

		O = 16.	H = 1.
Osmium	Os	191.	189.6
Oxygen	O	16.00	15.88
Palladium	Pd	106.5	105.7
Phosphorus	P	31.0	30.77
Platinum	Pt	194.8	193.3
Potassium	K	39.15	38.86
Praseodymium	Pr	140.5	139.4
Radium	Rd	225.	223.3
Rhodium	Rh	103.0	102.2
Rubidium	Rb	85.4	84.8
Ruthenium	Ru	101.7	100.9
Samarium	Sm	150.	148.9
Scandium	Sc	44.1	43.8
Selenium	Se	79.2	78.6
Silicon	Si	28.4	28.2
Silver	Ag	107.93	107.12
Sodium	Na	23.05	22.88
Strontium	Sr	87.6	86.94
Sulphur	S	32.06	31.83
Tantalum	Ta	183.	181.6
Tellurium	Te	127.6	126.6
Terbium	Tb	160.	158.8
Thallium	Tl	204.1	202.6
Thorium	Th	232.5	230.8
Thulium	Tm	171.	169.7
Tin	Sn	119.0	118.1
Titanium	Ti	48.1	47.7
Tungsten	W	184.	182.6
Uranium	U	238.5	236.7
Vanadium	V	51.2	50.8
Xenon	Xe	128.	127.
Ytterbium	Yb	173.0	171.7
Yttrium	Yt	89.0	88.3
Zinc	Zn	65.4	64.9
Zirconium	Zr	90.6	89.9

[CONTRIBUTIONS FROM THE LABORATORY OF THE PENNSYLVANIA STATE
COLLEGE AGRICULTURAL EXPERIMENT STATION.]

VIII. SOME CUBAN SOILS OF CHEMICAL INTEREST.

BY WM. FREAR AND C. P. BEISTLE.

Received October 18, 1902.

SOME time since, the writer received from Mr. Luis Marx, a Cuban tobacco grower, samples of a deep red soil from the

plantations San Antonio and Zorilla, in the municipality of Alquizar, in the southwestern part of the province of Havana. The results of the physical and chemical examination of these soils made by Mr. C. P. Beistle, under the direction of the writer, exhibit some peculiarities worthy of notice.

These soils were described as nearly virgin, deep and only slightly stony, and of a calcareous clay nature. The land lies high, is level, very permeable and never shows excess of standing water. The land is highly fertile, producing large crops of fine-leaved, elastic tobacco, numerous grasses and palms.

Dr. C. W. Hayes, of the United States Geological Survey, who recently made a reconnoissance of Cuba, states, in a letter to the writer, that the soils of the southern part of the province of Havana have a deep red color, and lie upon a horizontal or very gently undulating plain of subaerial denudation. No true coral reef rock has been noted in this part of the province, the larger part, probably, of the soil of this district being derived from a soft, friable chalk or chalky marl, though part of the limestone is a hard rock, projecting in angular points and weathered into a cavernous surface. The geological age of these rocks is not definitely ascertained; they are of a tertiary formation, probably corresponding to the Oligocene of the United States.

The soils considered in this paper have received no manurial application. The "surface" soils represent the upper twelve inches; the depth represented by the "subsoils" is not stated. The samples had been carefully sifted to remove coarse particles, before shipment.

SPECIFIC GRAVITY.

The specific gravity was determined by the usual pycnometric method, with results as follows:

	Specific gravity, 15.6° C.
San Antonio :	15.6° C.
Surface soil.....	2.677
Subsoil.....	2.681
Zorilla :	
Surface soil.....	2.714
Subsoil.....	2.711

The large amount of iron present is sufficient to account for

the rather high specific gravity. That there is little difference between the so-called surface and subsoils, is in accord with the fact that they are of similar color.

MECHANICAL ANALYSIS.

The subsoils were subjected to mechanical analysis by the Osborne beaker method, a tap-water of very slight alkalinity being used.

	San Antonio. Per cent.	Zorilla. Per cent.
Gravel (2-1 mm.)
Coarse sand (1-0.5 mm.).....	1.23	10.78
Medium sand (0.5-0.25 mm.)	13.63	12.75
Fine sand (0.25-0.1 mm.).....	} 32.80	30.84
Very fine sand (0.1-0.05 mm.)		
Silt (0.05-0.01 mm.).....	17.79	13.69
Fine silt (0.01-0.005 mm.).....	} 15.10	12.72
Clay (less than 0.005 mm.).....		
Loss upon ignition (organic matter, combined water, etc.)	19.45	19.22
	100.00	100.00

About five-eighths of the water-free soil (residue from ignition) belongs to the group of 'sand,' while the 'clay' constitutes less, probably, than one-eighth of the whole.

This state of subdivision should produce the permeable texture and ready drainage said to mark the soils in place.

While these figures well represent the present condition of these soils, the use of a deflocculating agent like the 4 per cent. ammonia water used for the determination of 'active humus' or *matière noire* led to a complete breaking down of the 'sandy' particles into the finest clay. So fine were these particles that 70 per cent. or upwards of the mineral matter in the several soils passed through double parchment filters and a clear filtrate was obtained only by use of a Pasteur filter. The apparently sandy or loamy condition of these soils at the present time is doubtless attributable to the flocculant action of the carbonates of lime and magnesia present.

CHEMICAL ANALYSIS.

The soils were analyzed by the methods of the Association of Official Agricultural Chemists, the acid solution being, however,

subjected to a greater number of evaporations and re-extractions to assure the complete removal of silica therefrom. The means of closely concordant, duplicate determinations are given in the following table:

CHEMICAL ANALYSES OF CUBAN SOILS.

	San Antonio. Surface. Per cent.	San Antonio. Subsoil. Per cent.	Zo-rilla. Surface. Per cent.	Zo-rilla. Subsoil. Per cent.
Moisture (loss at 100° C. in water-oven)....	1.42	2.58	0.57	0.81
(Composition of water-free soils.)				
Acid insoluble (not decomposed).....	7.420	15.910	15.930	13.050
Soluble silica (dissolved by Na ₂ CO ₃ solution)	27.080	19.820	17.450	19.690
Potash	0.190	0.110	0.165	0.155
Soda	0.140	0.135	0.220	0.210
Lime	0.270	0.370	0.350	0.370
Magnesia	0.190	0.140	0.210	0.130
Manganio-manganic oxide.....	0.118	0.086	0.070	0.081
Ferric oxide	16.630	15.750	17.150	17.490
Alumina.....	27.860	29.350	28.255	29.270
Phosphoric acid.....	0.555	0.470	0.475	0.440
Sulphuric acid.....	0.035	0.065	0.060	0.030
Carbonic acid.....	0.555	0.315	0.275	0.305
Chlorine.....	trace	trace	trace	0.000
Loss on ignition, corrected for CO ₂ expelled	18.912	16.808	19.566	18.930
	99.955	99.329	100.176	100.151
Phosphoric acid soluble in citric acid (1 per cent)	0.0087	0.0065	0.0060	0.0055
Potash soluble in citric acid (1 per cent.) ..	0.0098	0.0104	0.0125	0.0094
Nitrogen.....	0.255	0.145	0.230	0.165
Organic carbon.....	2.502	1.349	2.802	2.091
Organic matter corresponding (C × 1.724).	4.313	2.326	4.831	3.605
Water of combination :				
(a) Loss on ignition (corrected), less hygroscopic moisture and organic matter	14.599	14.482	14.735	15.325
(b) Total water obtained by combustion, less hygroscopic moisture and water derived from organic matter (assumed to contain 5 per cent. of hydrogen).....	15.249	15.331	14.484	13.723

Organic matter was determined by the method described by Van Bemmelen,¹ except that the hygroscopic moisture was de-

¹ *Landw. Versuchs-Sta.*, 37, 279.

terminated by the official method, instead of by drying *in vacuo* over sulphuric acid, as Van Bemmelen prefers.

The surface soils are distinctly richer in organic matter than the subsoils. There are not a very large number of recent analyses by this method on record for comparison. Van Bemmelen¹ found 2.65 to 5.07 per cent. in certain clay soils of Java and Sumatra. Warrington and Peake² found as much as 6.12 per cent. in an old pasture and as little as 0.65 per cent. in a clay subsoil. E. H. Hess,³ working under direction of the writer, found in the limestone clay lands of the Pennsylvania Experiment Station, from 2.53 to 3.09 per cent. according to their manurial treatment. These few data warrant the opinion, however, that these virgin Cuban soils contain rather more humus than the more worn clay lands of the humid region contain.

Owing to the impossibility of eliminating the water of combination of the large amount of mineral matter associated with the active humus in its ammoniacal solution, the separate determination of this part of the organic substance was given up.

The soils contain very little sulphur and chlorine and probably little ferrous iron. It may therefore be assumed that the loss upon ignition of the "water-free" soil represents quite accurately the result of destruction of the organic matter and the expulsion of water combined with the organic materials and the hydrous minerals. The combined water has been estimated by direct subtraction of the computed organic matter from the total loss upon ignition. A check computation has been made, based upon the total moisture obtained upon combustion, corrected for hygroscopic moisture; from this total, there was subtracted the water corresponding to the hydrogen of the organic matter, which was assumed, after Van Bemmelen,⁴ to contain 5 per cent. of this element. The results by the two methods differ beyond the limits of analytical error, thus failing to exhibit the surprising agreement that Van Bemmelen obtained in a variety of soils upon application of these methods.

The foregoing data are of especial interest in considering these soils as the products of certain geological processes. From this

¹ *Loc. cit.*

² Cited by Wiley, "Principles and Practice of Agricultural Analysis," Vol. I. p. 323.

³ Proc. Soc. Prom. Agr. Science, 1900.

⁴ *Loc. cit.*

point of view the extensive decomposition effected by the action of hot hydrochloric acid is especially significant. It is emphasized by the following tabular statement:

	San Antonio.		Zorilla.	
	Surface. Per cent.	Subsoil. Per cent.	Surface. Per cent.	Subsoil. Per cent.
Undecomposed mineral matter, insoluble in HCl and Na ₂ CO ₃ solution...	7.420	15.910	15.930	13.050
Decomposed mineral matter:				
Gelatinous silica..	27.080	19.820	17.450	19.690
Dissolved in HCl.	46.088	46.476	46.955	48.176
Carbon dioxide...	0.555	0.315	0.275	0.305
Water of combination (a).....	14.599	14.482	14.735	15.325
	<u>88.222</u>	<u>81.093</u>	<u>79.415</u>	<u>83.496</u>
Organic matter.....	4.313	2.326	4.831	3.605
	<u>99.955</u>	<u>99.329</u>	<u>100.176</u>	<u>100.151</u>

The high solubility observed, is clearly not due, as in highly calcareous soils, to the presence of large quantities of calcite, magnesite or gypsum. It appears to be partially explained by the large amounts of iron oxide¹ and possibly, by those of alumina present; closer consideration of the facts compels the rejection of this explanation; for the iron oxide and alumina constitute only about 36 and 60 per cent. respectively of the acid-soluble material, while Hilgard² found that they constitute about 42 and 52 per cent. respectively of the average acid-soluble material in 466 soils, chiefly of the Gulf States in which the tertiary formation occurs.

Nor can the extensive decomposition be attributed to solvent action upon such anhydrous silicates as chrysolite, leucite, labradorite, epidote, phlogopite or biotite, which are capable of complete or quite extensive decomposition by the hot acid employed; the quantities of alkalis and magnesia dissolved, are too small to account for any large percentage of such minerals.

One indicative feature of these soils is the large proportion of soluble silica they yield upon decomposition, ranging from 17.45 to 27.08 per cent. The limestone clay of Lancaster County has

¹ Cf. Grouven, Soils of Benkendorff, Prerau and Tillada, *Jahrb. Agr. Chem.*, **10**, 35.

² Bulletin 3, U. S. Weather Bureau, Division of Soils, p. 30.

been found to yield but 11.82 per cent;¹ Maxwell,² analyzing a composite sample representing twenty soils from the Northern United States, chiefly of the humid region, obtained only 7.284 per cent.; Hilgard³ found, in 119 soils from Tennessee, Mississippi, Louisiana, Indian Territory, and Texas, an average of 7.53 per cent., the accompanying insoluble matter being 74.74 per cent. Among the latter soils, however, thirteen show percentages of soluble silica ranging from 15.41 to 23.45 per cent., with accompanying insoluble matter, ranging from 34.8 to 53.19 per cent. The soluble silica in the Cuban soils is remarkable therefore for its large proportion to the entire soil, but not for exceptional quantity relative to the material decomposed by acid.

The large amount of water of hydration together with the ready decomposition of the soil under influence of hot acid, point to extensive weathering as the condition that has influenced the nature of the soil materials.

The results here observed may be due either to the slight resistance the original rock offered to weathering, to long exposure of more resistant rock, or to the separation of highly weathered material from that which has been less decomposed and its accumulation in the chalk beds from which these soils are derived.⁴

As instances of the first-class, the weathering of certain lavas may be cited. Maxwell⁵ has found dark red, lava soils of Hawaii composed of readily decomposable hydrous silicates and iron oxide, the average of 120 analyses showing only 21.034 per cent. of resistant mineral matter, 16.168 per cent. of soluble silica, 17.499 per cent. loss upon ignition due chiefly to water of hydration, and 22.942 and 16.831 per cent. respectively of iron oxide and alumina soluble in acid. Hiola⁶ and King⁷ have reported analyses of tufa subsoils from Kumaba and Shimosa, Japan, that are marked by great loss upon ignition, high soluble

¹ Report Pennsylvania Experiment Station, 1894, p. 160.

² "Lava and Soils of the Hawaiian Islands," (1898), p. 101.

³ X. Census, Vol. V.

⁴ The tendency of lime to aid in forming zeolitic minerals from more resistant materials, can not be accepted in explanation of the observed ease of decomposition in these soils, because limestone clays in general are far more resistant to the action of acids.

⁵ "Lavas and Soils of the Hawaiian Islands," (1898), p. 97.

⁶ *Mitth. deutsch. Ges. Naturw. Volkerkunde Ostaneria*, 1881: *Jahbr. Agr. Chem.*, 24, 25.

⁷ *Jahbr. Agr. Chem.*, 24, 22.

silica and very low acid-resistant substance, though in these soils, the alumina greatly exceeds the iron oxide. Not all volcanic soils show these characters, those of Sumatra and Java¹ being quite different.

The second hypothesis requires the parent rock to have been highly homogeneous and to have weathered under conditions that protect the weathered products from mechanical separation. The range in state of weathering exhibited by the several mineral materials of most sedimentary soils, raises grave doubt as to the occurrence anywhere of conditions that would permit the removal of calcareous materials, such as these soils have experienced, without the removal, at the same time, of the finer, more highly weathered siliceous materials from those less weathered.

On the other hand, very fine silt and clay representing the most highly weathered portions of rocks and soils separated mechanically from the coarser materials, show marked similarity in composition to these Cuban soils. Merrill² found the silts from decomposed granite, gneiss and diabase to be marked by high water of combination (8-14 per cent.), and of gelatinous silica (12-23 per cent.), with a resistant residue ranging from 59 per cent. in the case of granite to 16 per cent. in that of diabase; the acid-soluble alumina ranged from 9.2 to 24.9 per cent. and in each instance exceeded the iron oxide. Loughridge³ found, in the 21.64 per cent. of clay separated by mechanical analysis from a certain soil, conditions very different from those in the entire soil:

	Clay. Per cent.	Entire soil. Per cent.
Loss upon ignition.....	9.00	3.14
Acid-resistant mineral matter.....	15.96	70.53
Gelatinous silica.....	33.10	12.30
Acid-soluble material	58.06	14.66
	<hr/> 100.14	<hr/> 100.63

It would seem from these data last cited, that very fine silt carried far out into the gulf and deposited where the foraminiferous skeletons that form the chalk were accumulating, would give rise to a soil of the properties noted in these Cuban soils.

¹ Van Bemmelten, *Op. cit.*, 257 and 393.

² "Rocks and Rock-Weathering, and Soils," (1897), pp. 212-220.

³ Proceedings A. A. A. S., 22, 81; Wiley: "Principles and Practice of Agricultural Analysis," Vol. I, p. 247.

These red soils are not of purely local occurrence. A. E. Woods¹ notes the prevalence in Bermuda of peculiarly deep red soils, whose color changes upon long cultivation. Earle² reports a partial analysis of a Cuban soil, of locality not stated, which exhibits high water of combination, low magnesia and alkalis, low acid-insoluble material (including gelatinous silica) but high calcium carbonate—a soil resembling those above reported except that it still retains much of the associated calcareous material. Watts³ reports a red, limestone clay, tobacco soil from Mocho, Clarendon, Jamaica, that contains only 0.50 per cent. calcium carbonate, only 19 per cent. of acid-insoluble matter, including gelatinous silica, but which has 46 per cent. of iron and aluminum oxides and a large percentage of combined water.

While these soils may come under the Russian soil survey classification of laterites,⁴ and like the true laterites of India possess deep red color, their large humus content differentiates them from the latter, from which they differ also in other respects.⁵

The peculiar violet-red color of these soils may be due to the dehydrating effect of salt water which W. Spring⁶ and F. Katzer⁷ have observed in case of uncombined ferric oxyhydrate deposited in delta-formations and upon sea-bottoms. Dr. Hayes, in the letter earlier mentioned, notes, however, that much of the soil apparently derived from the same formation in more easterly parts of Cuba, has a gray instead of red color. This difference may possibly be due to changes upon exposure of the virgin soil, such as Woods mentions as occurring in Bermuda.

The writer has found no record of any analysis of a soil of the Oligocene portion of the tertiary formation in the United States. Analyses of a few Eocene soils from the central prairie region of Mississippi reported by Hilgard⁸ exhibit a very different composition.

¹ *Science*, June, 1902.

² Florida Experiment Station, Bulletin No. 19, p. 11.

³ Journal Jamaica Agricultural Society, (1899), pp. 17-23; Experiment Station Record, No. 10, pp. 933-934.

⁴ Cf. N. Sibirtzew, Mem. pres. au. Congres geol. Internat., St. Petersburg, 1897; *Jahrb. Agr. Chem.*, **42**, 66.

⁵ Cf. J. W. Leather: Agr. Ledger, (1898), No. 2, p. 83; Experiment Station Record, **10**, 421.

⁶ *N. Jahrb. Min.*, (1889), **1**, 47; *Jahrb. Agr. Chem.*, **42**, 49-50.

⁷ Petermann's geog. Mitth., 1897; *Jahrb. Agr. Chem.*, **42**, 51.

⁸ X. Census, Vol. V, p. 284.

MINERAL CHARACTER.

Attempts at separation into groups of minerals of different specific gravity by the use of Thoulet's solutions of 3.09 and 2.7 sp. gr., and at identification of the minerals present by microscopic means, were rendered abortive by reason of the flocculation of the fine particles and their deep coloration by iron. The use of hydrochloric acid to remove the iron was not attempted because of the readiness with which the silicates present, are decomposed. The separate groups obtained by mechanical analysis each contained from 57 to 60 per cent. of iron and aluminum oxides, so homogeneous were the flocculation aggregates.

The proportions of the several chemical constituents present throw a little light upon the possibilities of combination. The low solubility of the potash and phosphoric acid in 1 per cent. citric acid indicates that the former is chiefly combined with silica and the latter with iron oxide or alumina; its quantity corresponds to 1.16 to 1.45 per cent. of ferric orthophosphate. The carbonic acid is sufficient in most cases to combine with nearly all of the alkaline earths, and, in case of the San Antonio surface soil, also with most of the alkalis; the existence of a little ferrous carbonate seems probable; in like manner, the humus is probably sufficient to combine with most of the alkaline and earthy bases, so that the carbonic and humus acids must exist in partial combination with the iron; owing to the low combining power of the humus, it would not tie up any large proportion of the latter element.

No analytical data were obtained to establish the degree of oxidation of the iron present, but the deep red color points to a highly oxidized condition. No iron-containing silicates remain in the acid-resistant material, which is colorless.

Concerning the nature of the siliceous compounds present: No large part of the gelatinous silica can be derived from zeolitic combination, as the small quantities of alkalis and lime, and the very slight loss of water that occurs when the air-dried soil is heated at a temperature of 100° C. show.¹ Assuming that such zeolites are present as natrolite or phillipite, which require a minimum of lime, they could not make up more than 4.5 per cent. of the dry soil nor yield more than 0.70 per cent. of gelatinous silica.

¹ Cf. Hillebrand: Bulletin No. 176, U. S. Geol. Survey, p. 35.

Assuming that the iron is present as ferric oxide chiefly, the small quantities of gelatinous silica and alumina required for zeolitic combination may be disregarded and their ratios be directly considered to ascertain what evidence they offer as to their compounds present. The silica-alumina ratios in these soils range from 1.029 to 1.636, chiefly approximating the latter figure. The average ratio for the 119 southern soils analyzed by Hilgard¹ is 1:0.71; those for the common aluminous minerals decomposable by hydrochloric acid with a liberation of gelatinous silica, range from 1:0.42 to 1:0.85; allophane and chloritoid (ratios 1:1.71 and 1:1.46 respectively) are the most prominent exceptions, but its dark color and low hydration exclude the latter from playing any important part, while allophane has a too low specific gravity and too high hydration. Upon any of the hypotheses as to the combination of the bases other than alumina, the average specific gravity of these remaining minerals must lie between 2.2 and 2.5 and the water of hydration between 14.6 and 17.0 per cent.

Hilgard² found, in the Eocene soil of Mississippi earlier cited, a ratio of 1:1.34, approaching that of these Cuban soils, and noted in many southern clays an excess of alumina. He suggests the presence of gibbsite, a hydrated alumina, as a means of explaining both the composition and the cultural peculiarities of these lands. Assuming the presence of a decomposable aluminum silicate with a silica-alumina ratio and hydration like those of kaolinite, approximately one-half of the alumina of the Zorilla surface soil would be left to be accounted for; but the great hydration of gibbsite (34.5 per cent.) excludes it from acceptance as the source of the alumina.

Schloesing³ has employed a dilute solution of sodium hydroxide in recent studies upon the condition of alumina in French and Madagascar soils; kaolin and fatty clay gave up to this solvent an excess of silica over alumina and continued to do so upon repeated treatment; on the other hand, a certain ochreous type of Madagascar soils yielded from 1 to 2 per cent. of silica and 8 to nearly 12 per cent. of alumina in the first treatment, but an excess

¹ *Op. cit. supra.*

² *X. Census*, Vol. V, pp. 67 and 284.

³ *Compt. Rend.*, 132, 1203; *Bied. Centrbl.*, 30, 723-730.

of silica on repeated treatment; this he regards as indicating the presence of free alumina which is dissolved at once by the alkali. That soil was gravelly, however, and much of the alumina was extracted from the coarser materials separated by mechanical analysis; the land was fertile. Owing to lack of material, it has been impossible to apply this treatment to the Cuban soils; many other interesting observations have been omitted for the same reason. It is hoped that the peculiarities of these widely extended West Indian soils here reported, may lead others to more thoroughly study them.

A few words respecting the fertility of these Cuban soils: Their present content of calcium and magnesium carbonates is sufficient to keep them permeable, to provide for nitrification and to furnish all of these elements that may be needed to keep the soil sweet and the plants well fed. Magnesia is less abundant than lime, a condition very commonly reversed in the soils of the Gulf States. Potash is low but, owing to the presence of the lime, may not exhibit deficiency for some time. Phosphoric acid is unusually abundant, but of low availability because of its combination with iron or aluminum. These lands will, for this reason, as well as to insure continuance of permeability, require occasional calcareous manuring. Nitrogen is present in liberal supply.

[CONTRIBUTION FROM THE LABORATORY OF THE PENNSYLVANIA STATE
COLLEGE AGRICULTURAL EXPERIMENT STATION, No. 9.]

THE EFFECTS OF FERMENTATION UPON THE COMPOSITION OF CIDER AND VINEGAR.

BY C. A. BROWNE, JR.

Received October 24, 1902.

THE present work comprises the results obtained in connection with an experiment begun at this Experiment Station in the Fall of 1898, which had for its object a chemical study of the cask methods of producing cider and vinegar, as ordinarily practiced in the rural sections of this country. So far as known, no experiments have been published thus far towards this end.¹

PLAN OF THE EXPERIMENT.

The juice for the experiment was prepared wholly from one

¹ Reference should be made to Bulletin No. 127, of the Va. Agr. Expt. Station, by W. B. Alwood and R. J. Davidson, entitled "Observations on the Production of Vinegar in Cellars," which has since come to the writer's attention.