suitable disturbance a sufficiently undercooled melt should crystallize directly to wollastonite. In fact, we have in one or two instances thus obtained well developed rosettes which the microscope showed were optically negative, and in one case the whole charge excepting a few surface grains yielded wollastonite. That wollastonite rarely forms in this way is due, first, to the difficulty of undercooling the melt sufficiently, and second, to the release of the heat of fusion which tends to raise the temperature again beyond the inversion point.

The addition to calcium silicate of fluorides or borates in the proper proportion (to which some investigators have resorted), of course lowers the temperature of crystallization; and it is to this influence rather than to any mysterious "mineralizing" action that the synthesis of natural wollastonite is to be ascribed. It seems not impossible also that for a similar reason Gorgeu may have obtained it together with chlorosilicates, as he claims to have done, by the addition of calcium chloride. So in the glasses of commerce which contain much sodium silicate, a slow cooling sometimes gives rise to crystals of wollastonite below the inversion point.

Although the *temperature at which wollastonite may crystallize from a magma* is conditioned by the composition of the latter, it may be worth while to call attention to the fact that the value of the *inversion temperature* as a point of reference in geology is not impaired by the varying complexity in the composition of the magma, inasmuch as this temperature has to do with an equilibrium between two solid states of calcium metasilicate, and has no relation to the solution out of which either form crystallizes. It will of course be slightly affected by pressure in the usual way, and also to some extent by the impurities which, in small quantity, are found in the natural mineral, provided these are really dissolved in it.

IMPORTANT PROPERTIES OF THE TWO FORMS OF CALCIUM METASILICATE.

Symmetry.		Inversion Point.	Melting Point.	Specific Gravity at 25° compared with water at 25°.		
				Cryst. from an undercooled melt.	Cryst. from $Ca(VO_3)_2$.	Molten.
Wollastonite	monoclinic optically negative	1180°	....	2·915	*a.* 2·914 *b.* 2·912	----
Pseudo-Wollastonite	probably monoclinic pseudo-hexagonal optically positive	"	1512°	....	....	2·912

Optical Study.

In the thin sections which were made from the various preparations of calcium metasilicate, both forms, wollastonite and pseudo-wollastonite, were recognized, and determined by their optical properties alone, their morphological features being too indefinite and inconstant to be of service. Fortunately several of the optical characteristics of the two minerals differ sufficiently to render the separation under the microscope relatively simple.

Textually the preparations show considerable variation, although in general the artificial wollastonite occurs in fibrous or long prismatic aggregates, while the pseudo-wollastonite is more coarsely crystalline and granular in appearance. Radial spherulites of wollastonite in which the crystals are elongated parallel to the axis of symmetry (*b*) were observed frequently, especially in the sections of wollastonite from crystallized glass.

In size the crystals range from the finest cryptocrystalline aggregates to individuals several millimeters in length. As a rule the crystals formed out of a melt are larger than those produced by heating the silicate glass.

Wollastonite.—Under the microscope the artificial wollastonite resembles closely natural wollastonite and often presents its characteristic arrangement of divergent fibers. The colorless laths are usually transparent and show perfect cleavage cracks parallel to their long direction. Twinning after a face in the orthodiagonal zone was recognized on several of the crystals. Two of the crystals formed from the melt of calcium metasilicate and calcium vanadate were of sufficient size (·1 x ·2 x ·5$^{\mathrm{mm}}$) to permit goniometric measurement of their faces.* Both crystals were elongated in the direction of the axis of symmetry (*b*) and showed evidences of cleavage after *u* (001) and *c* (100). On the first crystal, the forms *u* (001),† *v* (101), *t* ($\bar{1}$01), *a* ($\bar{1}$02) and *e* (110) were observed; on the second, which was less perfect, the forms *c* (100), *u* (001), *t* ($\bar{1}$01) and *a* ($\bar{1}$02) occurred, with two uncertain forms (302)? and (203)?. The forms (001) and ($\bar{1}$01) were the best developed and gave sharp reflexion signals. The faces of the other forms were smaller and less satisfactory in their measurement. The accordance of the observed interfacial angles with those of natural wollastonite, however, was sufficiently close to prove their identity. The following comparison of their polar angles shows differences which are not greater than had been anticipated from the inferior reflexion signals obtained.

			Artificial Wollastonite.		Natural Wollastonite.	
Letter	Symbol.	Miller.	ϕ	ρ	ϕ	ρ
u	0	001	90°00′	5°30′±5′	90°00′	5°30′
c	∞0	100	"	90 27	"	90 00
e	∞	110	43 10	89 58	43 39	90 00
v	+10	101	90 00	45 06	90 00	45 33
a	$-\frac{1}{2}0$	$\bar{1}$02	"	19 54	"	20 03
t	−10	$\bar{1}$01	"	39 29	"	39 35

The greatest and least refractive indices were determined by Schrœder van der Kolk's‡ method of refractive solutions to be about 1·621 and 1·636. Birefringence, about 0·015. Optic axial plane, perpendicular to the cleavage lines. Optical character of principal zone, both positive and negative. Optical character of mineral negative with optic axial angle in air, 2 E = 69°30′–70°00′, measured on several different prepara-

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* Goldschmidt's two-circled goniometer with reduction attachment was used.

† The crystallographic orientation of Goldschmidt's "Winkeltabelle," Berlin, 1897, pp. 286–287, has been followed in the notation.

‡ Kurze Anleitung zur Mikroskopischen Krystallbestimmung, Wiesbaden, 1898.

tions after the Bertrand-Mallard method. In certain sections the optic axial angle appeared to be smaller than in others, a fact for which no explanation has been found. Optic axial dispersion $\rho > \nu$. All of the above properties agree well with those of natural wollastonite and substantiate the thermal and chemical evidence of Messrs. Allen and White.

Several of the preparations of wollastonite were cryptocrystalline and could be identified only by their low birefringence and fibrous spherulitic character.

Pseudo-wollastonite appears either in the form of small irregular grains often tabular in shape or in short prisms or fibers arranged in parallel or divergent groups. The grains are transparent and show occasionally well developed basal and imperfect prismatic cleavage lines. Limiting refractive indices, about 1·615 and 1·645, as measured by the method of refractive liquids. Birefringence about 0·025–0·035, considerably higher than in wollastonite. It is interesting to note in this connection how slightly the mean refractive index of wollastonite differs from that of pseudo-wollastonite. Accurate optical measurement would be required to ascertain satisfactorily which mineral has the higher average index of refraction. The same conditions prevail in their specific gravities, where the differences observed might well be ascribed to experimental error.

Optical character, positive, with very small optic axial angle $2\,E = 0° - 8°$. Plates cut parallel to the basal pinacoid show in convergent polarized light an interference cross which can often be seen to open slightly on turning the stage. The optic axial angle thereby is so small that from it alone the mineral might be regarded uniaxial, the mere opening of the interference cross being an optical anomaly analogous to the irregularities noted in many minerals. This is the view taken by J. H. L. Vogt* in his studies on the formation of minerals in slags. His opinion was strengthened by the hexagonal form of the crystals and by the observed extinction parallel to the basal pinacoidal cleavage cracks. Doelter†, who also made an extended microscopic study of this silicate, came to the conclusion that the mineral was either hexagonal or orthorhombic in crystal system, his observations agreeing otherwise with those of Vogt. Bourgeois,‡ on the other hand, pronounced the mineral monoclinic. His work was accomplished before that of Doelter and Vogt and appears to have been less extensive in scope. After a brief mention of the essential optical features he describes the occurrence of twinning lamellæ in certain of the

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* Mineralbildung in Schmelzmassen, Kristiania, 1892, 57–59.

† N. Jahrb. f. Min. 1886, i, 119–122.

‡ Bull. Soc. Min., v, 14–15.

elongated crystals and interprets them as indicative of the monoclinic system. Doelter also mentions in passing the rare occurrence of twinning lamellæ in his preparations, but seems to have attached no significance to the fact. The present writer also observed in several of his sections sharp and occasionally polysynthetic, twinning lamellæ which were not unlike oligoclase feldspar twins in appearance. On a plate perpendicular to the optic normal the twinning lamellæ were normal to the plate and parallel to the basal pinacoid, their trace running parallel to the basal cleavage lines. The lamellæ showed an extinction angle $a : \mathfrak{a} = 2°$. Since the cleavage cracks are not perfect, the small extinction angle of 2° might easily be overlooked, under ordinary circumstances, and the extinction be considered parallel. In the hexagonal and orthorhombic crystal systems the basal pinacoid is a plane of symmetry and cannot act as a plane of twinning nor show an extinction angle, however small. The fact, then, that twinning after the basal pinacoid does occur in the pseudo-wollastonite crystals and does show an extinction angle, the double of which when taken between adjacent lamellæ is 4°, precludes the uniaxial and orthorhombic crystal systems. The writer considers the mineral with Bourgeois as probably monoclinic. The twinning law is analogous to that of Tschermak in the micas, where the basal pinacoid is also the plane of composition. Since its crystals frequently similate hexagonal forms, pseudo-wollastonite may well be treated as pseudo-hexagonal and probably monoclinic in form. It is not a modification of the natural monoclinic wollastonite. and differs from the latter profoundly in optical as well as crystallographical features.

Paramorphic changes.—The phenomenon of paramorphism, the change of crystal structure of a chemical substance in the solid state with consequent preservation of the crystal habit of the original form, is well illustrated in the inversion of wollastonite to pseudo-wollastonite. Since in certain paramorphic minerals it has been noted that a plane of symmetry or other direction may be common to both simulated and simulating mineral, several experiments were made to ascertain whether any crystallographic or other relations exist between the original wollastonite crystals and the pseudo-wollastonite which replaces them. Cleavage fragments of natural wollastonite from Diana, N. Y., were heated in an electric arc and then cooled rapidly by plunging them into mercury. Sections from this preparation showed that the wollastonite had thereby passed into the pseudo-form without any apparent regularity. The fibers of the original wollastonite were unaltered up to that portion which had touched the electric arc, from which point outwards irregular grains of pseudo-wollastonite occurred without recognizable crystallographic grouping. The contact between the natural and pseudo form was sharp, indicating that the transition had taken place without any intermediate stage.

In a second experiment, natural wollastonite was heated in the electric furnace to 1260° and thus changed in the solid state to pseudo-wollastonite. The resulting mass consisted again of grains of the pseudo form, irregularly arranged, although indications of the original fibrous wollastonite texture are still indistinctly shown.

The conditions were altered in still another experiment by heating artificial wollastonite crystals, which had been obtained by crystallizing the silicate glass, to the inversion temperature (1190°) for about an hour. The resulting preparation was instructive in showing the paramorphic change in its incipient stage. The original larger crystals were filled with particles and clusters of the pseudo-form, arranged without apparent regard to the host. Had the preparation been allowed to remain at the inversion temperature for a longer period of time, the change would undoubtedly have progressed until all original wollastonite fragments had been completely replaced by innumerable pseudo-wollastonite grains.

As the above experiments were made with cleavage fragments of natural and artificial wollastonite which are not so well adapted to show paramorphism as crystals, artificial crystals of wollastonite obtained from the calcium vanadate flux were heated in the electric resistance furnace above the inversion temperature, and the product examined. The original crystals were elongated parallel to the axis of symmetry (b) and were bounded chiefly by forms of the orthodome zone with perhaps the unit prism and unit clinodome forms. After the alteration, each one of the original wollastonite crystals was found to have changed entirely to one pseudo-wollastonite individual alone, and rarely to two or more grains, as is usually the case, a remarkable fact which may be due perhaps to the minute size of the original crystals and to the equality of specific volumes of the two forms. In one instance a basal section of the pseudo-form was contained in the orthodiagonal zone of the original mineral, while in another plate cut perpendicular to the optic normal, sharp twinning lamellae were visible, the traces of which ran parallel to a unit prism or clinodome form terminating the crystal and making an angle of 29° with the direction of elongation of the simulated crystal. From these and other observations, it is evident that, generally speaking, in paramorphic change the planes of symmetry of the two forms do not coincide. Certain crystallographic directions, however, may or may not retain their character during the change.

The paramorphic change of pseudo-wollastonite to wollastonite, which is the more imporant from the geologist's standpoint, could not be observed, since the conditions under which it was effected involved solution and precipitation, and did not occur in the solid state.

Summary.

The chief results attained by the optical study of the calcium metasilicate preparates were:

1. Identification of artificial wollastonite, whose properties agree precisely with those of natural wollastonite.

2. Determination of the pseudo-hexagonal, probably monoclinic, crystal system of the second form of $CaSiO_3$; in its crystals the occurrence of distinct and often repeated twinning lamellae parallel to the basal pinacoid and with an extinction angle $a : \mathfrak{a} = 2°$, was considered the decisive factor.

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