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Carbon isotopic compositions of pore and matrix carbonates in carbonate nodules, and origin of carbonate formation

LIU Lian[1,2*], YIN QiuZhen[1,3], WU HaiBin[1] & GUO ZhengTang[1]

[1] *Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China;*
[2] *Graduate University of the Chinese Academy of Sciences, Beijing 100049, China;*
[3] *Institut d'Astronomie et de Géophysique G. Lemaître, Université catholique de Louvain, Chemin du Cyclotron 2, 1348 Louvain-la-Neuve, Belgium*

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Carbon isotopes of pedogenic carbonate are often used to study paleoenvironments, but the existence of detrital carbonate changes the carbon isotopic composition. To develop an experimental method to determine existence of detrital carbonate in carbonate nodules, and to avoid it during isotope analysis, 23 pedogenic carbonate nodules in Miocene loess from the Loess Plateau of China were studied through micromorphology and carbon isotope analysis. The difference in carbon isotopic composition between matrix carbonate (B) and pore carbonate (A) ($\delta^{13}C_{(B-A)}$) ranges from 0.27‰ to 0.44‰ in nodules containing detrital carbonate and –0.16‰ to 0.13‰ in nodules where detrital carbonate is absent. The latter is within measurement error, but the former is beyond it. Here we propose an isotopic approach to determine if nodules contain detrital carbonate: if $\delta^{13}C_{(B-A)}$ is within the measurement error, the nodules do not contain detrital carbonate, and vice versa. We suggest that it is better to analyze pore carbonate instead of matrix carbonate when using carbon isotope of carbonate nodules to reconstruct paleoenvironments.

carbonate nodule, pedogenic carbonate, detrital carbonate, carbon isotope

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Carbonates in loess include detrital carbonates and pedogenic carbonates. Detrital carbonates derived from dust source areas and are preserved in loess as detrital minerals, and their carbon isotopic composition reflects the environment of the dust source area. Pedogenic carbonates are formed *in-situ* and are affected by later precipitation, eluviation and biological effects throughout the processes of loess deposition and pedogenesis [1], and their carbon isotopic composition reflects the local paleoenvironment in the region where the dust deposits [2]. The carbon isotopic composition of pedogenic carbonate is widely used in paleoclimate and paleovegetation reconstruction [2–5]. On the Loess Plateau of China, there are nearly continuous eolian deposits recording most of the past 22 million years [6]. They contain abundant pedogenic carbonates, which are of great value for paleoenvironment reconstruction [1,7]. The carbon isotopic compositions of pedogenic carbonates [4,8], bulk soil carbonates [9,10] and carbonate rhizoliths [11] have been used to reconstruct monsoon evolution [12,13], paleoclimate [8] and paleovegetation [4,9]. Because the carbon isotopic composition of detrital carbonate does not reflect paleoenvironmental conditions during pedogenesis and its values differ significantly from those of pedogenic carbonate, contamination of pedogenic carbonate by detrital carbonate leads to inaccurate interpretation of paleoclimate and paleovegetation [7]. Therefore, determining the existence of detrital carbonate in carbonate samples is fundamental for the paleoenvironment reconstruction.

Up to now, there have been two main methods for determining detrital carbonate. One is soil micromorphological

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*Corresponding author (email: liulian@mail.igcas.ac.cn) analysis. For example, Wen [1] distinguished most of the detrital carbonates and pedogenic carbonates in loess in thin sections based on their mineral characteristics. Another method is carbon isotope analysis. Cerling et al. [2] studied the carbon isotopic compositions of soil organic matter and soil carbonate in Pleistocene soil profiles in northern America and Pakistan, and concluded that if the difference in carbon isotopic composition between soil organic matter and soil carbonate is between 14‰ and 16‰, it is reasonable to exclude the existence of detrital carbonate in the carbonate nodule. Zheng et al. [14] suggested that carbonates in a compact, dense, non-layered nodule, which had consistent carbon isotopic compositions in different parts, did not contain detrital carbonate. Carbonate nodules are distributed widely in loess. Pore carbonates are mainly pedogenic [15], but the carbonates in the loess matrix might contain detrital carbonates. The carbon isotopic compositions of the detrital carbonates and of the pedogenic carbonates are quite different, the former being significantly more positive than the latter [9,16]. Therefore, the difference in carbon isotopic composition between the pore carbonate and the matrix carbonate could reflect the existence of detrital carbonate.

Here we present an analysis of pedogenic carbonate nodules in Miocene loess from the Loess Plateau of China. We first determine the existence of detrital carbonate minerals in the nodule matrix through soil micromorphological analysis, and then measure carbon isotopic compositions of pore carbonate (A) and matrix carbonate (B) in the same nodule, and then calculate the difference between A and B ($\delta^{13}C_{(B\text{-}A)}$). We then compare the $\delta^{13}C_{(B\text{-}A)}$ value of nodules which contain detrital carbonate with the $\delta^{13}C_{(B\text{-}A)}$ value of nodules which do not, and propose a convenient isotope method for determining the existence of detrital carbonate in carbonate nodules on the Loess Plateau.

Twenty-three dense and hard carbonate nodules from the QA-I Miocene loess section were studied. The QA-I section is located 27 km northwest of Qinan city in Gansu Province, and covers a time interval spanning from 22 to 6.2 Ma [6]. The nodules were sampled from the nodule layers at the bottom of paleosol layers (Table 1).

Table 1 Relative depth of carbonate nodule samples in the QA-I section

Sample No.	Depth (m)	Sample No.	Depth (m)	Sample No.	Depth (m)
1	250.0	9	155.3	17	113.2
2	241.7	10	149.4	18	104.2
3	237.0	11	135.7	19	76.0
4	227.9	12	130.7	20	64.0
5	215.9	13	126.7	21	49.0
6	201.4	14	123.4	22	17.8
7	187.1	15	120.4	23	0.8
8	162.7	16	115.7		

Micromorphological analysis of nodules was conducted using an Olympus BX-60 fluorescence polar light microscope. Methods for discriminating between pedogenic carbonate and detrital carbonate in thin sections are based on previous studies [7,15,17–20]. The 23 nodule samples were sawed to obtain fresh surfaces, washed in distilled water, and air dried. The pore carbonate (A) and matrix carbonate (B) were both sampled by using a dental drill on the fresh surface on the same nodule under the Olympus reflected light microscope. The pore carbonate sample was drilled from the transparent-semitransparent calcite micrite aggregations in the pores. The matrix carbonate sample was obtained by mixing several powder samples drilled from different places in the matrix in the same nodule. The sampling precision was 0.3 mm and the weight of each sample was ~40 mg. Carbonate powder samples were converted to CO_2 gas with 100% phosphoric acid in vacuum, at 25°C for more than 6 h. CO_2 for isotopic analysis was purified cryogenically and then measured on a Finnigan-MAT 252 Mass Spectrometer at the Stable Isotope Laboratory of the Institute of Geology and Geophysics, Chinese Academy of Sciences. The analysis process was calibrated using the national standard material GBW4405, and carbon isotopic ratio of carbonate was reported in the standard notation relative to the PDB standard. The measurement error was ±0.2‰. The carbon isotopic compositions of 46 carbonate samples were measured.

Thin section observations show that pores carbonates are in the form of coatings, hypocoatings and infillings. The coatings are equigranular micrite grains (<10 μm) on pore walls (Figure 1(a)); the hypocoatings are equigranular micrites (<4 μm) impregnating the matrix along pore channels; the micrite infillings are calcite micrites that fill pores. These are typical features of pedogenic carbonate [15], ensuring the pure pedogenic origin of the pore carbonate samples. The matrixes of the nodules are impregnated inhomogeneously by micrite pedogenic carbonates, and the coarse grains such as quartz and feldspar are observable. In the thin sections of the Samples 3, 4 and 13 detrital carbonates are found in the matrixes (<5% content). These detrital carbonate grains have a diameter <50 μm and a similar size to other detrital minerals (Figure 1(b)). These carbonate grains are smooth and have dissolved fringes, indicating chemical weathering to some degree.

The carbon isotopic compositions of the pore carbonate (A) and the matrix carbonate (B) from the 23 carbonate nodules were measured ($\delta^{13}C_A$, $\delta^{13}C_B$). The values of $\delta^{13}C_A$ and $\delta^{13}C_B$ vary from –7.23‰ to –4.02‰, and from –7.23‰ to –4.16‰ respectively. The former represents the carbonate isotopic composition of pore pedogenic carbonates, and the latter represents the carbonate isotopic composition of the mixture of detrital and pedogenic carbonates in the matrix of Samples 3, 4 and 13 and of the pure pedogenic carbonates in the matrix of the other samples. The difference in the carbon isotopic composition between the matrix and the pore carbonates ($\delta^{13}C_{(B\text{-}A)}$) is in the range of –0.16‰–0.44‰ (Figure 2). The $\delta^{13}C_{(B\text{-}A)}$ values of Samples 3, 4 and 13 where the detrital carbonate grains were found are 0.44‰, 0.32‰ and 0.27‰, respectively. The $\delta^{13}C_{(B\text{-}A)}$ values of the other samples where detrital carbonates were absent are in the range of –0.16‰–0.13‰ with an average of –0.01‰.

Pedogenic carbonates in loess carbonate nodules are derived from dissolution, migration and reprecipitation of detrital carbonates in the soil [21]. During pedogenic carbonate nodule formation, if there are remnant detrital carbonates in the soil groundmass the micrite pedogenic carbonates pack them when they precipitate, forming the nodules containing detrital carbonates. If the detrital carbonates are completely dissolved and there is no more remnant detrital carbonate in the soil groundmass when the micrite pedogenic carbonates impregnate the soil, the nodules which do not contain detrital carbonate are formed. During nodule formation, carbonate solution migrates along pores and impregnates the surrounding soil. When the soil dries, carbonate precipitates in pores forming coatings or infillings. Carbon isotopic compositions of loess pedogenic carbonate and of detrital carbonate differ significantly. The former ranges from –10‰ to –4‰ [9], and the latter is ~0 [16].

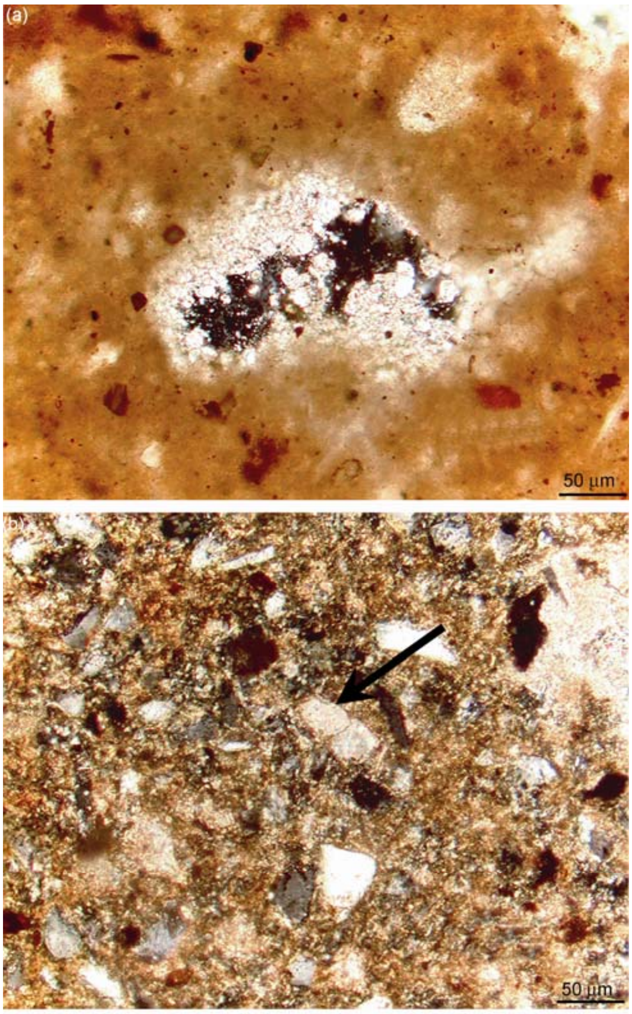

Figure 1 Micromorphological features of carbonate nodules. (a) Pedogenic carbonate micrite coatings in a pore (No. 18 nodule, crossed polarized light); (b) detrital carbonate grains in the matrix (No. 3 nodule, crossed polarized light).

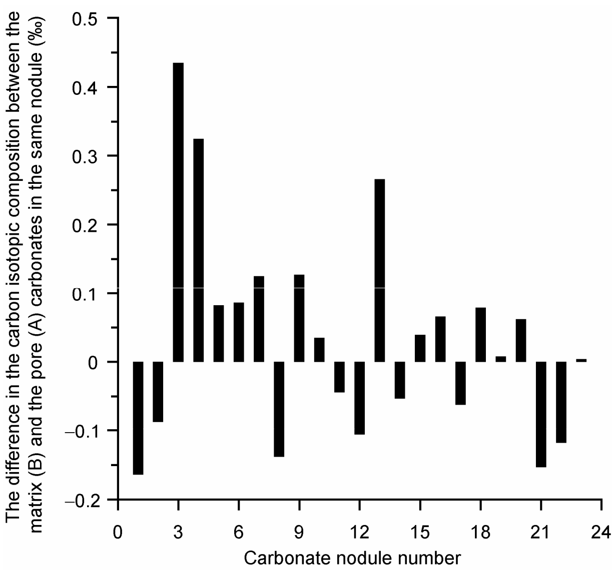

Figure 2 Difference in carbon isotopic composition between the matrix (B) and the pore (A) carbonates for the 23 samples.

Micromorphological observations and carbon isotope analysis show a correlation between the two carbonate forms. The $\delta^{13}C_{(B\text{-}A)}$ values of carbonate nodules without detrital carbonate vary from –0.16‰ to 0.13‰ with an average of –0.01‰. These values are within the measurement error (±0.2‰), indicating that the carbon isotopic compositions of pore carbonate and matrix carbonate are quite similar. This is not surprising because both the carbonate in the pore and the carbonate in the matrix are of pedogenic origin and should have similar carbon isotopic compositions. The $\delta^{13}C_{(B\text{-}A)}$ values of carbonate nodules with detrital carbonates vary from 0.27‰ to 0.44‰. These are larger than the measurement error. The higher values in the matrix are due to contamination by detrital carbonate, which has a more positive carbon isotopic value than the pedogenic carbonate. The $\delta^{13}C_{(B\text{-}A)}$ values are affected by the content of detrital carbonate in the matrix. The more the detrital carbonates, the higher the $\delta^{13}C_{(B\text{-}A)}$ values. Because paleosols in the Miocene loess have undergone strong weathering and eluviation [15], the carbonate nodules contain mainly pedogenic carbonates with only minor detrital carbonates. The $\delta^{13}C_{(B\text{-}A)}$ values are therefore quite low for these samples.

Using micromorphological and carbon isotope analyses of pedogenic carbonate nodules in Miocene loess from the Loess Plateau of China, we found that the $\delta^{13}C_{(B\text{-}A)}$ values of carbonate nodules without detrital carbonate were in the range –0.16‰–0.13‰ with an average of –0.01‰. They were within measurement error, indicating that the carbon isotopic compositions of the pore and the matrix carbonates are similar. The $\delta^{13}C_{(B\text{-}A)}$ values of the carbonate nodules with detrital carbonate are in the range 0.27‰–0.44‰. These values are relative larger and beyond measurement error, indicating the influence of detrital carbonate on the carbon isotopic composition. We propose a convenient isotope method to determine the existence of detrital carbonate in the nodules: if the $\delta^{13}C_{(B\text{-}A)}$ values are within the measurement error, the nodules do not contain detrital carbonate, and vice versa. We suggest that it is better to analyze pore carbonate instead of matrix carbonate when using carbon isotope of carbonate nodules for paleoenvironmental reconstruction.

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