Agricultural Experiment Station

OF THE

University of Tennessee

BULLETIN No. 107 (Technical Series No. 3) JUNE, 1914

THE NON-EXISTENCE OF MAGNESIUM CARBONATE IN HUMID SOILS

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APPARATUS FOR MEASURING DECOMPOSITION OF SOIL CARBONATES

KNOXVILLE, TENNESSEE

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PART I
BASKET AND RIM STUDIES

INTRODUCTION

The investigations reported in this bulletin seem to warrant the conclusion that magnesium carbonate does not exist as a solid mineral component of soils of humid climates, because of inhibitory conditions; and that the supposed existence of native magnesium carbonate, analogous to that of calcium carbonate in virgin soils, is an unproved assumption rather than an established fact. The research further shows that excessive amounts of magnesium carbonate applied to soils as precipitated carbonate, dolomite, and magnesite are soon decomposed, due to the great affinity of magnesia for silica, acid silicates and titanium oxide.

The experiments were begun in the spring of 1912, and involved a study of the factors influencing lime-requirement determinations, three distinct types of soil being used in the study. The work was planned with a view of determining the value of the Veitch-method results[1] when applied to field practice, and the laboratory studies were to be supplemented by extensive basket and pot experiments.

PLAN OF ORIGINAL EXPERIMENTS

The soils selected for study were, a Cumberland loam showing a Veitch lime requirement of 3812 pounds of CaO per 3,500,000 pounds of soil, a Tellico fine sandy loam showing a need of 1061 pounds of CaO per 3,500,000 pounds of soil, and a silt loam of Chickamauga limestone origin showing a requirement of 1346 pounds CaO for 3,500,000 pounds of soil, moisture-free basis being used in the calculations given. The treatments consisted of applications of Kahlbaum's "C. P." calcium carbonate, as follows: (1) the amount indicated by the Veitch method; (2) the Veitch-method indication augmented

by one-third; (3) the Veitch-method indication plus 1785 pounds; and (4) the Veitch-method indication plus 16,070 pounds. The carbonate was well mixed with the soils and placed in paraffined wire baskets[2] in the open, but sheltered from storms by a canvas cover. In the basket work, three crops were chosen—wheat, common red clover, and clover resistant to anthracnose[3]. Three check baskets were used for each crop and soil, and three baskets for each crop and treatment of each of the three soils. Due to the excessive temperatures, the wire baskets were found to be impracticable for summer work, and the baskets were replaced by pots for the clover, the growth of which will be reported later.

Because of the enormous deposits of dolomite in Tennessee and the cheapness of the material, which is used extensively, the relative value of magnesium carbonate and its effect when applied to soils are of great importance. Accordingly, the procedure outlined for calcium carbonate was duplicated by using Kahlbaum's "C. P." normal magnesium carbonate, in amounts chemically equivalent to the calcium carbonate treatments.

Gardner and Brown[1] found after growing two clover crops in soils which had been treated with amounts of limestone sufficient to meet the requirements indicated by the Veitch method, that lime-requirement determinations subsequent to the clover crops indicated that the original Veitch-method requirement had been but 72 per cent satisfied by the limestone treatment.

In order to control the possible interfering factor of root growth, portions of the soils receiving various treatments were left exposed without cropping for one year. At the expiration of this period the fallow soils which had received the excessive treatment of calcium and magnesium carbonates were analyzed for carbonate CO_2 by the method described by MacIntire and Willis[5] and it was found that well within the limit of laboratory error, the excessive applications of magnesium carbonate had been entirely decomposed with dissipation of the CO_2 by simple contact with the fallow soils, which were protected from loss by leaching. Boiling for one minute with 1-15 phosphoric acid and applying the boiling blank of the untreated original soil, confirmed the results by the method cited. The residues of calcium carbonate and the dissipation of magnesium carbonate, in terms of calcium carbonate, are given in Table I.

The differences between the amounts of precipitated calcium carbonate actually decomposed and the amounts indicated by the Veitch method as needed to neutralize soil acidity are shown in Tables XIII, XIV and XV to be due to continued activity of precipitated calcium carbonate upon clays and other siliceous compounds, during long periods of contact without leaching, even after attaining strongly alkaline conditions. However, the decomposition of calcium carbonate falls far short of that produced in treatments of magnesium carbonate.

TABLE I—*Residual carbonates in soils treated with calcium carbonate as contrasted with the decomposition and the dissipation of the CO_2 of chemically equivalent amounts of magnesium carbonate—period of contact, 1 year*

Soil type	Wt. of soil m. f. basis	$MgCO_3$ indicated by the Veitch method to neutralize soil acidity	C. P. $MgCO_3$ applied	Carbonate CO_2 in $MgCO_3$-treated soils at end of 1 year	Carbonate CO_2 blank on original acid soil	Difference representing increase of carbonate CO_2 from treatment of $MgCO_3$	$MgCO_3$ increase calculated from CO_2 analyses	$MgCO_3$ applied in excess of the Veitch-method requirement	$MgCO_3$ lost by decomposition, excess above Veitch requirement	$MgCO_3$ loss above Veitch-method requirement =— lbs. per A — 3,500,000 lbs. of soil	$MgCO_3$ loss above Veitch-method requirement in terms of $CaCO_3$ lbs. per A — 3,500,000 lbs. of soil
	Grams a	Grams	Grams	Per cent	Per cent	Per cent	Grams	Grams b	Grams		
Loam	28312	39.5878	142.4001	.0277	.0285	—.0008	—.2065	102.8123	103.0188	12740	15166
Sandy L'm	29920	11.6836	115.2735	.0223	.0148	.0075	2.2440	103.5899	101.3459	11855	14113
Silty Loam	25501	14.4166	120.3256	.0287	.0200	.0087	2.2186	105.9090	103.6904	14227	16937
Average										12941	15405

Residual carbonate CO_2 from $CaCO_3$ c treatments

Soil type	Wt. of soil m. f. basis	$CaCO_3$ indicated by the Veitch method to neutralize soil acidity	C. P. $CaCO_3$ applied	Carbonate CO_2 in $CaCO_3$-treated soils at end of 1 year	CO_2 blank on original acid soil	Difference representing residue of carbonate CO_2 from $CaCO_3$ treatment	$CaCO_3$ residue calculated from CO_2 analyses	$CaCO_3$ applied in excess of the Veitch-method requirement	$CaCO_3$ lost by contact in excess of Veitch-method requirem'nt during 1 yr. period	$CaCO_3$ residue =— lbs. per 3,500,000 of soil	Difference between loss of $MgCO_3$ and increase of $CaCO_3$ in terms of $CaCO_3$ lbs. per 3,500,000 of soil
	Grams a	Grams	Grams	Per cent	Per cent	Per cent	Grams	Grams b	Grams		
Loam	28312	46.9918	169.0326	.1704	.0285	.1419	91.3061	122.0408	30.7347	11288	26454
Sandy L'm	29920	13.8688	136.8326	.1397	.0148	.1249	85.1591	122.9638	37.8047	9961	24074
Silty loam	25501	17.1129	142.8296	.0957	.0200	.0757	43.8734	125.7167	81.8433	6143	23080
Average										9131	24536

a All calculations on moisture-free basis.
b Variations in amounts of carbonate used in excess are due to moisture at time of treatments.
c Kahlbaum's moisture-freed carbonates used.

TABLE II—*Wheat crops grown upon soils of Table* I—*Average of 3 baskets of each treatment on each soil*

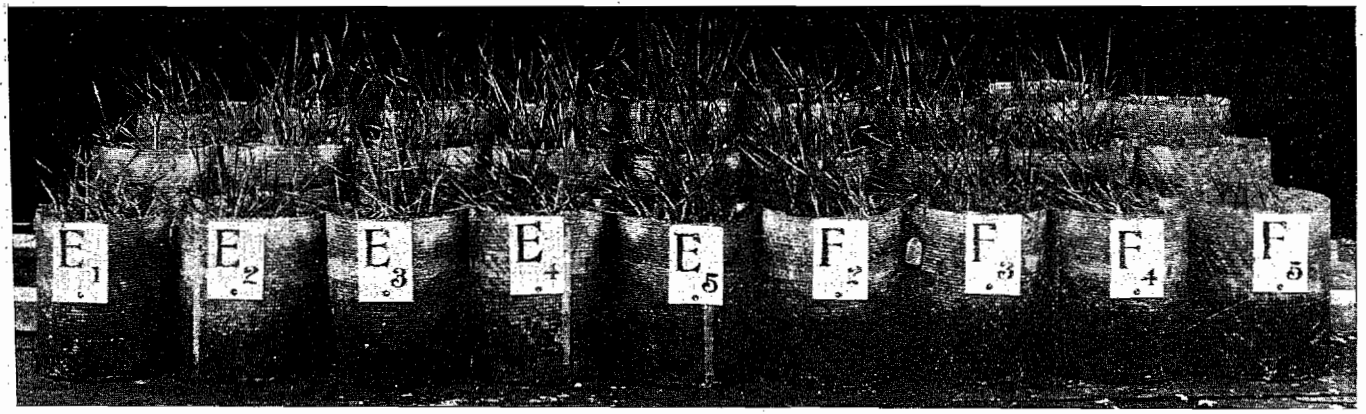
Calcium carbonate treatments

Type of soil	No lime		Veitch-method indication		Veitch +1-3		Veitch + 1785 lbs. $CaCO_3$ per A.		Veitch + 16070 lbs. $CaCO_3$ per A.	
	Green wt. Grams	M. F. wt. Grams	Green wt. Grams	M. F. wt. Grams	Green wt. Grams	M. F. wt. Grams	Green wt. Grams	M. F. wt. Grams	Green wt. Grams	M. F. wt. Grams
Loam	8.3165	1.5851	7.5897	1.3943	12.2786	2.2141	10.1301	1.7963	10.7935	1.6797
Silty loam	8.3974	2.1636	9.6762	2.5629	10.2303	2.3654	8.8323	2.2148	11.4773	2.3100
Sandy loam	16.2557	4.0649	20.0540	4.4463	20.8951	5.2933	23.9595	6.0634	30.2400	7.7355
Average 3 soils, 9 baskets	10.9899	2.6045	12.4399	2.8012	14.4680	3.2909	14.3073	3.3582	17.5036	3.9084

Magnesium carbonate chemically equivalent to $CaCO_3$ treatments

	No lime		Veitch-method indication		Veitch +1-3		Veitch + =1785 lbs. $CaCO_3$ per A.		Veitch + =16070 lbs. $CaCO_3$ per A.	
	Green wt. Grams	M. F. wt. Grams	Green wt. Grams	M. F. wt. Grams	Green wt. Grams	M. F. wt. Grams	Green wt. Grams	M. F. wt. Grams	Green wt. Grams	M. F. wt. Grams
Loam	8.3165	1.5851	9.7871	1.7025	8.3391	1.5829	10.9792	1.9086	3.4053	.7432
Silty loam	8.3974	2.1636	9.1349	2.2745	10.9109	2.5955	9.7620	2.3574	1.6581	.6829
Sandy loam	16.2557	4.0649	22.8715	6.2952	23.7871	6.1477	18.1945	5.1093	6.2412	2.3706
Average 3 soils, 9 baskets	10.9899	2.6045	13.9312	3.4241	14.3457	3.4420	12.9786	3.1251	3.7682	1.2656

PLATE 1—GROWTH OF WHEAT ON THE CARBONATE-TREATED SANDY LOAM OF TABLE I



Check	V	V + 1-3	V + 1768	V + 16070	V	V + 1-3	V + 1768	V + 16070
		$CaCO_3$				$MgCO_3$		

V—Lime requirement by the Veitch method. Numbers represent pounds per acre 3,500,000 pounds of soil. Crops sown Oct. 8, 1912; harvested Feb. 12, 1913. Magnesium-carbonate-treated baskets are devoid of any residual carbonates.

EFFECTS OF TREATMENT OF THE TWO PRECIPITATED CARBONATES UPON GROWTH OF WHEAT

The three soils treated as outlined with both calcium and magnesium carbonates were seeded to wheat 10 weeks after the addition of the carbonates, the growths being shown by figures of Table II. It will be noted that the average increase in growth resulting from the three treatments of calcium carbonate, other than the excessive amount, upon the three soils, is not quite so great as that from the three corresponding treatments of magnesium carbonate. The smallest of these three treatments of the carbonates is fully equivalent to the amounts applied in average agricultural practice in this State.

REPETITION OF THE CARBONATE TREATMENTS UNDER FIELD CONDITIONS, WITH MORE EXTENDED COMPARISONS

In another set of experiments the work was substantiated under field conditions. In these experiments iron rims 11 inches deep, 3 inches being above ground, equivalent in area to 1-10,000 of an acre, were used as containers for 200 pounds each of moisture-free soil, giving a soil depth of 8 inches. The original surface soil was removed and the rims were placed. The transported soil selected for study was mixed with the various treatments and laid in the rims upon the undisturbed red clay subsoil. Using growth of clover in previous field trials upon the same soil as an indication of lime requirement, instead of determinations by the Veitch method, high-grade analyzed burnt lime to the amount of 8 tons per acre was applied and thoroughly mixed in the upper 6 inches of the soil of four rims. Hydrated lime treatments were also made in quadruplicate, while precipitated calcium carbonate applications were made in duplicate. Precipitated magnesium carbonate, ground dolomite, and ground limestone were each applied in two quadruplicate sets, each treatment of each rim being chemically equivalent to the burnt lime applied as determined by analyses. The hydrate and various carbonate treatments were applied and mixed with the soil in the same manner as the burnt lime.

In applying the treatments great care was taken to make very uniform and thorough mixtures of the treatments with the soil in order that the samples subsequently taken for analysis might be truly representative.

Treatments of burnt and hydrated lime are not strictly comparable with ground limestone, because of the great difference in fineness, and for this reason the introduction of precipitated carbonate enhances the opportunity for comparisons between the caustic and neutral forms of lime. The "C. P." precipitated magnesium carbonate used was analyzed and found to correspond in composition to the

TABLE III—*Residual carbonates from treatments of various forms of lime and magnesium carbonate as determined by analyses upon newly-sampled moist loam soil. Contact period under field conditions, 8 weeks*

Lab. No.	Rim No.	Weig't of soil in each rim	Treatments — 28180 lbs. $CaCO_3$ per A.			Carbonate CO_2 from analysis of original unlimed soil	Carbonate CO_2 found by analysis at end of 8 weeks, m. f. basis	Carbonate CO_2 gain over original soil	Carbonate CO_2 gain calculated to $CaCO_3$ grams per rim	Carbonate CO_2 gain over original soil in terms of $CaCO_3$ lbs. per A. 2,000,000 of soil	Average gain of $CaCO_3$ from lime treatments. lbs. per A. 2,000,000 of soil
			Moisture conditions	Form of added substance	Weight of treatments per rim						
		Grams			Grams	Per cent	Per cent	Per cent			
2701	L 19	90720	No rain	CaO a	725.76	.0322 e	.4564	.4242	874.6136	19282	
2702	L 20	"	" "	$Ca(OH)_2$ b	976.94	"	.4547	.4225	871.1182	19204	
2704	L 25	"	" "	CaO	725.76	"	.4376	.4054	835.8611	18426	
2705	L 26	"	" "	$Ca(OH)_2$	976.94	"	.4377	.4055	836.0673	18432	
2706	L 27	"	" "	$CaCO_3$ c	1295.68	"	.4562	.4240	874.9944	19290	19170
2717	M 19	"	Rain and watered	CaO	725.76	"	.4440	.4118	849.0567	18718	
2718	M 20	"	" "	$Ca(OH)_2$	976.94	"	.4706	.4384	909.0109	20040	
2720	M 25	"	" "	CaO	725.76	"	.4612	.4290	884.5201	19500	
2721	M 26	"	" "	$Ca(OH)_2$	976.94	"	.4415	.4093	843.9022	18604	
2722	M 27	"	" "	$CaCO_3$	1295.68	"	.4768	.4446	916.6348	20208	
2707	L 32	"	No rain	$MgCO_3$ d	1238.07	"	.0337	.0015	3.0906	68	Average residue of $MgCO_3$ from precipitated carbonate treatments in equivalence of $CaCO_3$ lbs. per A. 2,000,000 of soil. (A) Moist samples, m. f. basis.....541 (B) By boiling composite air-dri'd spls. o
2723	M 32	"	rain and watered	"	"	"	.0354	.0032	6.5923	143	
2910	L 31	"	No rain	"	"	"	.0337	.0015	3.0906	68	
2912	M 31	"	Rain and watered	"	"	"	.0402	.0080	16.4821	363	
2908	K 31	"	Exposed	"	"	"	.0532	.0210	43.2683	954	
2909	K 32	"	"	"	"	"	.0474	.0152	31.3077	690	
2914	N 31	"	"	"	"	"	.0573	.0251	53.7763	1154	
2915	N 32	"	"	"	"	"	.0518	.0196	40.3941	890	

Difference between residues of carbonate CO_2 from $CaCO_3$ and $MgCO_3$ treatments, representing affinity of MgO for SiO_2, in terms of $CaCO_3$ lbs. per A 2,000,000 of soil.

(A)	(B)
18624	19170

a 97.92 per cent CaO.
b Made by slaking the analyzed burnt lime.
c 89.15 per cent $CaCO_3$ by analysis.
d Analysis gave $(MgCO_3)_4.Mg(OH)_2.5\ H_2O$ as composition of precipitated carbonate.
e Average 2 rims, 4 determinations.

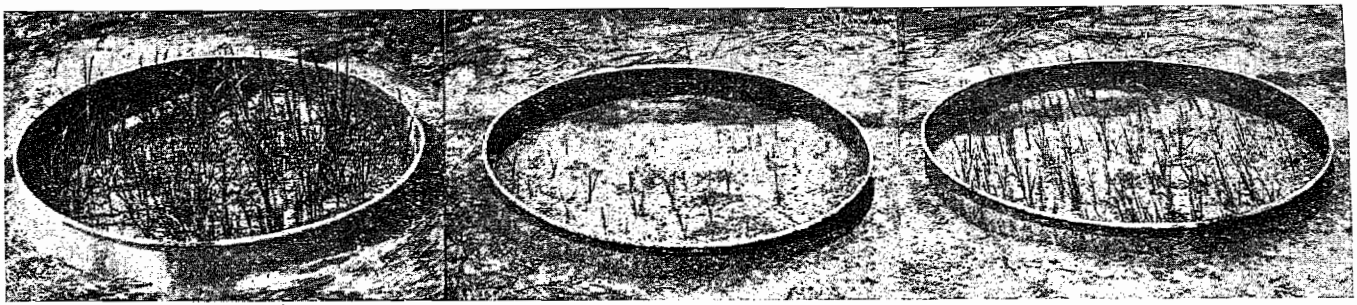
formula $(MgCO_3)_4$, $Mg(OH)_2 . 5 (H_2O)$ and computations from this analysis, assuming conversion of the hydrate to carbonate or its direct activity in correcting soil acidity, reduce the treatment of 1238.07 grams per rim to 1082.97 grams of normal carbonate. In the rim experiments the Cumberland loam of Table I was used and the soil of 8 rims was treated with the excessive applications of magnesium carbonate, equivalent in each case to 28,180 pounds of $CaCO_3$ per 2,000,000 of soil, 4 rims receiving carbonate alone and 4 receiving a supplementary treatment of barnyard manure. Four rims, 2 treated with magnesium carbonate alone and 2 with magnesium carbonate plus manure, were exposed to weather conditions during the experiment, the rainfall of 6 inches during June, July and August being uniformly distributed in showers and insufficient to cause any leaching during the 8 weeks' interval between treatment and sampling for CO_2 analyses. Two rims, one with magnesium carbonate alone and one with barnyard manure supplementary to the carbonate treatment, were protected from any rainfall, and 2 more, one of each treatment, were exposed to the weather and furnished with additional water to the extent of 8 inches, amounting to 14 inches in all, applied at various intervals in quantities insufficient, however, to cause leaching. The soil when placed in the rims contained 15.8 per cent moisture. When first applied the magnesium carbonate was in such bulk as to give to the soil a decidedly whitish appearance, which persisted for some days. On sampling at the end of 8 weeks, very minute white specks could be noticed throughout the soil treated with calcium carbonate, while no evidence of the presence of the more bulky magnesium carbonate could be noted. In Table III are given the results of the analyses, which were made in duplicate upon newly taken moist samples. The results were checked within a limit of error of .002 gram, in the aggregate increase of weight of the tubes used for collection of the gas, 25-gram charges of soil being used in the analyses.

DISCUSSION OF RESULTS OF TABLE III

Though it may be assumed that the analyses of the moist samples given in Table III mean that there actually exist in the treated soils minute amounts of residual magnesium carbonate still undecomposed at the end of 8 weeks, it should be emphasized that the limit of error, .002 gram, in weighing 2 tubes amounts to .008 per cent, which is increased to about .01 per cent on conversion of the results of the moist soil to the moisture-free basis. The possible slight occurrences of CO_2 in the soil moisture of the fertile loam are also included in the estimations. The writer believes, however that agricultural chemists familiar with the routine of the analyses would consider the entire set of magnesium-carbonate-treatment CO_2 determinations as within the limit of error and as checking the untreated soil. Samples of the untreated and originally thoroughly mixed soil in the same experi-

PLATE 2—COMPARISON BETWEEN THE EFFECTS OF PRECIPITATED CALCIUM AND MAGNESIUM CARBONATES UPON TALL OAT GRASS

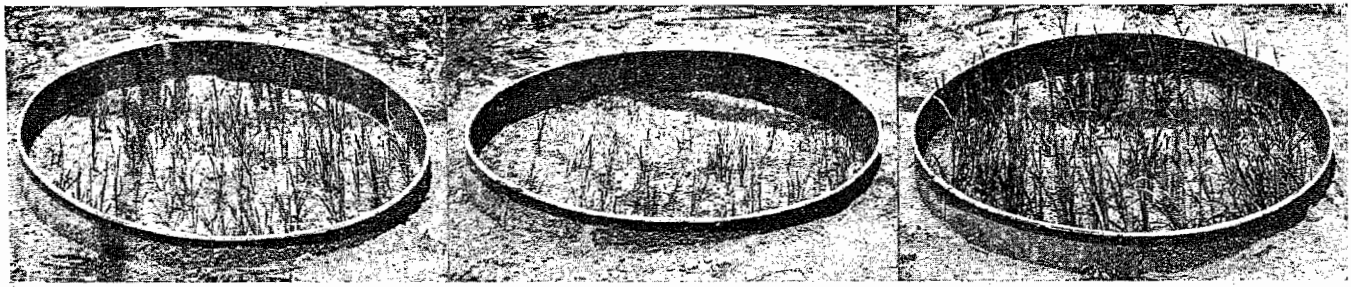
No carbonates in $MgCO_3$-treated soil at time of seeding



$CaCO_3$
28,180 lbs. per 2,000,000 of soil

MgCO3 equivalent to
28,180 of $CaCO_3$ per 2,000,000 of soil

No treatment



30 tons stable manure

MgCO3 equivalent to
28,180 lbs. $CaCO_3$ per 2,000,000 of soil and
30 tons stable manure

28,180 lbs. $CaCO_3$ per 2,000,000 of soil and
48 tons stable manure

ment have shown variations from week to week as great as can be found between the analyses of the blank and magnesium-carbonate-treated rims of Table III. Furthermore, duplicate determinations upon a composite of the air-dried samples from 6 untreated rims gave a carbonate CO_2 occurrence of .074 per cent by boiling for 1 minute with 1-15 phosphoric acid and aspiration for 15 minutes, while duplicates upon 2 air-dried composites of 4 rims each, of the 8 magnesium-carbonate-treated rims of Table III, gave CO_2 occurrences of but .0672 and .0660 per cent, an average of .0666 per cent, upon being subjected to the same analytical procedure as the blank, 25-gram charges of soil being used in each case.

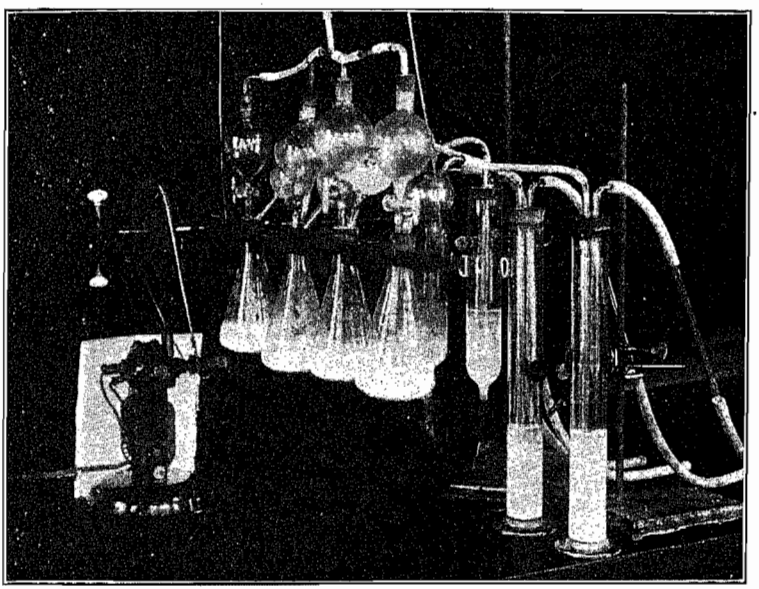
The carbonate determinations of Table III were also supplemented by further analyses. Twenty-five-gram charges of a composite sample of the 8 magnesium-carbonate-treated rims were subjected in duplicate to 4 hours' contact in cylinders with 500 cc of distilled water, saturated with CO_2, the soil being constantly agitated by a continuous flow of CO_2. These mixtures were immediately filtered at the end of the 4-hour period and titrated to neutrality against N-10 acid, methyl orange being used as an indicator. The duplicate determinations required 9 and 9 1-2 cc. The composite of the rims receiving precipitated calcium carbonate in amounts representing basicity equal to the magnesium carbonate, upon being treated at the same time in like manner to the magnesium carbonate composite, gave titrations of 48.6 and 48.7 cc. Table VIII shows that the precipitated carbonate of magnesium is more than 12 times as soluble as the precipitated carbonate of calcium; hence the absence of the applied precipitated magnesium carbonate is further substantiated. Table IX offers data tending to show the alkalinity found in the CO_2 extractions of magnesium carbonate treatments as being due to hydrolyzation and carbonation of the silicates of magnesium.

CONVERSIONS OF CALCIUM AND MAGNESIUM OXIDES TO CARBONATES WHEN APPLIED TO SOIL

The use by Hopkins[9] of finely divided magnesium carbonate in tests of the effect of magnesium upon plant growth is criticised by Gile[7], who attributes part of the injurious effects noted by Hopkins to causticity of the carbonate. Kearney and Cameron[8], however, recorded growth without apparent injury to the growing plants where the roots were immersed in a solution containing the suspended insoluble precipitated carbonate of magnesium, which was distinctly alkaline from the hydrate present. According to Sadler and Coblentz[9], "in moist air it (Mg O) readily absorbs moisture and CO_2, becoming converted into basic carbonate." Morley and Muir[10], Fresenius[11], and Loew[12] state that basic carbonate is formed from MgO in presence of water and CO_2. Loew further states, in objecting to the use of the precipitated carbonate in magnesium treatments, that ground dolomite

or magnesite should be used rather than "the artificially precipitated basic magnesium carbonates, which are very injurious, being easily absorbed, owing to their very fine pulverulent condition." In discussing the "Danger from using caustic magnesia and burned and hydrated magnesian lime," Wheeler[18] writes: "The preceding results show that caustic magnesia was toxic at first where it was used in large quantities, even on a soil evidently in slight need of magnesia, but that when sufficient opportunity had been afforded for it to become carbonated, it became useful."

PLATE 3



FOUR-UNIT FAN-MOTOR SHAKING APPARATUS USED FOR DETERMINING SOIL CARBONATES

The method is given in detail in Tenn. Sta. Bul. 100.

As supplementing the data bearing on the carbonation of burnt and hydrated lime reported in Table III, the carbonation of CaO in water solution, both with and without the presence of soil, was studied.

In order to test their relative rates of carbonation in water alone, 10-gram charges each of Kahlbaum's "C. P." freshly ignited oxides of calcium and magnesium were placed in separate graduated cylinders with 500 cc of distilled water and agitated by a current of CO_2 entering at the bottom of the cylinders, for a period of 4 hours. The solutions were then immediately filtered through Buchner funnels

with gentle suction, and their alkalinities determined in duplicate by titrations with standard acid, methyl orange being used as an indicator. *The average of the* 500-*cc duplicate extraction of MgO required* 1862.5 *cc of N*-10 *acid, while the CaO extractions required* 101 *cc of the same strength acid for neutralization, representing in equivalents, 18.63 and 1.01 grams, respectively, of calcium carbonate per litre* (See Table VIII). Oxide of magnesium being exceedingly insoluble in CO_2-free distilled water, the titrations clearly demonstrate the extensive reaction between MgO and carbonated water. While the comparison is based upon the amounts of the carbonates actually in solution and titrated as bicarbonates, it is very probably true that the entire charges, including the portions undissolved in the carbonated water, have been converted to the carbonate forms.

After thus demonstrating that magnesium oxide is readily carbonated in water and apparently more readily than lime, the procedure was repeated in the presence of definite amounts of a slightly alkaline

TABLE IV—*Comparison of carbonation of CaO and MgO in loam soil, CO_2 being supplied under laboratory conditions*

Treatments		Theoretical possible increase of CO_2 from treatment	Carbonate CO_2 occurrence by analyses after passage of CO_2	CO_2 liberated by acid from soil blank after passage of CO_2	Actu'l CO_2 increase due to carbonation of oxides	CO_2 increase of theory
CaO added	MgO added					
Grams	Grams	Grams	Grams	Grams	Grams	Per cent
.3531	---------	.2774	.2338	.0067	.2271	81.87
.2202	---------	.1730	.1713	.0067	.1646	95.14
.2698	---------	.2120	.1895	.0067	.1828	86.22
---------	.2514	.2767	.1618	.0067	.1551	56.05
---------	.2748	.3025	.1554	.0067	.1487	49.16
---------	.4210	.4634	.2244	.0067	.2177	46.98

soil. It is shown in Part II of this bulletin that magnesium carbonate reacts extensively with alkaline siliceous substances and decomposes when in contact therewith for a few weeks, and in order if possible to forestall the greater part of this anticipated reaction, the lime and magnesia were carbonated in contact with soil in the laboratory by the passage of CO_2 for 4-hour periods. Twenty-five-gram charges of soil which had received 2 tons of burnt lime per acre 9 months previously, and reacting alkaline to litmus, were placed in 300-c. c. Erlenmeyer flasks with 100 c. c of distilled water and treated with freshly ignited Kahlbaum's CaO and MgO, weighed from closed bottles. Currents of CO_2 were passed through the mixture of soil and water for 4 hours at room temperature and atmospheric pressure, duplicate blanks of the original soil being treated in the same manner. At the end of the period of contact with CO_2, the flasks were freed of CO_2 in solution by heating to boiling, cooled, and after standing overnight placed in a CO_2

train, the carbonate CO_2 being then liberated by 1-15 H_3PO_4, and determined gravimetrically.

The data of Table IV show a wide difference between the recoveries of CO_2 from the two carbonates. Although when tried in carbonated water alone, MgO showed an alkalinity about 18 times as great as that secured from CaO, as measured by the bicarbonates in solution, the recovery of CO_2 by acid from magnesium carbonate formed by carbonation of the MgO in the treated soil, is only about one-half that of the CO_2 liberated by acid from the carbonates resulting from the lime treatments. It is doubtless true that while all of the lime has been carbonated, a part of the calcium carbonate in solution has reacted with acid silicates and other acid salts of the soil (Tables XIV and XV), and that magnesium carbonate has acted in the same manner to a much greater extent. Then too, in the maximum charges of the triplicates upon both CaO and MgO, the carbonation actually effected is considerably more than would be required by the full amounts of CO_2 indicated by theory as needed for the complete carbonation of the smaller charges. It is quite apparent that the complete decomposition of magnesium carbonate upon long periods of contact with soil as shown in this bulletin has been accomplished in part very appreciably during the 4-hour period of contact with carbonated water and the standing overnight as carried out in the tests of Table IV.

Of the experiments available to the writer, only those of Frear[13] might be considered as parallel to those of Tables III and IV. Frear quotes Low and Davy as attributing toxicity of magnesian lime when applied to soils to the continued occurrence of the caustic form of magnesium. From his own experiments Frear concludes that magnesia carbonates more slowly than lime, and he attributes the harmful effect of magnesian lime to persistent causticity of magnesia.

In Dr. Frear's experiments "C. P." CaO and MgO in chemical equivalents were applied to soils, the reactions of which were not given, and contact permitted for 10 months, during 3 months of which time optimum moisture conditions were maintained. No check treatments of the carbonates of calcium and magnesium were used in the experiments cited. At the end of the 10-months period, analyses of the 9 soils treated with CaO gave a carbonate CO_2 content of .149 per cent, while an average of 8 of the same 9 treated with MgO (considering one analysis as typographical or other error) gave .051 per cent CO_2 as compared to .038 per cent CO_2 as the average of determinations on the 9 soils at the beginning of the experiment. In one instance, that of a muck soil, of the 9 lime treatments no increase of CO_2 was found, while in 4 cases of the 8 analyses quoted, there was no accumulation of CO_2 where magnesium oxide was added. These analyses led Dr. Frear to the conclusion that MgO is persistently caustic when applied to soils.

From the results given in this bulletin it would appear that the apparent lack of carbonation in the quoted results of Frear might then,

be the result of one or both of two possibilities rather than the persistent causticity of the magnesia; either the oxide has in the presence of CO_2 and water become carbonated and the carbonate in turn decomposed by the siliceous material and titanium oxide of the soil, or soluble silicic acid and acid silicates have acted directly upon the relatively insoluble MgO, with the formation of magnesium silicates and also titanates, as will be later shown in Part II of this bulletin. Reference to Table III will show that during a period of 8 weeks under field conditions, the 8 applications of 16,000 pounds of burnt lime per 2,000,000 of soil and equivalent amounts of hydrated lime had carbonated to practically the identical carbonate occurrences found in the treatments with the precipitated calcium carbonate. This table also shows that during the same period there was effected the complete dissipation of the CO_2 of the precipitated magnesium carbonate, in amounts equivalent to 28,180 pounds of $CaCO_3$ per 2,000,000 of soil. It is therefore probable that had equivalent amounts of oxide of magnesium been carbonated during the 8-weeks period, the decomposition of the carbonate by silicic acid reaction would have prevented the finding of magnesium carbonate upon analysis.

From the data of Tables III, IV and VIII, it would seem to be fully substantiated that the conclusions of Low, Davy, and Frear concerning the period of causticity resulting from applications of burnt magnesian lime are erroneous, as are also those of Wheeler concerning the accumulation of magnesium carbonate from excessive treatments of caustic magnesia. The period of *temporary* toxicity noted is due rather to extensive distribution of magnesia as a result of the fineness of division of the readily carbonated oxide, which is very soluble in carbonated water. The lime content of burnt magnesian lime treatments above soil "acidity" requirements would continue then, largely in the form of the more soluble carbonate, while the magnesia portion would exist in the relatively insoluble form of magnesium silicate.

COMPARATIVE ACTIVITIES OF CHEMICALLY EQUIVALENT AMOUNTS OF GROUND LIMESTONE AND GROUND DOLOMITE OF SIMILAR MECHANICAL COMPOSITION UNDER FIELD CONDITIONS

The use of chemically equivalent amounts of limestone and dolomite in the rim treatments affords opportunity for study of the activity of magnesium carbonate, when applied in the form of dolomitic limestone. The two materials were made to correspond in mechanical make-up to a local commercial product of ground limestone. The compositions, mechanical and chemical, of the two limestones are given in Table V.

The analyses to determine residual carbonates resulting from the

limestone and dolomite treatments were made 9 months after application of the materials. No leaching took place during the first 2 months of the period. A composite of 6 cores from each rim was ground to pass a 100-mesh sieve prior to analysis. Careful examination of the soils before grinding showed a few pieces of both limestone and dolomite still undisintegrated. The consistent and marked differences in residual carbonates between the 8 limestone rims and the 8 dolomite rims show an unmistakable activity of the magnesium carbonate content of the dolomite upon siliceous materials. Though all treatments were subjected to leaching during the last 7 months of the time intervening between treatment and analyses, the differences in residual carbonates could not be accounted for by leaching, because the limestone is 1.62 times as soluble as the dolomite in carbonated water, as is shown in Table VIII. Laboratory investigations reported in Tables XIV and XV served to eliminate consideration of the influence of organic matter in the phenomenon.

The decomposition of the dolomite would probably mean more finely divided calcium carbonate residue from this rock than from limestone, and the residual calcium carbonate of dolomite would probably approach in activity that of the finely divided precipitated carbonate.

TABLE V—*Mechanical and chemical analyses of the limestone and dolomite used in field treatments*

Through 10 mesh	100%
10 mesh to 2 mm	30.69%
2 mm. to 1 mm	18.73%
1 mm. to 1-2 mm.	18.55%
Less than 1-2 mm	32.03%
	100.00%

	SiO_2	Fe_2O_3	CaO	MgO	CO_2 by analysis	CO_2 from determinations of CaO and MgO
Ground limestone	5.91	1.35	50.23	1.59	39.52	39.47
Ground dolomite	3.25	2.45	31.43	17.71	44.22	44.10

Tables III and VI also afford an interesting comparison of the effect of fineness and purity of calcium carbonate upon the extent of its reaction with siliceous materials. The precipitated carbonate at the end of an 8-weeks period with no leaching showed residual calcium carbonate amounting to 19,749 pounds per 2,000,000 of soil, while 7 months later, after exposure to fall and winter rains, the residual calcium carbonate from the applications of limestone amounted to 21,844 pounds per 2,000,000 of soil.

TABLE VI—*Residual carbonates from treatments of identical basicity, in forms of ground limestone and ground dolomite of similar mechanical composition upon a loam soil—period of contact, 9 months* [a]

Rim No.	M. f. soil	Treatments equivalent to 28180 lbs. of $CaCO_3$ per 2,000,000 of soil	Carbonate CO_2 untreated soil m. f. basis	Carbonate CO_2 at end of 9 months m. f. basis	Variations between extremes and averages of duplicates	Increase of carbonate CO_2 over original soil during 9 months, m. f. basis	Increase of carbonate CO_2 over original soil during 9 months.	CO_2 increase over original soil calculated to $CaCO_3$, lbs. per A. 2,000,000 lbs.	Average residue of CO_2 in terms of $CaCO_3$, lbs. per A. 2,000,000 pounds of soil from limestone treatment
	Grams		Per cent	Per cent	Per cent + or −	Per cent	Grams per rim		
K 22	90720	Ground limestone & manure	.0394	.4883	.0064	.4489	407.24	20404	
L 22	"	" " " "	"	.5072	.0072	.4678	424.39	21264	
M 22	"	" " " "	"	.5285	.0072	.4891	443.71	22232	
N 22	"	" " " "	"	.4864	.0034	.4470	405.52	20318	
K 28	"	" " ———	.0318	.5616	.0012	.5298	480.63	24082	
L 28	"	" " ———	"	.5214	.0060	.4896	444.17	22545	21844
M 28	"	" " ———	"	.4599	.0016	.4281	388.37	19459	
N 28	"	" " ———	"	.5696	.0042	.5378	522.74	24445	
K 23	"	Ground dolomite & manure	.0394	.2620	.0002	.2226	201.94	10118	
L 23	"	" " " "	"	.2694	.0052	.2300	208.66	10454	
M 23	"	" " " "	"	.3284	.0056	.2890	261.18	13136	Average residue of CO_2 in terms of $CaCO_3$, lbs. per A. 2,000,000 pounds of soil from dolomite treatment
N 23	"	" " " "	"	.2744	.0028	.2350	213.19	10681	
K 29	"	" " ———	.0318	.3499	.0078	.3181	288.58	14459	
L 29	"	" " ———	"	.3521	.0112	.3203	290.58	14559	
M 29	"	" " ———	"	.2660	.0098	.2342	212.47	10645	11680
N 29	"	" " ———	"	.2383	.0030	.2065	187.34	9386	
Difference—representing dissipation of CO_2 from magnesium carbonate in dolomite, terms of $CaCO_3$									10164

a Solubilities of 100-mesh carbonates, represented by ratio of 1 to 1.62 for dolomite and limestone, respectively.

DECOMPOSITION OF MAGNESITE BY SOILS[a]

In the study of the activity of mineral carbonate of magnesium upon soils, 400 grams each of the three original "acid" soils of Table I were subjected to moist contact with 10 grams of analyzed 100-mesh magnesite in Erlenmeyer flasks at room temperatures. Thirty-gram charges of these moist mixtures were analyzed for residual carbonates at the end of 35 days, at the end of 65 days, and again after 138 days, correction being made in the calculations for the boiling blank on the original "acid" soils. It should be noted that none of the methods ordinarily used for carbonate CO_2 could be utilized in analyzing the magnesite. It was necesary to boil for 30 minutes to insure complete decomposition of the mineral. The amounts of magnesite decomposed by the soils were then compared with the Veitch-method requirements of magnesite. The extent of the decomposition above the amounts indicated by the Veitch method are shown in Table VII. The analyses indicate that magnesite undergoes the same decomposition as the magnesium carbonate of dolomite and precipitated carbonate, though less rapidly than the precipitated carbonate.

The activity of magnesite under field conditions is being further studied.

CAUSE OF TOXICITY IN THE SOILS OF TABLES I AND III
(Plates 1 and 2)

The rim experiment cited in Table III upon one of the soils used in the basket experiments of Table I, showed that about twice as much carbonate of magnesium as was used in the baskets underwent complete decomposition within 8 weeks. The soils in the baskets were in contact with the excessive magnesium treatments, equivalent to about one-half of the rim treatments, for about 10 weeks prior to seeding of wheat. The conclusion is therefore drawn that magnesium carbonate had been dissipated through combination with siliceous materials prior to seeding of wheat and that the toxicity shown in Table II and Plate 1 is attributable to excessive amounts and great fineness of division of magnesium silicate, and is *not* due to presence of an excess of *carbonate of magnesium*, nor to an excess of caustic hydrate impurities of the precipitated carbonate, for this hydrate would have been converted to the bicarbonate, and this in turn decomposed by contact with siliceous materials. The tall oat grass shown in Plate 2 was sown in the magnesium-carbonate-treated rims, 10 months after treatments. The analyses of Table III show that this carbonate treatment, equivalent to 28,180 pounds of $CaCO_3$ per 2,000,000 of soil, was decomposed within 8 weeks, and the harmful effect upon the growth of grass cannot therefore be attributed to the continued presence of magnesium carbonate.

That the decomposition of magnesium carbonate is due not alone to acid silicates but to silica (SiO_2) and titanium oxide (TiO_2) in the

[a] Suggested to the writer, in personal correspondence, by Dr. H. J. Wheeler.

TABLE VII—*Decomposition of magnesite by contact with moist soils under laboratory conditions* a

Soil type		Total grams of air-dried soil	$MgCO_3$ indicated by Veitch method to neutralize soil acidity, m. f. basis		$MgCO_3$ added	Decomposition of $MgCO_3$— determined by analyses of residual carbonates, m. f. basis. CO_2 liberated from 30-gram charges by boiling 30 minutes with 1-15 H_3PO_4										
						After 30 days' contact				After 65 days' contact				After 138 days' contact			
							Excess of Veitch				Excess of Veitch				Excess of Veitch		
			Per cent	Grams	Grams	Grams	Grams	Per ct.	Lbs. per 2,000,000 of soil	Grams	Grams	Per ct.	Lbs. per 2,000,000 of soil	Grams	Grams	Per ct.	Lbs. per 2,000,000 of soil
Sandy clay loam	(A)	400	.0454	.1736	9.424	.5755	.4019	.105	2100	.6538	.4702	.123	2460	1.4288	1.2552	.328	6560
	(B)	400	.0454	.1736	9.424	.4979	.3243	.085	1700	.7070	.5334	.139	2780	1.3978	1.2244	.320	6400
	Av.	400	.0454	.1736	9.424	.5367	.3631	.095	1900	.6804	.5018	.131	2620	1.4133	1.2398	.324	6480
Silty loam	(A)	400	.0564	.2100	9.424	1.4082	1.1982	.322	6440	1.5313	1.8213	.355	7100	2.2449	2.0349	.547	10940
	(B)	400	.0564	.2100	9.424	1.5229	1.3129	.352	7040	1.5789	1.3693	.368	7360	2.3625	2.1525	.578	11560
	Av.	400	.0564	.2100	9.424	1.4656	1.2556	.337	6740	1.5551	1.3453	.362	7230	2.3037	2.0937	.563	11250
Loam	(A)	400	.1633	.5939	9.424	.9143	.3205	.088	1760	.9666	.3728	.102	2040	1.5802	.9863	.271	5420
	(B)	400	.1633	.5939	9.424	.9396	.3458	.095	1900	.9982	.4344	.119	2380	1.4822	.8884	.244	4880
	Av.	400	.1633	.5939	9.424	.9270	.3332	.092	1830	.9824	.4036	.111	2210	1.5312	.9374	.258	5150

a The flasks were shaken during the second and third contact periods.

presence of moisture is later shown in Part II of this bulletin (Tables XIII and XV) It is also shown later in this bulletin that though magnesium is present in the form of silicates as a solid in the soil mass, the silicates of magnesium in the presence of carbonated water will yield $MgCO_3$, and it is very probably true that in case of abundant amounts of CO_2 the hydrolyzation of the magnesium silicate may result in minute amounts of magnesium carbonate in the soil water, especially where magnesium silicate predominates over the occurrence of calcium silicate and where calcium carbonate is absent.

RELATIVE SOLUBILITIES IN CARBONATED WATER, OF THE CAUSTIC AND NEUTRAL MATERIALS USED THROUGHOUT THE EXPERIMENTS

As stated by Loew[14], and as shown in Table VIII, precipitated magnesium carbonate is many times more soluble than precipitated calcium carbonate in carbonated water, and had the magnesium carbonate persisted in the soil in this finely divided state in the rim treatments it would have been leached out more readily than calcium carbonate when treated with carbonated water. The figures for the solubility of calcium carbonate as given by different investigators vary considerably, but in all cases the amounts of calcium carbonate dissolved from forms other than native minerals, are far less than from similar forms of magnesium. Bischof[15] found 1.8 gram of $CaCO_3$ dissolved in a litre of carbonated water when using commercial burnt lime and 2.8 grams of calcium carbonate when using pure CaO; Treadwell and Reuter[15] found 1.3 grams of $CaCO_3$ per litre dissolved in carbonated water at normal pressure, and temperature of 13°C; while Anderson[16] has shown that the solubility of calcium carbonate is directly dependent upon the fineness of the material extracted with carbonated water. Engel and Ville[17] give 28.45 grams of $MgCO_3$ per litre as being dissolved in carbonated water at atmospheric pressure and 13°C.

As relating to the relative solubilities of the various forms of calcium and magnesium used in the experiments reported, the analyses of Table VIII are offered. Ten-gram charges in duplicate of each of the substances used were placed in graduated cylinders with 500 cc of distilled water and the masses of the materials agitated by a constant current of CO_2 entering through tubes leading to the bottoms of the cylinders. At the end of the four hours of contact at room temperature, 25°C, the mixtures were immediately filtered through Buchner funnels by gentle suction and the alkalinities of the filtrates determined by titration against N-10 acid, methyl orange being used as an indicator.

The comparisons between the finely divided burnt lime and oxide of magnesium, both being freshly burnt Kahlbaum's "C. P." products, and the precipitated carbonates, are extremely interesting as contrasted with the relative solubilities of the native carbonates ground to

TABLE VIII—*Comparisons of solubilities of calcium and magnesium compounds in carbonated water—period of contact 4 hours—10-gram charges*

Substance	C. P. CaO		C. P. MgO		Precip. $CaCO_3$		Precip. $MgCO_3$		Limestone 100-mesh		Dolomite 100-mesh		Magnesite 100-mesh	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
CC N-10 acid	100	102	1855	1870	117.4	117.2	1445	1432.5	88.6	90.8	55.8	55.0	28	27.5
=Ca CO_3 grams per L	1.00	1.02	18.55	18.70	1.17	1.17	14.45	14.33	.89	.91	.56	.55	.28	.28
Length of crystals, mm					.0003		.0002		.005		.004		.003	

pass 100 mesh. The decided influence of the degree of fineness, determined from microscopic examination (camera-lucida attachment), is very striking. The figures upon the relative solubility of magnesite and limestone are closely in accord with those of Wheeler[18].

LACK OF EVIDENCE AS TO THE EXISTENCE OF MAGNESIUM CARBONATE IN SOILS

References on the part of many authorities to the existence of calcium and magnesium carbonates in soils are numerous, but the writer has been able to find but one definite and positive statement of the existence of magnesium carbonate where data are presented as proof of its occurrence. The existence of magnesium carbonate in soils, as analogous to calcium carbonate occurrences, has been assumed heretofore rather than proved. The citation referred to emanates from Argentina, and was published by Phipson in "The Chemical News"[19], 1902.

The work of Phipson was upon 8 soils, "taken with great care at the depth of one foot from the surface," and his analyses show as an average 1.09 per cent of CaO and 1.03 per cent of MgO.

From these analyses he concluded, "It is evident from these results that the lime is present as *dolomite*, which is not readily assimilated."

It is not without interest, however, to note that no reference to occurrence of CO_2 or its estimation is made, and the inference is that the determinations of CaO and MgO were from acid digestion of the soil, the conclusion as to the existence of carbonates resulting probably from the effervescence of the calcium carbonate. Loew[20] has reported an analysis of a soil near the Porto Rico Station, giving .60 per cent of CaO and 3.32 per cent of MgO, though the soil was *acid*. Acidity in such cases was considered by Loew[21] in later work as being due to acid silicates.

A four-day HCl 1.115 digestion in the cold of calcium and magnesium mineral silicates of Table IX, and of a composite from the 8 magnesium-carbonate-treated but carbonate-CO_2-free soils of Table III, gave large amounts of both calcium and magnesium dissolved from the silicate forms.

From 10-gram charges each of wollastonite and serpentine, 81 per cent of total CaO and 82 per cent of total MgO from the respective minerals were recovered by the cold acid digestion.

Since magnesium silicate is readily soluble in HCl, the data are not conclusive proof of the occurrence of magnesium carbonate, even in the subsoil under the conditions cited, and manifestly the conclusions of Phipson were not fully justified.

ABSENCE OF MAGNESIUM CARBONATE FROM VIRGIN SOILS

It seems eminently fair to assume from the observed extensive decomposition of the excessive amounts of precipitated magnesium car-

bonate and dolomite used in the basket and rim experiments that the natural processes being evolved for hundreds and thousands of years in surface soils would have effected the same decompositions of any residual carbonate of magnesium from the original soil-forming calcareous sandstone, limestone or dolomite.

Gaither[22], in a very comprehensive study of a large number of Ohio soils, concluded that there is a definite correlation between soil acidity, as shown by the litmus-paper test, and the absence of carbonates as shown by the Marr method. In examinations of many types of Eastern soils the writer has observed that it is a very rare exception to find a soil reacting alkaline to litmus, unless the soil has recently received lime treatment. It would seem then that many of our cultivated soils are without residues of native mineral carbonates of either calcium or magnesium.

The work of Gaither[22] and the results reported by MacIntire and Willis[5] indicate that in many cases of soil analyses the figures offered as representing carbonate CO_2 were not derived from carbonates, but from action of boiling acid upon soil organic matter.

The trace of magnesium as carbonate possibly existing in the soil solution upon long contacts of magnesium silicates with carbonated soil-water, and resulting from hydrolyzation and carbonation of silicate of magnesium, is not determinable upon the samples used in laboratory procedure.

Apparently an excess of silicates and, as will later be shown, of titanium oxide, is inhibitory to the long-continued presence of magnesium carbonate in soils, and we therefore feel compelled to conclude that none of the carbonate CO_2 found in dried virgin soils, as analyzed in the laboratory, can be accredited to combination with magnesium as magnesium carbonate.

POSSIBLE EXCEPTIONS TO THE CONVERSION OF MAGNESIUM CARBONATE TO SILICATES IN SOILS

In case of peaty soil underlaid by hardpan, which prevents efficient natural drainage, it may be that the usually large amounts of organic matter and the relatively small amounts of silica with which the carbonate has opportunity for contact may permit the retention of magnesium carbonate to an appreciable extent and that any toxic action upon plant growth observed subsequent to excessive applications of burnt magnesian lime or dolomite might be attributed to presence of magnesia dissolved as bicarbonate. In other words, absence or presence of but relatively meager amounts of silica and acid silicates would permit the existence of magnesium carbonate when excessively applied, though efficient drainage would mean its ready leaching, especially when formed from the finely divided burnt magnesian lime.

Because of the lack of opportunity for study of arid soils, the possibility of the existence of magnesium carbonate in such soils might

be assumed, though the observations of Hilgard[23] tend to show even more unfavorable conditions for the retention of magnesium carbonate in arid soils than in those of humid climates. Cameron and Bell[24] have shown that magnesium forms several soluble double salts with the alkali carbonates. This would probably mean a greater distribution and surface exposure of any applied magnesium carbonate to silica and acid silicates in arid soils than would be presented in field practice under humid conditions.

From numerous analyses, Hilgard found that the soluble silica in arid soils is about twice as great as that in humid soils, and that the same holds true of hydrous silicates, which in this bulletin will be shown to decompose magnesium carbonate readily by mere contact without CO_2 to effect solution of the carbonate. Tables XIV and XV show decidedly greater activity between acid silicates and magnesium carbonate, than between acid silicates and calcium carbonate, and it would therefore seem that the existence of magnesium carbonate in arid soils would be even less probable than in soils of humid climates. This, however, is a point to be further investigated.

It is also very probable that in subsoils near the native occurrences of substrata of limestone carrying some small amounts of magnesium carbonate, or formations of dolomitic character, that magnesium carbonate may occur in rock fragments which are still to undergo complete disintegration. Through personal communications, the writer has been informed by Mr. J. W. White, of the Pennsylvania Station, that he has secured samples of subsoil from one plat where the "mother rock" occurred within 2 feet of the surface, and that CaO determination would not account for all of the CO_2 resulting from analysis of the alkaline subsoil. On the other hand, from personal experience on the same plats, sampling to a depth of 7, 14 and 21 inches upon the 24 plats reported in Table XVI, the writer observed several large lumps of wet, swollen occurrences of stone as large as an orange, which on being easily perforated by the sampling auger at first glance appeared to be white clay, and which might easily have been included in the sampling, but for the personal observation and supervision of the collection of samples. The results of Table XVI show from the composite of 480 borings from subsoils 14 and 21 inches deep on the 24 plats, that even in the heaviest lime treatments the total CO_2, from analyses of these subsoils close to the native rock occurrence, is not sufficient in any of the 48 instances to account for the total lime as being in combination as carbonate, without considering the magnesium occurrence.

The results of Table XIII show that the texture of the soil influences the rapidity of the decomposition of the soil carbonates, and it is possible that in the coarse sandy soils of the coastal plains where hydrated silica occurrences are meager, the magnesium carbonate of treatments may remain for an appreciable length of time before being lost by

drainage or decomposition through reaction with the coarser siliceous materials. However, the sandy loam (Table I), from a peach orchard, completely dissipated the CO_2 of the carbonate of magnesium to an equivalence of 16,070 pounds of calcium carbonate per acre in excess of the Veitch-method indication, and upon being further treated in the laboratory the same magnesium-treated soil accomplishes still further decomposition, as shown in Table XIII. This sandy soil, however, contains considerable red clay.

THE SOLUBILITIES OF SILICATES OF CALCIUM AND MAGNESIUM IN CARBONATED WATER

Since it is evident that magnesium occurs in soils as magnesium silicate and not as magnesium carbonate, the question of the solubility of magnesium silicates in carbonated water assumes important proportions. In order to study the comparative solubilities of carbonate-free mineral silicates of calcium and magnesium with the carbonates of the two elements, the data of Table IX were secured. The various charges of the materials were introduced into graduated cylinders with 500 cc of distilled water. Carbon dioxide entering through glass tubes, extending to the bottoms of the cylinders, kept most of the material in suspension during the 4-hour period of the passage of the gas. The analyses show that silicates of calcium and magnesium undergo hydrolyzation and carbonation to an appreciable extent, the soluble silica in no case accounting for more than a small proportion of the amounts which would be in combination with the bases, even assuming that the silica occurring in the carbonated water is in combination with the bases as dissolved silicates, instead of occurring as soluble hydrated silica. It is also evident from the analyses of the calcium and magnesium silicates that where CO_2 is present in abundance, the presence of one silicate is neither inhibitory nor depressing to the action of carbonated water upon the other. The analyses further show that where the amounts of CO_2 introduced and the periods of contact are the same, variations in amounts of the silicate of same fineness constitute an important factor in determining the extent of reaction. This will evidently explain why in certain instances good stands of clover are maintained upon soil analyzing moderately well in total CaO, but acid to litmus and showing lime requirements upon dried samples in the laboratory. It is fair to assume from the analyses of the relatively coarse mineral silicates that with abundant supplies of calcium silicate under field conditions, the hydrolyzation and subsequent carbonation of the lime of the silicate will produce media of sufficient degree of alkalinity to maintain good growths of clover and other legumes. It is doubtless true that growing plants assimilate part of their store of magnesia as magnesium carbonate in the same manner.

This utilization of the lime of calcium silicate probably accounts

TABLE IX—*Comparisons of solubilities of finely ground mineral carbonates and silicates of calcium and magnesium in carbonated water—period of contact, 4 hours*

Substance	Wollastonite $CaSiO_3$ 10 grams	Limestone $CaCO_3$ 10 grams	Serpentine $MgSiO_3$ 10 grams	Magnesite $MgCO_3$ 10 grams	Wollastonite and serpentine each 10 grams	Precipitated chalk $CaCO_3$ 10 grams	Precipitated chalk and serpentine each 10 grams	Wollastonite 20 grams
N-10 acid to neutralize	54.2	90	21.6	28	69.35	117.3	121.2	92.2
Alkalinity = grams $CaCO_3$ per L.	.542	.90	.216	.28	.6935	1.173	1.212	.922
Grams of SiO_2 per L. in filtrate of carbonated water	.0566		.0162		.0840	.0020	.0254	

in part for the benefits derived by legumes from applications of Thomas slag, which has been shown to contain considerable of calcium silicate.

THE CONSERVATION OF MAGNESIA IN SOILS

In noting the excess of magnesia over lime as characteristic of tropical soils, Hilgard[25] attributes this to the "more ready solubility of lime in carbonated water," but he also says that dolomites weather more readily than limestones. However, Loew[21] cites an analysis of an "acid" soil near the Porto Rico Station, as giving .60 per cent of CaO and 3.32 per cent of MgO. Frear[26] states that dolomites as a rule weather more slowly than pure limestones, "though there are exceptions to the rule." It is probably true that compactness, degree of crystallization and purity of a limestone or dolomite have much to do with its weathering. As shown in the solubilities given in Table VIII, the limestone used in these experiments is appreciably more soluble in carbonated water than the dolomite. From the discovery of the decomposition of magnesium carbonate when in contact with alkaline siliceous substances, together with the solubilities of Table VIII, it seems probable that at first the weathering of limestone is much more rapid than that of dolomite, but as the weathering of dolomite proceeds with increasing occurrence of siliceous impurities in the rock residue, the decomposition of the dolomite may be stimulated by the additional activity resulting from the affinity of magnesia for silica (Tables XIII, XIV and XV,) and the decomposition of dolomite at the later period may be expedited beyond the extent of the limestone disintegration, as a result of the magnesia-silica reaction. Prof. C. A. Mooers, from twenty years' observation in the extensive Tennessee areas of soils derived from limestone and dolomite, has noted the greater depth of the dolomitic soils as compared with those of limestone derivations, and the frequency of the outcrops of limestone as contrasted with the less common dolomite outcrops. His investigations have further shown no excessive retention of magnesium in soils of dolomitic origin, their usual comparatively low productiveness being attributed by him to poverty of phosphoric acid. Hilgard[25] states that less magnesia than lime is found in soil leachings, and Hall[27] established from investigation upon drainage waters that but from 5 to 20 pounds of magnesia per acre per annum is lost by leaching, and that this is not appreciably increased by fertilizer treatments of magnesia.

The work of Lyon and Bizzell[28], Way[29], Clarke[30], and Zoller and Ulbricht, quoted by Frear[31], shows that lime is much more extensively leached than is magnesia. Tennessee soils derived from high-grade marble, the native rock analyzing 99 per cent $CaCO_3$, have less of residual CaO than of MgO. Hopkins[32], citing results of the Illinois State Water Survey, gives, from 90 analyses of well waters, 330

pounds of calcium and 130 pounds of magnesium as the leaching per acre per annum from estimated average rainfall. This is equivalent to a loss of 462 pounds per acre per annum of CaO and 217 pounds of MgO, a ratio of 2.21 to 1, while the determined solubilities of calcium silicate (wollastonite) and magnesium silicate (serpentine) in carbonated water were 2.10 to 1. The presence of native or applied calcium carbonate in soils would, of course, tend to increase the given ratio of lime to magnesia in drainage waters.

It is evident from the given solubilities of the various forms of magnesium carbonate, that were the carbonate existing in the soil, its leaching would be comparable with that of lime, and this fact, together with the decomposition of magnesium carbonate shown in Tables I, III, VI, VII, XIII, XIV and XV, forces upon us the conclusion that the occurrence of magnesium in the soil mass is in the form of silicate and not in the form of carbonate.

It appears, therefore, that the loss of magnesia from soils is the result either of the direct solubility of magnesium silicate or of the hydrolyzation and subsequent carbonation of the silicate when acted upon by carbonated soil water. The solubilities of the silicates of Table IX were, however, altogether negligible when in contact for 4 hours with distilled water at room temperature and at boiling temperature. Furthermore, the analyses of Table IX indicate that by far the largest proportion of soluble magnesia derived from action of carbonated water upon magnesium silicate (serpentine) is due to the presence of magnesium bicarbonate formed from the hydrolysis of the silicate. In the bicarbonate form, the magnesium would then be leached from the soils without subsequent conversion to the silicate, where drainage is sufficiently rapid.

THE DECOMPOSITION OF SOLUBLE SALTS OF MAGNESIUM BY SILICATES, WITH THE FORMATION OF INSOLUBLE MAGNESIUM SILICATES

Wagner[33] states that the successful use of Stassfurt salts containing magnesium chlorides and sulphates is dependent upon the presence of an excess of lime. Loew[13], quoting the observations of Schultz-Lupitz, concerning the corrective effects of lime applied to soils receiving kainit and carnalit, attributes the beneficial influences to correction of lime-magnesia ratio. The observations of Fleischer[34], who noted a greater benefit derived from the application of kainit in fall over spring treatment, indicated either a leaching of the harmful constituents of kainit and carnalit or their conversion and retention in the soil in some less soluble form. Loew[13] suggested the partial leaching of magnesium over winter, or the conversion of the soluble magnesium salts to the "less noxious carbonate," as accounting for the observation cited. Hall[27] found, however, but little leaching of magnesia, which seemed not to be appreciably affected by additions

of magnesia as sulphate. It was thought possible by the writer that magnesium sulphate and chloride might by mass action in the presence of an excess of carbonate of lime undergo a partial conversion to magnesium carbonate, with the replacement of the lime as the base with the acid radicle of the original magnesium salts, and that the resultant magnesium carbonate might then react with silicates, forming insoluble magnesium silicate. This reaction, however, was not produced in qualitative trials in the laboratory.

It was noted by Keitt[35] that kainit salts when mixed with basic slag are rendered insoluble in water. Hall[30] has shown that basic slag is not represented by the formula $Ca_4P_2O_9$, as was formerly held, but by the formula $(CaO)_5P_2O_5SiO_2$. This led the writer to try the reaction between calcium silicate and magnesium sulphate and magnesium

TABLE X—*Recovery of magnesia from magnesium sulphate contact-treatments with wollastonite and serpentine—Co_2-free distilled-water extraction*

Treatments	10 grams wollastonite + .5000 gram MgO as MgSO4	20 grams wollastonite + .5000 gram MgO as MgSO4	10 grams serpentine + .5000 gram MgO as MgSO4	20 grams serpentine + .5000 gram MgO as MgSO4
Grams MgO recovered in solution	.4891	.4732	.4913	.4804
Grams CaO replaced by MgO and found in solution	.0174	.0376	.0069	.0187

chloride. Ten and twenty-gram charges of calcium silicate (wollastonite) were in contact for 2 hours with .5 gram of freshly ignited "C. P." MgO converted to the neutral chloride and sulphate and dissolved in 150 cc of distilled water. The mixtures were then filtered, and it was found that appreciable amounts of soluble magnesia were rendered insoluble, and that lime was liberated instead. Pastes of the mixtures of magnesium sulphate and each of two mineral silicates, wollastonite and serpentine, in the same amounts were then permitted to stand for 14 days. The mixtures were then extracted with CO_2-free water and the extract analyzed, the magnesium determinations being made in quadruplicate.

The serpentine was used as a check upon any physical absorption, but the sample proved to contain some lime. The magnesia recovered and the lime liberated by the treatments are given in Table X. The influence of the amount and surface exposure of the silicates is plainly demonstrated by the analyses of Table X, which show direct propor-

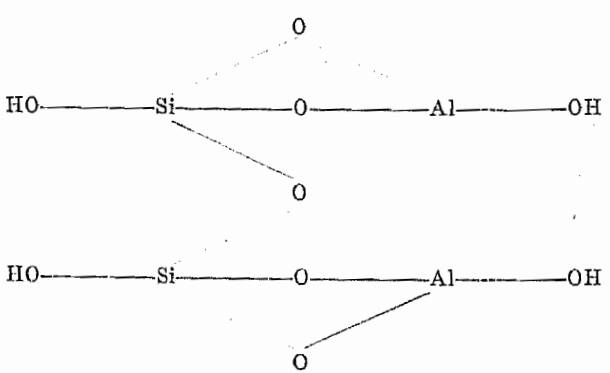
tion between the lime obtained in solution and the amount of silicates used in making the pastes, the amount of magnesia being a constant. Water blanks upon the two minerals show negligible extractions.

It would thus seem that the reason for the disappearance over winter of the temporary sterility attributed to applications of kainit and carnalit is accounted for by the affinity of MgO for SiO_2, and direct action between the soluble magnesium salts and calcium and possibly other silicates, resulting in the formation of the insoluble magnesium silicates.

PART II
LABORATORY INVESTIGATIONS

STUDIES OF THE MATERIALS EFFECTING DECOMPOSITION OF SOIL CARBONATES

The existence in the soil of acids, and acid-salts, including acid silicates, such as clays, is usually conceded by soil chemists and is mentioned in the standard works upon soils. The activity of clays in effecting the decomposition of soluble carbonates was noted by Morse and Curry[37]. They found that the bases were removed from solutions with the formation of bicarbonates or free CO_2 and concluded that the amounts of bases removed from solutions are dependent upon the concentration of the carbonate solutions. Loew[38] advanced the designation "argillic" acid and accounted for the dual acid and alkaline activities of clay by the formula—



Having in mind the well-known affinity of magnesia as magnesium chloride for silica in the dry, when dehydrating silica at temperatures above 120°C, the writer determined to study the effects of magnesium carbonate over lengthy periods and at room temperatures upon hydrated and dehydrated quartz of different degrees of fineness, as well as hydrated and dehydrated clays and other silicates occurring in soils. Calcium carbonate was also tried, the precipitated analyzed salts of both calcium and magnesium being used, except where the use of dolomite was specified.

PRELIMINARY STUDIES AS TO THE APPROXIMATE MOISTURE CONTENT GIVING MAXIMUM ACTIVITY BETWEEN SILICEOUS MATERIALS AND CARBONATES

The plan followed in determining activities between carbonates and the various soils and soil constituents was to bring the carbonates into contact with the various substances in CO_2-free atmosphere in air-tight Erlenmeyer flasks, from which subsequent to treatments the atmosphere was exhausted at intervals, and any liberated CO_2 drawn off by suction and determined gravimetrically in soda-lime U tubes (see frontispiece). The first test was made to determine the moisture condition giving the greatest activity, a loam soil being used for contact with precipitated magnesium carbonate. In order to eliminate the biological influences without introducing the factor of heat, treatments of neutral benzoate of soda were made to obtain sterile conditions in the preliminary experiments to determine the amount of moisture favoring the maximum activity. The benzoate of soda for each charge of soil was made by the conversion of .4 gram of benzoic acid to sodium benzoate.

Three moisture conditions, air-dry, estimated "optimum" of 15 per cent, and 200 cc in addition to 15 per cent air-dry basis, were maintained upon 200-gram charges of a loam soil, which had been in contact for a year with a large excess of calcium carbonate, (Table I). The benzoate of soda was introduced in solution into each of the nine 200-gram soil charges. Three charges were restored to air-dry condition, three to estimated "optimum" and three were given the excess of 200 cc above "optimum" moisture. The 9 charges, representing the three moisture conditions in triplicate, were placed in 500-cc Erlenmeyer flasks, which were stopped with two-hole rubber stoppers, through which were inserted glass tubes, the in-takes extending to the bottom of the flasks. The intakes and outgoes were connected with Geisler stopcocks, and cotton filters were placed in the tubing to prevent any dust being aspirated off from the dry treatments. The magnesium carbonate was thoroughly mixed throughout the charges and the atmosphere of the flasks freed of CO_2. The flasks were then closed and permitted to stand for one week, after which time and at regular intervals thereafter the CO_2 was drawn off and determined by the apparatus shown in the frontispiece. The excess moisture flasks were periodically agitated during aspiration to facilitate expulsion of CO_2 from solution. The averages of triplicate determinations covering a period of contact of 152 days are given in Table XI. The CO_2 in each of the magnesium carbonate treatments amounted to .7396 grams. It will be seen, however, that the CO_2 liberated from the "optimum" moisture flasks was considerably in excess of that amount, *seeming* at first to indicate an absorption of the base from

TABLE XI—*CO_2 evolved from contact of 2 grams $MgCO_3$ with 200 grams of the alkaline loam soil of Table I, in the presence of sodium benzoate*

Treatment	Grams of CO_2 evolved after												
	7 Days	14 Days	21 Days	28 Days	35 Days	42 Days	56 Days	63 Days	77 Days	95 Days	109 Days	116 Days	152 Days
Air-dried	.0051	.0060	.0078	.0091	.0120	.0141	.0162	.0184	.0198	.0254	.0283	.0373	.0522
"Optimum"	.1793	.4100	.5507	.7272	.8916	1.0536	1.1851	1.2606	1.3285	1.3690	1.4141	1.4712	1.5046
200 cc excess H_2O	.0247	.0709	.0984	.1145	.1454	.1819	.2268	.2665	.3156	.3671	.4262	.4726	------

sodium benzoate and liberation of the acid radicle, which in turn apparently acted upon the large amount of residual calcium carbonate in the soil, resulting from treatment prior to that of magnesium carbonate and benzoate of soda.

This observation seemed interesting in its apparent relation to selective absorption, and the reason for the excess of CO_2 above the amount of that applied as $MgCO_3$ was further studied (Table XII).

CO_2 EVOLVED BY CONTACT OF ACID AND ALKALINE SOILS WHEN TREATED WITH NEUTRAL SODIUM BENZOATE

In Table XII are given the activities of sodium benzoate treatments on the original acid loam soil and on the two carbonate-treated soils of Table I, of which the acid and magnesium-carbonate-treated soils were shown by analysis to be free of carbonate CO_2, while the calcium-carbonate-treated soil contained a considerable excess of carbonate. Two hundred grams of moist soil were treated in each case as described for the analyses of Table XI. It is evident from the analyses of Table XII that the CO_2 evolved in excess of the amount supplied by the magnesium carbonate, in the carbonate and benzoate treatments with "opium" moisture content shown in Table XI, cannot be due to the action of the benzoic acid radicle upon the excess of calcium carbonate, since greater amounts of CO_2 are evolved by decomposition of the sodium benzoate in both original acid soil and the alkaline magnesium-treated carbonate-free soil than from the soil

TABLE XII—*Evolution of CO_2 from contact of sodium benzoate with an "acid" loam before and after calcium and magnesium carbonate treatments of Table* I

Soil	Reaction to litmus	Previous treatment	Grams CO2 evolved after				
			14 days	28 days	56 days	92 days	147 days
Loam	Acid	None	.1837	.2727	.4002	.4662	.5001
"	Alkaline	$MgCO_3$	.1087	.2197	.3082	.3904	.5014
"	Alkaline	$CaCO_3$	.0927	.1049	.1948	.2544	.3407

containing an excess of calcium carbonate. In fact the excess of carbonate appears to have a somewhat depressing effect upon the CO_2 evolution. The conversion to CO_2 of the total carbon in .4 gram of the original benzoic acid as the sodium benzoate of the treatment, would give a theoretical carbon occurrence of .2752 gram, while .1366 gram of carbon has been evolved in the average CO_2 evolutions of the two carbonate-free soils of Table XII. Assuming the benzoate of soda to be the source of the carbon of the CO_2 evolved, rather than the soil, it is evident that oxygen has been secured from a source other than carbonates. Oxidation by the atmospheric oxygen of the flasks was suggested by the fact that suction was characteristic of all the treatments involving benzoate of soda, though it was not notice-

able in the case of the minerals used in the Erlenmeyer flasks experiments.

MAGNESIUM CARBONATE IN MOIST CONTACT AT ROOM TEMPERATURES WITH VARIOUS SILICEOUS SUBSTANCES MADE STERILE BY HEAT

Tables XI and XII demonstrated that "optimum" water content gave favorable conditions for activity between soil and magnesium carbonate, and that the presence of sodium benzoate involves complications. The use of sodium benzoate was then discontinued. Further contacts of the earthy carbonates and siliceous materials were made in Erlenmeyer flasks with "optimum" moisture content, sterilization being effected by heat in an autoclave, after the introduction and mixing of the carbonates with the charges of siliceous materials. The materials used to decompose earthy carbonates in this series were coarse and very fine white quartz sand, SiO_2 (silt, E. & A.), crude kaolin, clay and alkaline soil of the three types of Table I. The treatments were, (a) 2.5 grams of $MgCO_3$, (b) 2.5 grams of $MgCO_3$ and 2 grams of $CaCO_3$, and (c) 3 grams of dolomite, the analysis of which is given in Table V. *The three soils used had already received treatments of magnesium carbonate equivalent to* 16,070 *pounds per acre of* $CaCO_3$ *in excess of the Veitch-method requirement and had been subjected to this contact for a period of one year without leaching, being however, free of carbonates at the beginning of the second treatment of Table* XIII, *as shown by the analyses of Table* I.

DISCUSSION OF RESULTS OF TABLE XIII

The data of Table XIII eliminate consideration of biological influences and indicate clearly that the reaction responsible for the decomposition of magnesium carbonate is due largely to silica and silicates. The reaction is shown to be dependent upon the fineness of both the carbonate and the siliceous materials. The presence of calcium carbonate does not appear to be inhibitory to the reaction. While in most cases there seems to be less of CO_2 evolved from the mixtures of precipitated carbonates of calcium and magnesium, this is probably accounted for by the fact that the carbonate of lime contains some hydrated oxide of calcium, which would combine with a part of the CO_2 evolved. It will be shown later in this bulletin that to a lesser degree calcium carbonate appears also to act upon silica.

Had the reactions responsible for the data given resulted from soils alone, either the possible activity of carbonates upon soil organic matter or the influence of CO_2 upon the solubility of the precipitated $MgCO_3$ might be advanced as a factor in the evolution of CO_2, but the contacts were effected in many other cases than those cited in Table XIII, with absolute freedom from organic matter and CO_2 gas. If the reaction involved in the decomposition of the carbonates be considered

TABLE XIII—*CO_2 evolved from earthy carbonates in contact with siliceous materials at room temperatures, under sterile conditions*

Siliceous materials 200 grams	Reaction	Treatments	Grams CO_2 evolved after c										Equivalent in $CaCO_3$	
			7 days	14 days	21 days	28 days	42 days	63 days	79 days	111 days	150 days	205 days	Grams	Lbs. per 2,000,000 of soil
Coarse sand	Alkaline	$MgCO_3$ e	.0009	.0044	.0065	.0118	.0153	.0192	.0260	.0358	.0393	.0397	.0902	902
" "	"	" and $CaCO_3$ e	.0032	.0083	.0120	.0163	.0217	.0288	.0356	.0430	.0490	.0539	.1225	1225
" "	"	Dolomite e	.0033	.0055	.0063	.0124	.0213	.0275	.0341	.0377	.0454	.0502	.1141	1141
Very fine sand	Alkaline	$MgCO_3$	.0082	.0126	.0216	.0343	.0546	.0619	.0664	.0827	.0923	.1000	.2272	2272
" " "	"	" and $CaCO_3$	.0033	.0079	.0129	.0265	.0393	.0568	.0615	.0669	.0780	.0912	.2072	2072
" " "	"	Dolomite	.0024	.0117	.0132	.0163	.0267	.0278	.0311	.0332	.0377	.0419	.0952	952
Silt	Alkaline	$MgCO_3$	.0413	.0558	.0825	.1102	.1491	.1682	.1828	.1891	.2050	.2268	.5155	5155
"	"	" and $CaCO_3$	.0044	.0205	-----	.0399	.0534	.0666	.0868	.0937	-----	.1037	.2357	d 2357
"	"	Dolomite	.0024	.0055	.0208	.0345	.0502	.0581	.0638	.0677	.0371	.0985	.2238	2238
Clay	Alkaline	$MgCO_3$	.1651	.2242	.2799	.3349	.4236	.4468	.4503	.4712	.4846	.4971	1.1297	11297
"	"	" and $CaCO_3$	.1202	.1759	.2250	.2464	.3268	.3608	.3706	.3834	.3896	.4061	.9229	9229
"	"	Dolomite	.1816	.2115	.2377	.2594	.2836	.3063	.3094	.3199	.3308	.3526	.8013	8013
Kaolin	Alkaline	$MgCO_3$	.0338	.0789	-----	.1029	.1193	.1441	-----	.1536	.1652	b.1807	.4107	4107
"	"	" and $CaCO_3$	.0251	.0655	-----	.0803	.0958	.1062	-----	.1265	.1337	b.1518	.3450	3450
"	"	Dolomite	.0262	.0475	-----	.0662	.1040	.1175	-----	.1264	.1323	b.1563	.3552	3552
Loam a	Alkaline	$MgCO_3$	.0563	.1092	.1820	.2382	.3153	.3657	.3969	.4152	.4353	.4569	1.0384	10384
"	"	" and $CaCO_3$	.0825	.1384	.2055	.2686	.3364	.3579	.3727	.4045	.4191	.4370	.9932	9932
"	"	Dolomite	.0267	.0479	.0790	.1109	.1304	.1527	.1587	lost	.1840	.2139	.4861	4861
Sandy loam a	Alkaline	$MgCO_3$	.0282	.0472	.0579	.0846	.1278	.1458	.1575	.1702	.1978	.2336	.5309	5309
" "	"	" and $CaCO_3$	.0241	.0436	.0638	.0903	.1012	.1198	.1308	.1425	.1601	.1857	.4224	4224
" "	"	Dolomite	.0165	.0493	.0548	.0677	.0874	.1057	.1262	.1273	.1414	.1734	.3941	3941
Silty loam a	Alkaline	$MgCO_3$	.0379	.0907	.1325	.1815	.2554	.3101	.3255	.3346	.3406	.3766	.8559	8559
" "	"	" and $CaCO_3$	.0390	.0709	.0990	.1573	.1974	.2291	5.289	.2807	.2916	.3346	.7604	7604
" "	"	Dolomite	.0169	.0410	.0660	.0952	.1426	.1776	.1891	lost	.2137	.2486	.5536	5536

a One year previously treated with excess of $MgCO_3$ = 16070 lbs per acre $CaCO_3$ above Veitch requirement.
b Total period 14 days less than other 7 sets due to later beginning.
c Occasionally shaken at intervals other than 79-111 days.
d Two weeks less contact than other two silt treatment due to loss of original.
e $MgCO_3$, 2.5 grams; $CaCO_3$, 2 grams; dolomite, 3 grams.

as a function of solubility, it would appear that the solubility of the siliceous materials is as much the controlling factor as the solubility of the earthy carbonates, if not more so.

ACTIVITY OF SILICON DIOXIDE

In his treatise upon the synthetical preparations of crystalline alkali silicates, Morey[39] writes:

"It must be emphasized, however, that conclusions in regard to the relative strength of silicic acid based on the apparent degree of hydrolysis of such solutions are not necessarily valid; indeed, there is ground for the belief that silicic acid is considerably stronger than has generally been supposed."

Frear[40] quotes Hilgard as finding high lime content accompanying soluble silica and alumina in prairie soils of Alabama, Mississippi and Texas. According to Frear[40], quoting Storer, old mortars are often found to contain notable quantities of hydrous silicates, so that "caustic lime must be able to attack even the strongly resistant grains of sand." The experiments of Stockhardt are also quoted to the effect that caustic lime attacks powdered quartz as well as gelatinous silica. Wagner[41] cites experiments of Petzholdt, von Schrotter and Walters as proving that the hardening of mortar is in part due to the formation of calcium silicate, and the superiority of the mortar in structures built by the Romans is attributed to the mixing of sand with newly hydrated lime as contrasted to present-day methods. Sadler and Coblentz[42], and Spiller[43] assert that the setting of mortar is independent of the formation of calcium silicates and is due entirely to the carbonation of the hydrated lime. Though the influence of the formation of calcium silicate upon the setting of the mortar appears to be a disputed point, there is apparently no contradiction as to the actual formation of a compound resulting from the contact of caustic lime with quartz. It would appear from the data of this article that the observations noted as to the activity of the lime upon silica may be in part attributed to the action of carbonated lime upon siliceous materials. At least, CO_2 is evolved from contact of pure SiO_2 and "C. P." $CaCO_3$ under moist conditions at room temperatures. The evolutions of CO_2 from contact of silica with $MgCO_3$, noted in Table XIII, demonstrate that there is a decided affinity of MgO for SiO_2 and that the silicic acid radicle extensively replaces that of carbonic acid. As might be expected, the 100-mesh dolomite, relatively coarse as compared to the precipitated salts, was less active in most cases, but its CO_2 evoltuions were quite appreciable.

FURTHER STUDIES UPON THE DECOMPOSITION OF CARBONATES AS EFFECTED BY VARIOUS SOIL MINERAL CONSTITUENTS

After observing the decomposition of applied carbonates, with the elimination of both biological activities and influence of the

presence of organic matter, as shown in Table XIII, various soil mineral materials were studied in relation to their activities upon precipitated magnesium and calcium carbonates. Two hundred grams of each of the finely ground mineral materials were used for the contact treatments designated in Tables XIV and XV without sterilization in 500-cc Erlenmeyer flasks.

Weigner[44], in his studies of absorption by silicates, which he considers as a chemical reaction when regarded as an exchange of bases, concluded that dehydration lessened absorption, and that fineness of the silicate has but little influence upon absorption. In order to include observations of the comparative activities of the original substances, with action subsequent to dehydration, the various materials were ignited in platinum in a muffled furnace, for 16 hours. Gooch, Rickert and Kerzirian[45] found that all water is driven from hydrated silica in 30 minutes' heating of small charges over an ordinary Bunsen flame, but because of the bulk of the charges used the ignitions in the experiments reported were continued for an overnight period of 16 hours. Water equivalent to that of hydration was restored, and the moisture made equivalent to that of the unignited materials just before the carbonate treatments were applied.

Because of the usual occurrence in soils of appreciable amounts of titanium oxide and its close relationship to SiO_2, a pure form of titanium ore, 98 per cent TiO_2, was included among the substances used. The writer endeavored to secure acid-titanates, but was unable to secure the ore sought. According to Hopkins[46], of the 2 per cent of the solid crust of the earth other than silica and silicates, a large part is due to the occurrence of titanium, and, quoting the Geological Survey, he gives for an average 5300 pounds of titanium for 2,000,000 of soil in four loess soils from Illinois, Mississippi, Iowa and Missouri. The writer has found large quantities of titanium in the Hagerstown silty clay loam of limestone origin at the Pennsylvania Station. Dunnington[47] asserts that the element occurs universally. Hall[48] states that examinations of most sands show occurrences of rutile. Wait[49] found the element as a constituent of a large number of plant ashes and natural occurrences of coal. He has also shown the writer data from a number of analyses of clays, the TiO_2 percentages of which vary from 2.8 per cent to 4 per cent.

Solutions of sodium silicate were also tried as to their action in contact with the earthy carbonates. Hendrick's[50] analyses of commercial water glass indicate that the substance is principally an acid silicate, $NaHSiO_3$. With the 1 to 1 dilution as used, there was no evolution of CO_2 secured at room temperatures, but the lack of any apparent physical effect of the solution upon calcium carbonate, as contrasted with the slimy formation resulting from the magnesium-carbonate treatment, was very noticeable.

TABLE XIV—*Decomposition of magnesium and calcium carbonates by long periods of contact with earthy materials under "optimum" moisture conditions at room temperatures*

Siliceous materials	Grams used	Reaction	Treatment of substance before addition of carbonates	Carb'ate treatm't MgCO3 21-2 grms CaCO3, 2 grams	Grams CO_2 evolved after					CO_2 loss in terms of $CaCO_3$, grams	CO_2 loss in terms of $CaCO_3$, lbs. per A. 2,000,000 of soil
					14 days	28 days	56 days	a 78 days	a 133 days		
Red clay	200	Alk.	None	MgCO3	.2242	.3349	.4352	.4545	.4605	1.0466	10466
				CaCO3	.0247	.0466	.0567	.0606	.0677	.1538	1538
Loam	200	Alk.	1-yr. cont'ct xs of CaCO3—carb'n-free by oxygen	MgCO3	.0214	.0462	.0727	.1053	.1262	.2868	2868
				CaCO3	.0127	.0233	.0277	.0302	.0351	.0797	797
Loam	200	Alk.	1 yr. after large excess MgCO3, ignited 16 hrs.	MgCO3	.0229	.0342	.0590	.0789	.0994	.2259	2259
				CaCO3	.0210	.0318	.0409	.0566	.0680	.1545	1545
Kaolin	200	Alk.	Ignited 16 hours	MgCO3	.0097	.0320	.0473	.0561	.0613	.1393	1393
				CaCO3	.0170	.0281	.0379	.0457	.0574	.1304	1304
Kaolin	200	Alk.	None	MgCO3	.0789	.1029	.1319	.1344	.1485	.3375	3375
				CaCO3	.0052	.0071	.0219	.0483	.0560	.1272	1272
Kaolonite	200	Alk.	None	MgCO3	.0041	.0161	.0242	.0312	.0408	.0928	928
			Ignited 16 hours		.0100	.0159	.0237	.0310	.0428	.0972	972
Kaolonite	200	Alk.	Ignited 16 hours with 20 grams MgCO3	MgCO3	.0063	.0090	.0090	.0099	.0152	.0345	345
			20 " CaCO3		.0005	.0046	.0058	.0065	.0074	.0168	168
Bauxite	200	Alk.	None	MgCO3	.0403	.0674	.1681	.1496	.1838	.4177	4177
			Ignited 16 hours		.0052	.0067	.0126	.0195	.0324	.0736	736
Hornblend	200	Alk.	None	MgCO3	.0063	.0089	.0154	.0185	.0237	.0538	538
				CaCO3	0	.0044	.0065	.0092	.0131	.0297	297
Hornblend	200	Alk.	Ignited for 16 hours	MgCO3	.0016	.0032	.0032	.0060	.0085	.0193	193
				CaCO3	.0025	.0036	.0046	.0050	.0078	.0177	177

a Flasks not agitated during the period of 78 to 133 days.

TABLE XV—*Decomposition of magnesium and calcium carbonates by long periods of contact with earthy materials under "optimum" moisture conditions at room temperatures*

Siliceous materials	Grams used	Reaction	Treatment of substance before addition of carbonates	Carb'ate treatm't MgCO3, 21-2 grms CaCO3, 2 grams	Grams CO_2 evolved after					CO_2 loss in terms of $CaCO_3$ Grams	CO_2 loss in terms of $CaCO_3$ lbs. per a 2,000,000 of soil
					14 days	28 days	56 days	a 78 days	a 133 days		
Rutile	200	Alk.	None	$MgCO_3$	.0608	.0941	.1191	.1469	.1803	.4097	2731
"	"	"	"	$CaCO_3$	.0060	.0133	.0203	.0368	.0479	.1089	726
Opal	200	Alk.	None	$MgCO_3$	.0102	.0190	.0272	.0370	.0425	.0965	965
"	"	"	"	$CaCO_3$	.0096	.0176	.0320	.0411	.0523	.1188	1188
Opal	200	Alk.	Ignited 16 hours	$MgCO_3$	.0045	.0093	.0171	.0216	.0271	.0616	616
"	"	"	" 16 "	$CaCO_3$	.0053	.0112	.0153	.0206	.0264	.0600	600
Silt	200	Alk.	None	$MgCO_3$	.0558	.1102	.1587	.1834	.2013	.4575	4575
"	"	"	"	$CaCO_3$	.0728	.0937	.1174	.1428	.1789	.4066	4066
Red clay	200	Alk.	None	$MgCO_3$	.2242	.3349	.4352	.4545	.4801	b.1091	1091
" "	"	"	Ignited 16 hours	"	.0121	.0183	.0261	.0336	.0468	b.1036	1036
Soapstone	200	Alk.	None	$MgCO_3$	.0029	.0068	.0140	.0181	.0211	.0479	479
"	"	"	"	$CaCO_3$	.0084	.0126	.0169	.0229	.0308	.0700	700
Kaolinite	200	Alk.	None	$MgCO_3$	.0041	.0161	.0242	.0312	.0408	.0927	927
"	"	"	"	$CaCO_3$	.0097	------	.0148	.0179	.0231	.0525	525
Serpentine	200	Alk.	None	$MgCO_3$	.0238	.0322	.0614	.0722	.0930	.2113	2113
"	"	"	"	$CaCO_3$	.0018	.0065	.0076	.0157	.0246	.0559	559
Serpentine	200	Alk.	Ignited 16 hours	$MgCO_3$	.0033	.0041	.0094	.0139	.0369	.0838	838
"	"	"	" 16 "	$CaCO_3$	.0037	.0037	.0037	.0037	.0037	.0084	84
Alum. silicate	200	Acid	None	$MgCO_3$	.0426	------	.2053	.2253	.2266	.5150	5150
" "	"	"	Ignited 16 hours	"	.0454	------	.0945	.1305	.1744	.3963	3963
Rutile	200	Alk.	Ignited 8 hours	$MgCO_3$	.0020	.0079	------	------	b.0186	b.0287	b287
"	"	"	" 8 "	$CaCO_3$	.0040	.0078	------	------	b.0125	b.0422	b422

a Flasks agitated during the period of 78 to 133 days.
b Total period of contact, 91 days.

DISCUSSION OF THE ACTIVITIES BETWEEN THE CARBONATES AND SILICEOUS MATERIALS

Inspection of Tables XIV and XV demonstrates that the condition of the siliceous materials with reference to their hydration has an appreciable influence upon the activities shown, especially in the case of clay. It is also noted, however, that after ignition the silica seemed able to recover sufficient water to effect its chemical combination with the bases of the carbonates. Although in every case of ignition the evolution of CO_2 from carbonate treatment is reduced, the action of magnesium carbonate after ignition is still quite appreciable, and greater throughout than the activity of calcium carbonate, as measured by the evolution of CO_2. The acid silicates, including even the magnesium silicate (serpentine), show a decidedly greater decomposing effect upon magnesium carbonate than upon calcium carbonate. There seems to be no great difference between the measures of activity of calcium and magnesium carbonates in combining with silt and hydrated SiO_2 (opal), but the greater affinity of magnesia for TiO_2 is plainly indicated. The two loam soils of Table XIV are those of Table I and for a year they had been in contact with excessive calcium and magnesium treatments. However, at the time of the treatment given in Table XIV there were present no residual carbonates from the original magnesium carbonate treatment of Table I. The 16-hour ignitions of the two soils were accomplished in a muffle furnace as in the cases previously cited, but the gentle ignitions with oxygen, which was used in an attempt to eliminate organic matter at a temperature not effecting dehydration, were accomplished by gentle relay heatings in platinum dishes in the open, a current of oxygen being supplied to the soil mass.

It is a matter of no great surprise that the calcium and magnesium carbonates in large quantities with large surface exposure should act as do the more soluble carbonates, as shown by Morse and Curry[51], when brought into contact with acid or hydrated silicates, resulting in liberation of CO_2; but the decomposition of the two carbonates, relatively insoluble in the absence of CO_2, resulting from their being brought in exceedingly dilute solutions to the relatively insoluble SiO_2 or the reverse, is an interesting phenomenon. Aberson[52] concluded, from his studies of the functions of absorption, that the phenomenon is a function of the surface of colloidal substances. Weigner[53] in his conclusions as to the lack of effect of fineness of silicates in influencing their activities, considers the phenomenon as a chemical reaction, and he noted the quick attaining of an equilibrium between the silica "gels" and ammonium salts. The limits of the activities of the excessive treatments of the earthy carbonates and siliceous materials studied have not been as yet, either quickly or entirely attained in our investigations, and the extent of the decompositions is the subject of further studies planned. It was observed that agitations be-

PLATE 4

ERLENMEYER FLASKS CONTAINING THE MIXTURES OF PRECIPITATED EARTHY CARBONATES AND SILICEOUS MATERIALS

tween the periods of withdrawal of the CO_2 from the atmosphere of the Erlenmeyer flasks, caused considerable increase in the gas evolved over that obtained by permitting the mixtures to remain in the flasks without disturbance. The observations made by the writer have led to the conclusion that the reaction shown to transpire as the result of contact between magnesium carbonate and pure SiO_2 and TiO_2 is, considered as absorption, a chemical phenomenon rather than one of physical nature.

Inspection of Table XV shows that the dehydration of pure SiO_2 and TiO_2 has a diminishing effect upon the decomposition of the earthy carbonates. The degree of fineness of materials, and the extent of hydration, which the pure dehydrated silica seems capable of recovering in some measure upon being moistened, are apparently the factors controlling the extent of the phenomenon of decomposition of the carbonates, especially of magnesium carbonate.

Since the data of Tables XIV and XV were tabulated it has been found that some of the dehydrated materials, especially serpentine, are increasing their activities, as measured by the CO_2 evolved. The TiO_2 of Table XV has subsequently been treated for 10 days with an excess of caustic soda, then freed of the alkali and treated as was the original oxide with precipitated magnesium carbonate. At the end of 104 days 140 milligrams of CO_2 were drawn off from 300 grams of rutile. The finding concerning TiO_2 and SiO_2 suggests parallel activities of the oxides of Zirconium, Germanium, and other metals of the same chemical group.

CONVERSION OF $CaCO_3$ TO SILICATES IN SOILS IN FIELD PRACTICE

Laboratory investigations reported in this bulletin have shown that the magnesia of magnesium carbonate has a decidedly greater affinity for SiO_2 and silicates, and for TiO_2, than has the lime of calcium carbonate; but the activity of calcium carbonate, though more slow, is continued and extensive in the ultimate, especially in soils rich in clay. The cumulative conversions of calcium carbonate to forms other than carbonate in practice, are shown in Table XVI, the analyses being from peroxide fusions by the writer upon soils of the lime-treated plats of the General Fertilizer Experiments of the Pennsylvania Station, and are offered through courtesy of Prof. F. D. Gardner, head of the Department of Agronomy of the Pennsylvania Station. These analyses, as yet unpublished, are to appear in the delayed 1911-1912 report of the Pennsylvania Station. The 2-ton-per-acre applications of burnt lime were made every 4 years to the corn, while the ground limestone treatments were made every 2 years upon the corn and wheat, the rotation being corn, oats, wheat and grass. The analyses were upon composite samples of 40 borings, 10 from each of the 4 plats receiving each specified treatment. Of

TABLE XVI—*Analyses of 24 plats, of the Pennsylvania Station, showing pounds per acre of lime occurring as carbonates, as compared with total and other forms, after 32 years' treatment*

Composites of plats on all 4 tiers

Plat No.	16			22			23			24			33			34		
Treatment	Manure 6 tons			Burnt lime 2 tons Manure 6 tons			Burnt lime 2 tons			None			Gypsum 320 lbs.			Ground limestone 4 tons		
	Total CaO	CaO as $CaCO_3$	CaO in other forms	Total CaO	CaO as $CaCO_3$	CaO in other forms	Total CaO	CaO as $CaCO_3$	CaO in other forms	Total CaO	CaO as $CaCO_3$	CaO in other forms	Total CaO	CaO as $CaCO_3$	CaO in other forms	Total CaO	CaO as $CaCO_3$	CaO in other forms
0—7 inches	7576	1641	5935	20045	9267	10778	21192	10912	10280	7883	1902	5981	7985	1459	6526	19573	9741	9832
7—14 "	7924	1693	6231	11548	5105	6443	2188	2188	7701	7043	1067	5976	7228	1641	5587	13165	4505	8660
14—21 "	8906	3802	5104	9912	2265	7647	2474	2474	6207	7043	1902	5141	7760	1380	6380	10319	4167	6152
0—21 inches	24406	7136	17270	41505	16637	24868	15574	15574	24188	21969	4871	17098	22973	4480	18493	43057	18413	24644
Variation from check	+ 2437	+ 2265	+ 172	+ 19536	+ 11766	+ 7770	+ 17793	+ 10703	+ 7090	------	------	------	+ 1004	+ 391	+ 1395	+ 21088	+ 13542	+ 7546
Increase of CaO, percentage of application	------	------	------	61.1	36.8	24.3	55.6	39.7	15.9	------	------	------	51.0	0	51.0	62.8	40.3	22.5

the total amount of lime added, an average of the three basic-form treatments gives an accumulation of 20.9 per cent of the aggregate of treatments in forms other than carbonates. Of the conserved lime from treatments, nearly 35 per cent is found in siliceous and other combinations other than calcium carbonate. As the CO_2 determinations were made by boiling 1 minute with 1-15 H_3PO_4 without application of a blank for activity of the acid upon soil organic matter, the CO_2 results are undoubtedly higher than actual occurrence, and the absolute amounts of the other combinations of CaO are, therefore, greater than they are shown to be by the analyses. Some small amounts of the lime applied are probably combined in organic forms and much

TABLE XVII—*Total K_2O per acre in limed plats of the Pennsylvania Station after 32 years of treatment—Same samples as in Table XVI (J. L. Smith method)*

Plat No...	16	22	23	24	33	34
Treatment	Manure 6 tons	Manure a 6 tons Burnt lime 2 tons	Burnt lime 2 tons a	None	Gypsum 320 lbs.	Ground limestone 2 tons b
0-7 inches	75544	66574	66523	68253	72440	69154
7-14 "	72645	70076	68714	69673	67312	65653
14-21 "	65827	67721	66523	76136	66410	57705
0-21 "	214016	204371	201760	213062	206162	192412

a Every 4 years.
b Every 2 years.

has probably replaced potash in silicates, as shown in Table XVII. These data were secured, at the request of the writer, by Messrs. E. S. Erb and W. Thomas, under the direction of Dr. Wm. Frear.

INFLUENCE OF TIME IN THE DECOMPOSITION OF MAGNESIUM CARBONATE WHEN APPLIED TO SOILS

The indications from our work are that the retention in soils of magnesium in the form of carbonates in determinable amounts is of but brief duration, even with applications far in excess of requirements of practice. The first analyses of the rim treatments of the precipitated magnesium carbonate in excessive amounts were made 8 weeks after the applications, and at that time the entire applications, equivalent to about 16 tons per acre of fairly pure limestone, had disappeared without interference from leaching. The magnesia of magnesian lime would be expected to carbonate (Table VIII) and act in a similar manner to the precipitated carbonate.

The dolomite decomposition has been shown to be extensively, if not entirely, effected within 9 months, the first sampling period after treatment equivalent to 28,180 pounds of $CaCO_3$ per 2,000,000 of soil, while the activity of magnesite under field conditions is being made the subject of further study. It is to be expected that the mag-

nesium carbonate of the more dense dolomite and magnesite will require more time for decomposition than the finely divided precipitated magnesium carbonate, but their decompositions represent the identical reaction and will eventually occur. The time required in the accomplishment of the last named reactions would vary, of course, with the type of soil, the form and amount of treatment, and the mechanical handling of the soil. According to the laboratory analyses embodied in Table XIII, considering the CO_2 evolved from the dolomite treatment as coming from its magnesium carbonate content, in the case of the alkaline clay, nearly 2 tons of dolomite per acre 2,000,000 pounds, would have been decomposed in practice during the first week of contact.

The determinations of the limits of the magnesia-silica reaction and periods required for decomposition of various forms of magnesium carbonate, as influenced by soil type and composition, climatic and other factors, are yet to be determined.

RELATION OF THE FINDING CONCERNING THE DECOMPOSITION OF MAGNESIUM CARBONATE UPON OTHER INVESTIGATIONS

Since the announcement by Loew[63] of his hypothesis and the work of Loew and May[64] concerning the functions of calcium and magnesium in plant growth, much pot work upon the subject has been reported. Some investigators, notably those of the Imperial University and the Central Agricultural Experiment Station of Japan, have reported results which were considered by them as confirming Loew's hypothesis, while various other investigators in Europe and America have concluded that Loew's reasoning is fallacious and that his hypothesis has not been substantiated. Varying results have been reported from the use of soil and sand as media, while the treatments of finely divided precipitated magnesium carbonate have given results not in accord with those secured by the use of magnesite. In most of the investigations reported either magnesite, precipitated carbonate or sulphate has been used as a source of the applied magnesia.

Without entering into a discussion of the merits of Loew's hypothesis, it would appear from the data submitted in this bulletin that in many cases reasonings have been advanced upon the erroneous assumption of the continued presence of magnesium carbonate subsequent to its application to soils. The data presented indicate most emphatically that the presence of the usual soil components is altogether inhibitory to the continued existence of magnesium carbonate as a mineral solid in soils, when the magnesium carbonate is applied as the precipitated carbonate or as dolomite or magnesite.

It is apparent that when treatments of precipitated carbonate were made upon natural soils, the existence of magnesium carbonate was of but brief duration, while in the sand cultures the carbonate

remained much longer, because of the lesser activity of magnesia upon the relatively coarse grains of SiO_2 and because of the absence of the acid silicates and titanium oxide occurring in clays. The same would probably apply to the sulphates and chlorides of magnesium. Under all conditions the magnesium carbonate of dolomite and magnesite would probably remain longer than the carbonate of the precipitated salt before decomposition and conversion to silicate. However, the solubilities of magnesite and magnesium silicate (serpentine) in carbonated water, are not greatly different, and there would be no great disparity between the amount of magnesia available to plant growth from the native silicate and magnesite of equal fineness.

The solubility and fineness of a magnesium treatment have been shown to be very important factors in determining its toxic effect. Daikuhara[5] showed that when lime is present in soils as calcium carbonate, the necessary amount of magnesia when applied as magnesium sulphate is so small that the best ratio becomes 60 to 1. Although magnesia is decidedly less soluble as the silicate than as the original precipitated form, the fineness of the silicate resulting from the reaction of silica and the precipitated carbonate would still give appreciable availability of the magnesia through hydrolysis, as compared to the magnesia derived by solution of the relatively coarse mineral magnesite. The fineness of the original source of the applied magnesia would, though its influence upon the dissemination and surface exposure of the magnesium silicate resulting from treatment, affect the occurrence of magnesia available to plant growth. In other words, with a definite amount of CO_2 in soil moisture, the magnesia in solution would vary with the surface exposure of the silicate. Magnesium silicate derived from equal amounts of the magnesia as precipitated carbonate or magnesian lime would be more extensively disseminated than silicates derived from magnesite or dolomite as the source of the oxide. In soil cultures, then, the amount of magnesia coming in solution to the plant would depend upon the source of magnesia of the silicate and the amount of CO_2 present; the reaction of carbonate decomposition being shown to be reversible, resulting in the hydrolyzation and carbonation of the magnesium silicate.

The studies upon the relative solubilities of mineral calcium and magnesium silicates and the natural carbonates of the two elements demonstrated that calcium silicate is about 2½ times as soluble in carbonated water as magnesium silicate, and that ground limestone is about 1⅔ times as soluble as native calcium silicate (Tables VIII and IX). It would therefore seem that where equal amounts of lime and magnesia are found in soils, all of the lime in the mineral form of calcium carbonate and magnesia as native or converted magnesium silicate, the amount of calcium carbonate in *solution* and available to plant growth would be more than 4 times as great as magnesium carbonate (in terms of calcium carbonate, representing

equal alkalinity), whereas, were both occurrences of calcium and magnesium in the form of silicates, the ratio of the two compounds in solution would be represented in terms of calcium carbonate by 2½ to 1. The relations as to solubility are based upon assumptions that the compounds are of same fineness.

It is evidently established by the investigations here reported that the relative influences upon plant growth of the occurrences of lime and magnesia in soils, in their relation to each other, and jointly to the other essential elements, are entirely dependent upon the amount and form (silicates or carbonates) of the calcium occurrences and the amount of CO_2 in the soil to effect carbonation and solution of the hydrolyzed magnesium, which in its solid, inorganic chemical form in the soil mass is shown to be almost entirely a constant; i. e., magnesium silicate.

THE MAGNESIA-SILICA REACTION AS APPLIED TO PRACTICE

Given practical application, the research shows that when lime and magnesia are applied to soils in amounts in excess of those required to correct soil "acidity," magnesia is entirely converted to silicates, while lime is found partly as carbonate and partly as silicate, both of which are much more readily leached than is magnesium silicate. Where excessive treatments of lime and magnesia are given, as burnt magnesia-lime or as dolomite, or when these materials are repeatedly applied to the same soil, there will be at some future time an accumulation of the more insoluble magnesium silicates, while the lime will have been extensively lost by leaching. This accumulation of magnesia above the amount of lime conserved would mean eventually a condition which would be toxic to plant growth, and which would require remedial lime treatment in the future, though the soil might still be alkaline to litmus. Type of soil and climatic conditions would influence the factor of time required for the attainment of this probable toxicity. It is not apparent, however, that any deleterious conditions would be expected to materialize for many years as a result of the use of dolomite or burnt magnesian lime in the amounts ordinarily used in practice, nor do we find justification for giving preference to ground limestone over dolomitic limestone of equal basicity in conservative farm practice of the present.

SUMMARY AND CONCLUSIONS
PART I

The CO_2 of "C. P." precipitated magnesium carbonate, chemically equivalent to check treatments of 8 tons per acre of calcium carbonate in excess of the Veitch-method lime requirement, was dissipated by contact with fallow soils of three distinct types during a period of one year, without the interference of leaching.

The 8-ton-per-acre-equivalent applications of magnesium carbonate were decidedly toxic to wheat.

Repetition of the experiment under field conditions showed that in all of eight instances magnesium carbonate equivalent to 28,180 pounds of $CaCO_3$ per acre 2,000,000 of soil had been entirely decomposed at the end of 8 weeks without leaching, chemically equivalent amounts of burnt lime, hydrated lime and precipitated calcium carbonate being used as check treatments.

The precipitated magnesium carbonate exhibited no physical indications of the heavy treatment at the end of 8 weeks, while applications of chemically equivalent amounts of precipitated calcium carbonate were plainly discernible to the naked eye.

The 8-ton applications of burnt lime per 2,000,000 pounds of soil were shown to be completely carbonated within 8 weeks.

Magnesia was shown to be more readily converted to carbonate in soils than is lime.

The temporary toxicity usually attributed to magnesian lime and precipitated magnesium carbonate treatment was shown to be due, *not* to the persistence of causticity, which remains but briefly.

The harmful effects upon wheat and tall oat grass shown in Plates 1 and 2 were found to be due to finely divided and extensively diffused magnesium silicate, and *not to the applied magnesium carbonate*, which had been decomposed prior to the seedings.

Both the oxide and the precipitated carbonate of magnesium were many times more soluble in carbonated water than the corresponding forms of calcium; but in the case of the native mineral carbonates, limestone was 1.62 times as soluble as the dolomite and more than 3 times as soluble as the magnesite.

Decomposition of precipitated magnesium carbonate was found to be appreciably effected overnight by an alkaline loam soil under laboratory conditions. It was shown that magnesia is decidedly more active than lime upon the siliceous material of soils when the two bases are dissolved in carbonated water.

An average of eight treatments each of ground limestone and ground dolomite, of similar mechanical composition, and chemically equivalent in each case to 28,180 pounds of $CaCO_3$ per 2,000,000 of soil, gave 21,844 and 11,680 pounds, respectively, of residual calcium carbonate at the end of 9 months, though the limestone was 1.62 times as soluble as the dolomite in carbonated water.

The influence of purity and fineness of the applied materials upon the occurrence of residual carbonate is shown by the average residue of 19,170 pounds of $CaCO_3$ per 2,000,000 of soil, 8 weeks after application of chemically equivalent amounts of oxide, hydrate and precipitated carbonate of calcium without leaching, as compared to 21,844 pounds of residual calcium carbonate, 9 months after treatment of ground limestone of equal basicity.

That the decomposition of magnesium carbonate is not entirely a function of solubility of the carbonate is indicated by the comparison between the residual carbonates of limestone and dolomite treatments.

Amounts of magnesite, considerably in excess of the Veitch-method lime-requirement indication were decomposed by moist contact with each of the 3 soils of Table I.

If the magnesia-silica reaction be considered as a function of solubility, the solubility of the silica seems as important as that of magnesium carbonate in effecting of the reaction.

The solubilities of the mineral calcium and magnesium silicates used were negligible in CO_2-free water at normal and boiling temperatures.

Hydrolysis of calcium and magnesium silicates is accomplished to an appreciable extent in carbonated water, calcium silicate yielding much greater alkalinity than magnesium silicate.

An abundance of calcium silicate seems to function in producing alkalinity as well in carbonated water as one-half of an equal amount of calcium carbonate of the same fineness and of comparable purity.

Where an excess of CO_2 is maintained as the constant, the hydrolyzation of a mechanical mixture of the two silicates seems to be effected as though hydrolyses were accomplished separately.

With excess of CO_2 as the constant, the alkalinity produced by the hydrolyzation of either of the two silicates varies with the mass of the silicate.

No conclusive proof of the existence of magnesium carbonate in soils could be found in previously published data.

The occurrence of magnesia in the carbonate-free magnesium-carbonate-treated soils was shown by extraction in the cold with HCl, sp. gr. 1.115. The carbonate-free wollastonite and serpentine used gave large amounts of CaO and MgO dissolved by the same treatment.

The observations have led to the conclusion that soil activities

extending over thousands of years have completely decomposed any residual carbonate of magnesium in virgin soils, and that applications in practice are soon decomposed, even under decidedly calcareous conditions without drainage; that is, except for the minute quantities in soil moisture, resulting from hydrolyzation of silicates, or immediately after carbonate treatment, before decomposition has been effected, magnesium is not to be found in the carbonate form in surface soils.

The experiments indicate that with the greater occurrence of clays and hydrated silicates in the upper subsoil, magnesium carbonate would be even more quickly decomposed there than in the surface soil.

Possible exceptions to absence of magnesium carbonate, due to its decomposition by siliceous materials, are noted in unstudied arid soils, which, however, would appear to react as do humid soils, though more extensively; in peaty soils, very deficient in silica; in the coarse sand of the coastal plains, especially soon after magnesia treatment; and where subsoil rock has not completely disintegrated.

The loss of magnesia from soils is shown to be attributable to the hydrolyzation of magnesium silicate and its leaching in the bicarbonate form.

The greater loss of lime from calcareous soils is shown to be due to the decidedly greater solubility of calcium carbonate over that of magnesium silicate, while in "acid" soils the lime lost is also greater than the magnesia, because of the more ready hydrolysis and carbonation of calcium silicate over that of magnesium silicate.

The application of soluble, neutral sulphate and chloride in solution, and in form of paste, to insoluble calcium silicate, resulted in the formation of insoluble magnesium silicate, with the liberation of lime to the sulphuric acid radicle.

With the soluble magnesium salt as a constant the formation of the insoluble magnesium silicate was proportional to the mass of calcium silicate used.

The above reaction probably explains the temporary sterility following field treatment of Stassfurt salts without lime.

PART II

In original studies as to the causes for the entire dissipation of the CO_2 of magnesium carbonate when in contact with soils, benzoate of soda was used to maintain sterile conditions in the treated soils, but it was found that this salt could not be used because of complications.

When in moist contact with an alkaline loam soil, previously receiving heavy treatments of precipitated magnesium carbonate, neutral sodium benzoate was decomposed with oxidation and copious evolutions of CO_2. The same soil in its original acid condition acted in the same manner.

Sand, both coarse and fine, clay, kaolin, silt and three soils pre-

viously excessively treated with $MgCO_3$ (Table I) effected the decomposition of precipitated magnesium carbonate by moist contact at room temperatures both with and without the presence of precipitated calcium carbonate, each substance being alkaline and sterile by heat.

Dolomite in contact with the above materials under moist and sterile conditions at room temperature also evolved CO_2.

Pure alkaline SiO_2, hydrated and dehydrated, evolved CO_2 from moist contact with precipitated carbonates of calcium and magnesium and dolomite at room temperatures.

The magnesia of precipitated magnesium carbonate showed decidedly greater affinity for TiO_2 than did the lime of precipitated calcium carbonate; the decomposition of magnesium carbonate being extentively effected by moist contact at room temperatures with alkaline TiO_2.

The constant decomposition of carbonate of magnesium observed in the preliminary pot and field work seems due to the great affinity of magnesia for SiO_2, hydrated silicates, and TiO_2.

Hydrated silicates gave greater decomposition before dehydration than afterward, though appreciable decompositions were effected even after dehydration.

Clay, opal, loam soil, kaolin, kaolinite, bauxite, hornblend, rutile, silt, soapstone, serpentine, and C. P. aluminum silicate gave appreciable decomposition of the precipitated magnesium carbonate before and after ignition for 16-hour periods, the magnesium carbonate being almost invariably more active than precipitated calcium carbonate under both hydrated and dehydrated conditions.

Magnesium silicate (serpentine) was appreciably active upon magnesium carbonate, indicating that the possible extent of the activity between soil and magnesium carbonate is far beyond the limits to which the reaction has been subjected in our field experiments.

Soils strongly alkaline from excess of calcium carbonate effect the decomposition of magnesium carbonate.

Citations from unpublished analytical results secured from the Pennsylvania Station plats show that the action of burnt and carbonated lime upon siliceous materials, with formation of silicates of calcium, is extensive and cumulative in field practice.

The finding concerning magnesium carbonate decomposition, when applied to different pot culture work, has considerable bearing thereon, explaining what otherwise would be decided variations and discrepancies in previous work involving magnesia treatment.

The results indicate that ground dolomite might be used even in excessive amounts without any immediate toxic effect upon plant growth. However, the greater loss of lime by leaching of carbonate and hydrolyzed silicates, would produce at some future time conditions which would necessitate extensive liming to overcome magnesia poisoning.

REFERENCES

1 J. A. C. S., 1902, vol. 24, p. 1120.
2 Bur. of Soils, Bul. 23, p. 32.
3 Tenn. Station, Bul. 75.
4 Pa. Station, Report 1910-1911, p. 72.
5 Tenn. Station, Bul. 100.
6 Soil Fert. and Perm. Ag., p. 171.
7 Porto Rico Station, Bul. 12, p. 9.
8 U. S. Dept. of Agr., Report 71, 1902, p. 26.
9 Phar. and Med. Chem., vol. I, p. 447 (3rd Edit.).
10 Watts. Dict. of Chem., vol. 3, p. 162.
11 Quant. Chem. Anal., vol. 1, p. 179.
12 Bur. of Plant. Ind., Bul. 1, pp. 17, 35 and 13.
13 Pa. Station, Report 1899-1900, pp. 74 and 149.
14 Bur. of Plant Ind., Bul. 1, pp. 15 and 35.
15 Zeit. Anorg. Chem., 17, 170 (1898).
16 Proc. Roy. Soc. Edinburgh, 16, 319 (1889).
17 Compt. rend., 93, 340 (1881).
18 Manures and Fertilizers, pp. 326 and 328.
19 Chem. News and Jour. Phys. Research, 1902, vol. 86, no 2234, p. 148.
20 Porto Rico Station, Cir. 10, p. 15.
21 Porto Rico Station, Bul. 13, p. 5.
22 Jour. Ind. and Eng. Chem., vol. 5, no. 2.
23 The Soil, p. 386.
24 Bur. of Soils, Bul. 49, p. 64.
25 Soils, pp. 405, 42 and 24.
26 Pa. Station, Report 1899-1900, p. 25.
27 The Soil, p. 225.
28 Jour. Ind. and Eng. Chem., vol. 3, no. 10, p. 742.
29 Jour. Roy. Agr. Soc., 17, 133.
30 U. S. Geol. Survey, no. 330, Series E.
31 Pa. Station, Report 1899-1900, p. 68.
32 Ill. Station, Soil Report no. 6, p. 43.
33 Jahrb. fur. Agr. Chemie, 1897, p. 254.
34 Bot. Jahresber. f., 1886.
35 Science, Mar 6, 1914, and S. C. Station Bul. 173, p. 43.
36 Fertilizers and Manures, pp. 130-132.
37 N. H. Station, Report 1907-1908, p. 271.
38 Porto Rico Station, Bul. 13, p. 6.
39 J. A. C. S., 36, no. 2, p. 216.
40 Pa. Station, Report 1899-1900, pp. 69 and 109.
41 Chem. Tech., p. 668.
42 Phar. and Med. Chem., vol. 1, p. 424.
43 Chem. News, 18, 112.
44 Jour. Chem. Soc., London, 102, 1912, no. 600, 2, p. 891.
45 Amer. Jour. Sci., 36, 598.
46 Soil Fert. and Perm. Ag., pp. 46 and 69.
47 Amer. Jour. Sci., Dec. (1891), Chem. News, 65, 65.
48 The Soil, p. 33.
49 J. A. C. S., 18, 402.
50 Jour. Agr. Sci., vol. 2, 1907, p. 100.
51 N. H. Station, Report 1907-1908, p. 271.
52 Abs. Jour. Soc. Chem. Ind., 31, 1912, no. 5, p. 243.
53 Flora, 1892, p. 286.; Landw. Jahrb, 1892, p. 561.
54 Bur. of Plant Ind., Bul. 1.
55 Bul. Imp. Cent. Agr. Exp. Station, Japan, vol. I, 1907, no. 2, p. 87.