

Dolomitization in Semi-arid Hawaiian Soils¹

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INTRODUCTION

SOILS DEVELOPED under a limited rainfall usually show the influence of salinization by calcium or sodium salts. In the presence of appreciable quantities of sodium salts, soil carbonates are converted to sodium carbonate and give rise to a condition known as black alkali. Recently workers have found soils in which the salinization had been caused by magnesium salts. Ellis and Caldwell (1935) found a magnesium clay "solonetz" in certain Manitoba soils in which 80 to 90 per cent of the adsorbed cations were calcium and magnesium. In addition, the calcium-to-magnesium ratio in these soils varied from 1.6 to 1.0. Alicante (1933) reported a Philippine soil which contained twice as much magnesium as calcium in a soluble form. Kudrin and Rozanov (1938), working with "sierozem" soils, found a high content of adsorbed magnesium especially in the "solonchaks." Rost and Chang (1941) divided the solonchaks of the Red River Valley of Minnesota into two groups: those having 20 to 50 per cent of their exchangeable cations as magnesium and those having more than 85 per cent of their exchangeable cations as calcium. In addition, they found a direct relation between exchangeable magnesium and gypsum in the soil. Thus, there is evidence that magnesium salts may play an important role in the salinization processes in soil.

Salinization of a soil with magnesium salts

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would be expected to give rise to the formation of magnesium carbonate, a very insoluble compound of magnesium. However, if a magnesium sulfate salinization occurred in a soil rich in calcium carbonate, then dolomitization might occur in the soil with the formation of two relatively insoluble compounds, dolomite (double carbonate of calcium and magnesium) and gypsum. The results of some recent studies suggest that this process does occur in soils. Alway and Zetterberg (1935) found that the molecular ratio of calcium carbonate to magnesium carbonate varied from 1.51 to 4.80 in calcareous Minnesota soils. Later work on Minnesota soils (Sherman, 1937) showed the occurrence of dolomitization in soils which have a high water table of waters rich in magnesium sulfate. In some of these soils the molecular ratio of calcium carbonate to magnesium carbonate approached 1.0. The carbonates in the dolomitized area did not visibly effervesce when treated with cold dilute hydrochloric acid even though the soils contained as much as 40 per cent carbonates. When pure dolomite is treated with cold dilute hydrochloric acid, the ensuing effervescence is barely perceptible. This relative inaction of a carbonate to cold hydrochloric acid is characteristic of dolomite. The carbonates from the area rich in magnesium were identified as dolomite and distinguished from calcite and other carbonates by a stain technique (Sherman and Thiel, 1939). Pellets containing gypsum and long needle-like crystals of gypsum were found imbedded in the clay below the dolomitized layer of soil. The nature of the occurrence of gypsum in these forms suggested their secondary origin.

In Hawaii, Lyman and Dean (1938) have reported soils containing twice as much magnesium as calcium. They found these soils in low-lying areas which had been under salt water in the past. The authors have found other Hawaiian soils rich in magnesium in areas which had never been under sea water. These soils in general occur only in the dry areas of the Hawaiian Islands.

The dark gray soils of Lualualei Valley, Waianae Valley, and Makaha Valley on the west slope of the island of Oahu have a low calcium-to-magnesium ratio, as shown in the present study. Under a very limited annual rainfall of 16 to 20 inches per year, these soils were developed on alluvial materials brought down from the Waianae Range. These soils are intermingled with numerous outcrops of coral rock (95 per cent calcium carbonate) and a few outcrops of basaltic rocks. The soils developed on these materials (coral and basaltic rock) can be readily distinguished from the alluvial soils by color. The native vegetation in the area is that characteristic of semi-arid regions, the dominant vegetation being algarroba (mesquite). Because of the highly dispersed condition of the soil and the consequent retarded penetration of water, the "A" and "B" horizons of the soil profile have been very poorly developed. Crystals of gypsum were found in some of the subsoils. In soil above the layer containing gypsum, the carbonates gave a very weak effervescence when treated with cold dilute hydrochloric acid and a violent effervescence with hot acid. This test would indicate the presence of dolomite in this soil.

The object of this study is to determine whether dolomitization is taking place, and if so, to what extent it is occurring in these soils and its possible relationship to soil-forming processes.

EXPERIMENTAL METHODS

Soil samples from several areas of soils having a high percentage of their exchange-

able cations as magnesium were collected, on the basis of profiles which showed evidence of dolomitization. These samples were analyzed for water-soluble salts, for exchangeable cations, and for the composition of the carbonates.

1. Water-soluble salts were leached from the soil by shaking 25 grams of soil with a liter of distilled water and allowing the mixture to stand overnight. It was then filtered on a Buchner funnel and the soil was washed with another liter of distilled water or until no test was given for sulfates in the leachate. The filtrate was evaporated to a small volume and the organic matter was destroyed by acid oxidations with a few drops of hydrogen peroxide. Calcium was determined by the standard volumetric method, using potassium permanganate as the oxidizing agent. Magnesium and sulfate were determined gravimetrically as magnesium pyrophosphate and barium sulfate, respectively.
2. Exchangeable cations were extracted by neutral normal ammonium acetate solution containing 70 per cent ethyl alcohol to reduce the solubility of the calcium carbonate. Calcium and magnesium were determined by the same methods as were used for the water-soluble ions. Potassium was determined volumetrically by the cobaltinitrite method (Volk and Truog, 1934), and sodium was determined gravimetrically as sodium zinc uranyl acetate (Barber, 1928).
3. The carbonate analysis was made by a method described for the analyses of dolomitic carbonates (Sherman, 1937). This method involved the determination of carbonate carbon dioxide by decomposing the carbonates with normal hydrochloric acid solution, followed by absorption of the carbon dioxide in a 0.5 N sodium hydroxide solution in an absorption tower. Before entering the tower, the carbon dioxide was passed through a silver sulfate-sulfuric acid solution to remove any hydrochloric acid fumes from the digestion flask. The digestion flasks were heated to boiling in order to insure the complete decomposition of the dolomite. After the decomposition of the carbonates, the sodium hydroxide solution in the absorption tower was drained into a volumetric flask. The tower was washed with five portions of hot carbon-dioxide-free distilled water to remove all the sodium hydroxide. The carbonates were precipitated in the volumetric flask by the addition of barium chloride and the solution was then made up to volume. The precipitate was allowed to settle and an aliquot was taken from the clear portion of the liquid. The excess sodium hydroxide was determined in the aliquot

by titration with a standard acid. A blank determination was made by the same method, using only the chemical reagents.

To determine the composition of the carbonates, another sample of soil was extracted with the amount of half-normal hydrochloric acid calculated as necessary to decompose the determined quantity of carbonates in the soil, this amount being based on carbonate-carbon dioxide determinations. To insure a slight excess of the acid, 0.1 ml. was added. Previous work has shown that only the carbonates are attacked by this quantity of acid (Sherman, 1937). The mixture was diluted with distilled water and then heated to boiling to insure the complete digestion of the carbonates. The mixture was filtered and the soil washed free of chloride with hot distilled water. Calcium and magnesium were determined in the filtrate by using the usual standard methods for these elements.

EXPERIMENTAL RESULTS

Samples of surface soils were collected from various parts of Lualualei Valley, Waianae Valley, and Makaha Valley on the island of Oahu, and in Table 1 is given the content of exchangeable calcium and magnesium in these soils. In every soil, magnesium constituted a very appreciable part of the cations, accounting for 20 to 45 per cent of the total exchangeable cations present in the soil.

Samples from a soil profile representing a typical area which showed indications of dolomitization were analyzed for composition of the water-soluble salts, quantity of each exchangeable cation, and composition

TABLE 1

THE CONTENT OF EXCHANGEABLE CALCIUM AND MAGNESIUM IN SURFACE SOILS FROM MAKAHA VALLEY, WAIANAE VALLEY, AND LUALUALEI VALLEY ON THE ISLAND OF OAHU

LOCATION OF SOIL	pH	EXCHANGEABLE Ca	EXCHANGEABLE Mg	RATIO Ca:Mg
		m.e./100 gm.	m.e./100 gm.	
Makaha Valley	7.3	22.12	16.06	1.38
Waianae Valley	7.1	24.15	19.69	1.23
	7.4	39.36	13.62	2.90
	6.3	27.40	14.21	1.93
	6.9	27.38	19.05	1.44
	7.3	36.80	14.69	2.50
	7.3	40.00	14.79	2.70
Lualualei Valley	7.1	56.80	16.15	3.49
	6.4	29.40	18.62	1.58
	6.9	31.98	19.16	1.67
	7.0	26.10	17.77	1.47
	7.8	33.89	9.89	3.43
	7.6	37.42	9.64	3.88

TABLE 2

THE COMPOSITION OF THE WATER-SOLUBLE SALTS OF A LUALUALEI VALLEY SOIL WHICH CONTAINS DOLOMITIC CARBONATES

DEPTH OF SOIL SAMPLES	pH	WATER-SOLUBLE SALTS M.E. PER 100 GM. SOIL			RATIO Ca:Mg
		Ca	Mg	SO ₄	
inches					
0-6	7.8	0.84	0.43	0.52	1.95
6-12	7.7	0.76	0.43	0.36	1.77
12-18	7.5	0.72	0.48	0.40	1.50
18-24	7.5	0.80	0.41	0.41	1.95
24-30	7.2	8.48	2.18	10.10	3.89
30-36	7.3	26.60	3.63	30.12	7.33
36-42	7.3	26.78	4.36	31.08	6.14

of the carbonates. The soil at a depth of 24 inches and deeper contained grains and needle-like crystals of gypsum. The carbonates in the soil above the zone of gypsum accumulation effervesced weakly when treated with cold dilute hydrochloric acid; this fact suggested the possibility that a high percentage of the total carbonates was in the form of dolomite. The data obtained in the analysis of this profile were similar to those obtained from similar soil profiles.

The data in Table 2 were obtained in the analysis of the water-soluble salts extracted from the soil samples of the selected profile. The greatest quantity of water-soluble salts was found in the part of the profile which contained the crystalline gypsum. The calcium and sulfate amounted to approximately 27 and 31 milliequivalents per 100 grams in this horizon. The water-soluble magnesium increased with the increase in sulfate but the increase was less than that shown by the calcium. The milliequivalents of water-soluble calcium and magnesium were equal to the milliequivalents of sulfate in soils rich in sulfate. This would suggest that both calcium and magnesium were combined with the sulfate in this part of the profile. The lowest calcium-to-magnesium ratio was found in the zone overlying the zone of gypsum accumulation.

In Table 3 are given the data obtained for the quantities of exchangeable cations in the soil from the different parts of the soil profile. The quantity of exchangeable calcium was found to be markedly greater in the soils from the part of the profile which showed the accumulation of gypsum. In this part of the profile, calcium amounted to 80 to 90 per cent of the total exchangeable cations in the soil, whereas in the soil above the zone of gypsum accumulation it amounted to 72 per cent of the total exchangeable cations. Exchangeable magnesium showed an opposite relationship, since it amounted to 25 per cent of the total exchangeable bases in the soils of the profile above the zone of gypsum accumulation and in the gypsum zone it accounted for 9 per cent of the cations. The ratio of exchangeable calcium to magnesium was the lowest in the soils above the zone of gypsum accumulation. The quantity of exchangeable potassium and sodium found in the soils of this profile was small, amounting to less than 4 per cent of total exchangeable cations.

The results of the analysis of the carbonate fraction are given in Table 4. The amount of total carbonates found in any soil horizon of this profile was not great. Analysis of carbonates in the soils of this area has failed to show a zone of carbonate accumulation in

TABLE 3

THE QUANTITY OF EXCHANGEABLE CATIONS AND THE PERCENTAGE OF EACH CATION OF THE TOTAL EXCHANGEABLE CATIONS IN A LUALUALEI VALLEY SOIL WHICH CONTAINS DOLOMITIC CARBONATES

DEPTH OF SOIL SAMPLES	EXCHANGEABLE CATIONS IN M.E. PER 100 GM.					RATIO Ca:Mg	PERCENTAGE OF TOTAL EXCHANGEABLE CATIONS			
	Ex-change capacity	Ca	Mg	K	Na		Ca	Mg	K	Na
inches										
0-6 ..	65.8	48.0	15.8	1.4	0.6	3.04	72.9	24.0	2.1	1.0
6-12 ..	57.2	40.8	14.5	1.0	0.9	2.81	71.3	25.3	1.7	1.6
12-18 ..	54.9	39.3	14.2	0.5	0.9	2.78	71.6	25.9	0.9	1.6
18-24 ..	48.0	34.5	12.1	0.3	1.1	2.85	71.8	25.2	0.6	2.3
24-30 ..	52.2	42.5	8.2	0.3	1.2	5.18	81.4	15.7	0.6	2.3
30-36 ..	74.4	66.4	6.5	0.2	1.3	10.21	89.2	8.7	0.3	2.0
36-42 ..	76.1	67.4	7.2	0.2	1.3	9.36	88.6	9.4	0.3	1.7

any soil profile. In this profile, magnesium carbonate was found in the greatest quantities in the soils above the zone of gypsum accumulation. The portion of carbonates in the form of dolomite was found to be greatest in the 12- to 18-inch layer of soil, which corresponded to the zone of weakest effervescence with cold dilute hydrochloric acid. The molecular ratio of calcium carbonate to magnesium carbonate was 1.12 for this layer. The carbonates were considered to be in the form of dolomite, since if they were a mixture of calcium and magnesium carbonates the quantity of calcium carbonate present would have been sufficient to give a very violent effervescence with cold dilute acid. Sherman and Thiel (1939) found that when carbonates of the soil were 87 per cent or more dolomite they gave a characteristic effervescence with cold dilute acid which was similar to that given by pure dolomite. Approximately 94 per cent of the carbonates in this soil layer are in the form of dolomite. In the soil from the zone of gypsum accumulation, calcium carbonate constituted approximately 80 per cent of the total carbonates.

DISCUSSION

This study has presented an instance of the dolomitization of a calcareous soil by the action of magnesium salts. The occurrence of dolomitization in soil, a process by which the double carbonate of calcium and magnesium is formed, has been established by chemical analysis of the soil carbonates, by weakness of effervescence of the carbonates when treated with cold dilute hydrochloric acid, and by the presence of one of the two end products of the process in the soil, gypsum. The formation of dolomite in these soils is associated with the soil-forming processes, since the materials which make up the alluvial parent material do not contain dolomite as a mineral. The soil is rich in magnesium silicate minerals and thus provides a source of magnesium as soil weathering progresses.

The mechanism by which the dolomite is formed may need some explanation, since calcium exceeds magnesium in both the water-soluble salts and exchangeable cations. The soils of this area receive most of their precipitation during very short intervals of

TABLE 4

THE COMPOSITION OF THE SOIL CARBONATES OF A LUALUALEI VALLEY SOIL WHICH CONTAINS DOLOMITIC CARBONATES

DEPTH OF SOIL SAMPLES	SO ₄	PERCENT-AGE SATURATION WITH Ca+Mg	CARBONATE ANALYSIS				Ratio Mols CaCO ₃ to Mols MgCO ₃
			Effervescence in cold dilute HCl	Total carbonates	MgCO ₃	Carbonates as dolomite	
inches	m.e./100 gm.	per cent		gm. /100 gm. soil	gm. /100 gm. soil	per cent of total	
0-6 . .	0.52	96.9	strong	6.06	1.50	54.1	2.56
6-12 . .	0.36	96.6	weak	4.62	1.35	63.9	2.03
12-18 . .	0.40	97.5	very weak	3.44	1.47	93.9	1.12
18-24 . .	0.41	97.0	weak	0.87	0.21	51.7	2.64
24-30 . .	10.10	97.1	strong	0.84	0.09	23.8	6.82
30-36 . .	30.12	97.9	very strong	2.55	0.23	19.6	8.60
36-42 . .	31.08	98.0	very strong	3.67	0.28	16.6	10.27

the year. Each year these soils become very dry, often to the extent that they show wide and deep cracks. During these periods of drought the salts are brought toward the surface by capillary rise of water. In the process of drying, much of the calcium salt is precipitated at lower levels, while the magnesium salt, owing to its higher solubility, remains in solution. At such periods the soluble magnesium may exceed the soluble calcium and thus create conditions favorable to the formation of dolomite by the action of magnesium sulfate on calcium carbonate. When the soils become wet the salts are leached to a lower level in the soil, from which the more soluble salts (magnesium) can rise again. This would be a possible explanation of the gypsum accumulation in the subsoil of these soils and of the formation of dolomite directly above the gypsum layer.

The formation of dolomite and gypsum as end products of this process should be expected under arid or semi-arid conditions, since these two compounds represent the most insoluble compounds of calcium and magnesium which could be formed in the presence of calcium carbonate. According to Leather (1913), the presence of magnesite together with calcite in soil is extremely doubtful and if magnesite did exist it would only be present in traces. It has been found that when the dolomitic carbonates are treated with acid they give up calcium and magnesium carbonate in approximately a 1:1 ratio. This fact and the effervescence which is characteristic of dolomite establish the identity of the type of carbonate formed. The formation of gypsum will result from the action of magnesium sulfate on the calcium carbonate and its precipitation from solution during wetting and drying of the soil. This process would lead to the formation of gypsum in the crystalline forms found in these soils.

Dolomitization in soils can be expected to occur under soil conditions similar to those described in this report. It is likely that dolomitization has occurred to some extent in many calcareous soils.

CONCLUSIONS

As a result of this study of the composition of the soil carbonates in a representative soil profile from Lualualei Valley, Makaha Valley, and Waianae Valley, the following conclusions may be drawn:

1. Dolomitization of the carbonates has been established by the chemical composition of the soil carbonates, by the effervescence in cold dilute hydrochloric acid characteristic of dolomite, and by the presence of one of the two relatively insoluble end products, gypsum, which will be produced when this process occurs in the presence of sulfates and calcium carbonate.
2. In the soil horizons where dolomitization has occurred, 50 to 94 per cent of the carbonates are in the form of dolomite.
3. In order that the process of dolomitization may occur, the presence of soluble magnesium salts is required. The soils of this area were found to be rich in magnesium, since this cation accounted for 20 to 45 per cent of the exchangeable cations in the soil. The drying of the soil during dry weather concentrates and increases the soluble magnesium until it exceeds the calcium in solution due to the precipitation of calcium as gypsum, and thus leads to conditions favorable to the formation of dolomite. Periodic rainy and dry seasons are essential to the dolomitization process.
4. The soil below the zone where the dolomitic carbonates exist contained numerous pellets filled with crystalline gypsum and crystals of gypsum. In this zone of gypsum accumulation the calcium-to-magnesium ratio is very high.

REFERENCES

- ALICANTE, M. M. A survey of the soils in the district of the Philippine Milling Company, Mindoro. *Philippine Sugar Assoc. Res. Bur., Ann. Rpt. Div.*, 1933: 69-72, 1933.
- ALWAY, F. J., and JEAN M. ZETTERBERG. Relative amounts of calcium carbonate and magnesium carbonate in some Minnesota subsoils. *Soil Sci.* 39: 9-14, 1935.
- BARBER, H. H., and I. M. KOLTHOFF. A specific reagent for the rapid determination of sodium. *Amer. Chem. Soc. Jour.* 50: 1625-1631, 1928.
- ELLIS, J. H., and O. G. CALDWELL. Magnesium clay "solonetz." *Third Internatl. Cong. Soil Sci. Trans.* 1: 348-350, 1935.
- KUDRIN, S. A., and A. N. ROZANOV. The characterization of serozems having a high content of adsorbed magnesium. *Pedology* (8): 836-855, 1938.
- LEATHER, J. W. Soil problems. *Pusa Agr. Res. Inst. and Col., Sci. Rpts.*, 1913-14: 16-17, 1913. [Abstract, *U. S. Off. Expt. Stat., Expt. Sta. Rec.* 33: 513, 1915.]
- LYMAN, CLARENCE, and L. A. DEAN. The calcium-magnesium ratio of some Hawaiian soils. *Hawaii Univ. Agr. Expt. Sta. Rpt.*, 1938: 49, 1938.
- ROST, C. O., and P. C. CHANG. Exchangeable bases of solonchak of the Red River Valley. *Soil Sci. Soc. Amer. Proc.* 6: 354-359, 1941.
- SHERMAN, G. DONALD. *The occurrence of dolomite in the subsoils of the Red River Valley.* [Master's thesis on file at University of Minnesota, 1937.]
- and G. A. THIEL. Dolomitization of glacio-lucustrine silts of Lake Agassiz. *Geol. Soc. Amer. Bul.* 50: 1535-1552, 1939.
- VOLK, N. J., and E. TRUOG. A rapid chemical method for determining the readily available potash of soils. *Amer. Soc. Agron. Jour.* 26: 537-546, 1934.