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Pedogenic carbonate in Chernozemic soils and landscapes of southeastern Saskatchewan

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Wang, D. and Anderson, D. W. 2000. Pedogenic carbonate in Chernozemic soils and landscapes of southeastern Saskatchewan. *Can. J. Soil Sci.* **80**: 251–261. The objective of this study was to characterize soil carbonates and estimate their accumulation by using a method based on $\delta^{13}\text{C}$ values of soil carbonate in pedons and landscapes. Dark Brown Chernozem soils of the Amulet Association (with mixed C_3 and C_4 plants) and native Black Chernozem soils of the Oxbow Association (with a pure C_3 plants) were included. Six soil samples representing the Cca and Ck horizons of the Oxbow and Amulet Associations were chosen for detailed pedogenic carbonate studies, which include particle size fractionation, mineralogical identification, surface morphology examination, and stable carbon isotopic compositions analysis on the particle size fractions.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses of the fractionated particle sizes indicated that dolomite dominates the carbonate occurring in the Ck horizons, and is mainly in medium and coarse silt fractions. In the Cca horizons, carbonate in clay and fine silt fractions is mostly calcite, whereas dolomite dominates the carbonates in medium and coarse silt fractions. Calcitic coatings on the surfaces of both silt and sand particles were observed. Stable carbon isotope ratio ($\delta^{13}\text{C}$ value) of carbonate was -8‰ in the clay fraction of Cca horizons in which carbonate is dominated by calcite. Carbonate in the fine particle size fractions of the Cca horizons is dominated by calcite and has the most depleted $\delta^{13}\text{C}$ values, indicating that pedogenic carbonate occurs as calcite and mainly in the fine particle size fractions. In contrast, carbonates from coarse silts of Ck horizons were composed solely of dolomite and had the most enriched $\delta^{13}\text{C}$ values (-1.1 to -1.4‰), a character of lithogenic carbonate. On a landscape basis, carbonate occurs mainly in the Cca horizons in mid- and upper slope soils as a result of moisture movement and ground water fluxes. Soils in the depressions were more leached and contained small amounts of carbonate, mostly in the 60- to 90-cm depth. Calculations from the $\delta^{13}\text{C}$ values of soil carbonates indicate that about 50–68% of the carbonate in the Cca horizons of middle slope soils is of pedogenic origin, which is equivalent to a CaCO_3 storage of 136–188 kg m^{-2} . In contrast, 5 to 39% (0–36 kg m^{-2} CaCO_3) of carbonate stored in the lower slope soils is of pedogenic origin. Thirty-one to fifty percent of the carbonate (equivalent to 100–134 kg m^{-2} CaCO_3) in upper slope soils is of pedogenic origin.

Key words: Carbonate, pedogenic, calcite, dolomite, $\delta^{13}\text{C}$ value, XRD, SEM, landscape

Wang, D. et Anderson, D. W. 2000. Caractérisation des carbonates d'origine pédogénétique dans des sols et des paysages chernozémiques du sud-est de la Saskatchewan. *Can. J. Soil Sci.* **80**: 251–261. L'objet de nos travaux était de caractériser les carbonates du sol et d'évaluer leur accumulation au moyen d'une méthode basée sur les valeurs $\delta^{13}\text{C}$ des carbonates, dans divers sols et paysages. Les sols étudiés étaient des Chernozems brun foncé de l'association Amulet (plantes en C_3 et en C_4) et des chernozems noirs de l'association Oxbow (plantes en C_3 exclusivement). Six échantillons de sol représentatifs des horizons Cca et Ck des deux associations étaient prélevés pour analyse détaillée des carbonates, notamment, sur la granulométrie, sur l'identification minéralogique, sur l'examen de la morphologie de surface et sur les effets de la composition en isotopes de carbone stables sur les diverses fractions granulométriques. Les analyses par diffraction des rayons X (DRX) et par microscopie électronique à balayage (MEB) des fractions granulométriques révélaient que dans l'horizon Ck les carbonates consistent essentiellement en dolomite qui se retrouve principalement dans les fractions limon moyen et limon grossier. Dans les horizons Cca, le carbonate des fractions argile et limon fin consiste surtout en calcite, la dolomite dominant dans les fractions limon moyen et limon grossier. Des revêtements calcitiques étaient observés à la surface des particules de limon et de sable. Le ratio d'isotopes de carbone stables ($\delta^{13}\text{C}$) des carbonates était de 8‰ dans la fraction argile des horizons Cca à dominance de calcite. Les carbonates présents dans les fractions fines des horizons Cca sont à dominance de calcite et c'est eux qui démontrent les valeurs $\delta^{13}\text{C}$ les plus basses, ce qui laisse à conclure que le carbonate d'origine pédogénétique consiste en calcite et se retrouve principalement dans les fractions granulométriques fines. En revanche, les carbonates des limons grossiers des horizons Ck étaient exclusivement sous forme de dolomite et manifestaient les valeurs $\delta^{13}\text{C}$ les plus riches ($-1,1\text{‰}$ à $-1,4\text{‰}$), ce qui est typique des carbonates issus de la roche mère. Dans une perspective de paysage, les carbonates se retrouvaient principalement dans les horizons Cca des sols en milieux et en hauts de pente, résultat du mouvement de l'eau dans les sols et du flux de l'eau souterraine. Dans les dépressions, les sols étaient plus lessivés et ne contenaient que de petites quantités de carbonate, surtout dans la tranche de profondeur de 60 à 90 cm. Les chiffres des valeurs $\delta^{13}\text{C}$ révèlent qu'environ 50 à 68% des carbonates présents dans les horizons Cca des milieux de pente sont d'origine pédogénétique, ce qui correspond à une accumulation de 136 à 188 kg m^{-2} de CaCO_3 . En revanche, seulement 5 à 39% (0 à 36 kg m^{-2} CaCO_3) des carbonates stockés dans les bas de pente sont d'origine pédogénétique alors que pour les hauts de pente la proportion se situe entre 30 et 50%.

Mots clés: Carbonate, pédogénétique, calcite, dolomite, valeur $\delta^{13}\text{C}$, diffraction des rayons X, MEB, paysage

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Table 1. Properties of the six horizons for the detailed pedogenic carbonate study

Sample	Horizon	Depth (m)	CaCO ₃ equiv. (g kg ⁻¹)	Slope	Vegetation type	Soil Association
1	Ox-Ck ^z	2.00–2.30	190	Lower	C3	Oxbow
2	Ox-Cca ^z -1	0.60–0.80	334	Middle	C3	Oxbow
3	Ox-Cca-2	0.23–0.45	390	Upper	C3	Oxbow
4	Am-Ck	1.6–1.65	139	Upper	C3 & C4	Amulet
5	Am-Cca-1	0.15–0.35	349	Upper	C3 & C4	Amulet
6	Am-Cca-2	0.10–0.5	299	Upper ^y	C3 & C4	Amulet

^zCk horizons contain carbonates (lithogenic), whereas Cca or calcic horizons contains more carbonate than the parent material, a consequence of build up of pedogenic carbonate.

^yThis soil is located on a south-facing slope. All others are located on north-facing slopes.

ately fine-textured till in southeastern Saskatchewan. One toposequence was selected from the Oxbow Association of the Black soil zone, and the other was from the Amulet Association of the Dark Brown soil zone. The Oxbow transect includes Rego Black, Calcareous Black, Orthic Black and Gleysolic profiles in sequence from the crest to the depression. The Amulet Association has Rego and Orthic Dark Brown soils, and Gleysolic profiles in sequence on a similar landscape. Soils on these toposequences were described and sampled by genetic horizons from the selected pedons (Fig. 1). A set of three samples from each toposequence was selected for a detailed study of pedogenic carbonates, consisting of one deep Ck horizon that has been little affected by pedogenic processes, and two Cca horizons that have the maximum carbonate accumulations of all soils in the toposequences (Table 1).

In order to estimate pedogenic carbonate distribution and storage on a landscape basis, a third site was selected adjacent to the Oxbow toposequence, and three parallel subtransects from the knoll to the center of the depression were sampled. Each of these transects includes 10 pedons with a distance interval of 5 m. A 90-cm core sample from each pedon was taken with a truck-mounted sampler. Bulk soil samples were collected from depths of 0–15, 15–30, 30–60 and 60–90 cm. Soil samples were air-dried and ground to pass a 2-mm sieve, with subsamples ground to <425 µm for carbonate determination and $\delta^{13}\text{C}$ value analysis.

Particle size fractionation was performed on the six samples selected for detailed study of pedogenic carbonates. Soils (50 g air-dried) were pretreated with 30% H₂O₂ to remove organic matter, and then ultrasonically dispersed with a Braunsionic 1510 system at 300 W for 30 min. After dispersion, the sample was sieved to separate sand (2000–50 µm), and then fractionated by centrifugation and sedimentation into clay (<2.0 µm), fine silt (2–5 µm), medium silt (5–20 µm) and coarse silt (20–50 µm) fractions.

Soil organic C and total C were determined with LECO CR-12 carbon analyzer, with inorganic C content calculated by the difference (Wang and Anderson 1998b). Two subsamples were combusted at temperatures of 840 and 1100°C for organic C and total C, respectively. The CO₂ released from sample combustion is measured by an infrared cell and the C content (%) is determined by integrating the CO₂ released during the combustion process (LECO, MI). Equivalent CaCO₃ content was calculated from inorganic C content of the samples.

The mineralogy of soil carbonates in each particle size fraction was identified with XRD analysis. The XRD analysis was carried out with Rigaku X-ray diffractometer, by selecting CuK α radiation with a graphite crystal monochromator (Rigaku, Tokyo). The surface morphology of soil carbonates was examined under a SEM. The soil particle separates were glued onto the sample holders, and then coated with gold for 5 min in a vacuum coating chamber.

The $\delta^{13}\text{C}$ value analysis of carbonates involved a conversion of the C to purified CO₂, and followed by a measurement of the stable C isotope ratio with a mass spectrometer. The C in carbonate was converted into CO₂ by adding orthophosphoric acid (H₃PO₄) to the sample under vacuum in a Y-shaped reaction chamber. The reaction was allowed to occur overnight. The evolved CO₂ was purified in a cold trap and sealed in Pyrex glass tube (Rask and Schoenau 1993). The $\delta^{13}\text{C}$ value of the CO₂ was measured on a VG-SIRA 12 mass spectrometer. All the $\delta^{13}\text{C}$ values are reported relative to the international standard Pee Dee Belemnite. The overall precision for repeated measurements of a standard sample was $\leq 0.2\text{‰}$.

The $\delta^{13}\text{C}$ values were measured on all the particle size fractions of the six selected samples, and all the bulk samples that contained significant amounts of carbonates from the Oxbow site. The proportion of pedogenic carbonates was calculated based on the $\delta^{13}\text{C}$ values of soil carbonate and soil organic matter, by using a fractionation factor of +16.5‰, determined on pedogenic carbonate in carbonate pendants from the same soils (Wang and Anderson 1998a). The mass of pedogenic carbonates in soil horizons and landscape positions was estimated by multiplying the total carbonate stored in the horizon or landscape positions with a factor for the proportion of pedogenic carbonate as determined by the $\delta^{13}\text{C}$ values.

RESULTS AND DISCUSSION

Mechanical Composition and Carbonate Distribution

The higher CaCO₃ contents in the Oxbow soils relative to the Amulet soils represent the regional difference in glacial deposits (Table 2). The carbonates in the Ck horizons are mainly of lithogenic origin and occur mainly in silt fractions, as noted previously by Rostad and St. Arnaud (1970). The CaCO₃ content of fine silt and clay fractions of Cca horizons ranges from 315 to 571 g kg⁻¹, and is 69 to 100% pedogenic carbonate, based on $\delta^{13}\text{C}$ values.

Fig. 2. X-ray diffractograms showing carbonate minerals in soil separates.

Fig. 4. Comparison of the surface morphology of fine-, mid-, and coarse-silt fractions from horizons of Cca (A, B and C) and Ck (D, E and F).

sions (Richardson et al. 1992). The large quantity of pedogenic carbonates occurring in the middle slope position has been explained by upward and lateral fluxes of bicarbonate-enriched ground water, driven by constant and rapid evapo-

ration at soil surface in arid and semi-arid regions (Miller et al. 1985; Richardson et al. 1992). Pedogenic carbonates can also precipitate in soils by upward flux of moisture without ground water involvement. Soluble constituents

Fig. 6. The $\delta^{13}\text{C}$ value, inorganic C content and the percentage of pedogenic origin from the Amulet toposequence. The number in parenthesis is the CaCO_3 content in grams per kilogram soil; and the upper number is the percent pedogenic carbonate in the horizon.

Gleysol and Orthic Black profiles have lost most of their carbonate, and that remaining is mainly lithogenic carbonate at the 60- to 90-cm depth. In contrast, the middle slope soils now contain more carbonate than they had at the start of soil formation. The additional carbonate is pedogenic carbonate, mainly in the 30- to 60-cm depth. Net gains of carbonate on upper slope soils were noted as well. A likely hypothesis is the weathering of CaCO_3 in the surface horizons, its downwards translocation to precipitate as pedogenic carbonate in the subsoil, followed by the gradual erosion of the carbonate-depleted surface horizon. Weathering of Ca-bearing silicates can also result in pedogenic carbonate formation. Based on an earlier study, about 20% of Ca-feldspars in Black Chernozemic soils have been weathered (St. Arnaud and Sudom 1981), and the released Ca may well have been precipitated as pedogenic carbonate.

The $\delta^{13}\text{C}$ values of the carbonates from the Oxbow site range from -1.4‰ in the Ckg horizon (60 to 90 cm) in the soil at 0 m, an indication of mainly lithogenic carbonates, to a value of -8.0‰ in the Cca horizons (15 to 30 cm) of the middle slope soils, indicating maximum amounts of pedogenic carbonate accumulated (Table 3). The carbonates present in the Ck horizons in the depressional and the lower

slope soils are believed to be the last traces of lithogenic carbonate. In the middle slope soils (at an elevation of 1.2 to 1.4 m relative to the lowest point within the landscape), the most depleted $\delta^{13}\text{C}$ values reflect the strongest accumulation of pedogenic carbonates. The $\delta^{13}\text{C}$ values of carbonate in upper slope soils range from -3.9‰ to -6.2‰ in the 0- to 60-cm depth, which implies that about 34 to 50% of the carbonate in the soils is of pedogenic origin. Pedogenic carbonates in this landscape occur mainly in the upper 60 cm as there is an inadequate amount of moisture available to translocate carbonates deeper. Based on the carbonate content and the $\delta^{13}\text{C}$ values, most pedogenic carbonates occur in the middle and upper slope soils (Table 3). At the middle slope position (20 to 30 m from the depression), about 136 to 188 kg of pedogenic carbonate is stored in an area of 1 m^2 to a depth of 90 cm (Fig. 7), with a maximum accumulation at the depth of 30–60 cm. In the upper slope area (35 to 45 m from depression), the storage of pedogenic carbonate is about 100 to 134 kg m^{-2} . In contrast, the soils in the lower slope area (0–15 m from depression) have only 0–36 kg m^{-2} of pedogenic carbonate, which occurs mainly in deeper horizons. The large amount of pedogenic carbonate in soils of the upper slope area seems to have resulted partially from