Application of Carbon Isotopes in Loess-paleosol Sequences in Palaeoenvironmental Research

Yi Hu1, 2, 3, 4

1 Shaanxi Land Engineering Construction Group Co., Ltd., Xi’an, China
2 Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi’an, China
3 Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural and Resource, Xi’an, China
4 Shaanxi Provincial Land Consolidation Engineering Technology Research Center, Xi’an, China

490234215@qq.com

Abstract. Loess-paleosol sequences at the Chinese Loess Plateau have been proved the best-preserved carriers of palaeoenvironmental information. Studies on carbon isotopes in loess-paleosol sequences could obtain useful information for palaeobotany and palaeoclimatology and reconstruction of palaeoenvironment. This literature review points out some imperfections of previous studies and suggests that future studies regarding relationship between carbon isotopes and other climate factors, carbon isotopic fractionation during transformation of plant materials to soil organic matter under different ecological conditions, and carbon isotopes in modern soils of Chinese Loess Plateau should be given priority.

1. Introduction
Study and reconstruction of palaeoenvironment is the scientific basis for understanding history of environmental development on this planet and predicting tendency of environmental development in the future. Deposits or fossils that survived ancient geological process, such as deep-layered loess-paleosol in northern China, keep a record of dated environmental information and are thus important carriers in palaeoenvironmental studies.

Carbon is the most important element in the biosphere and is the foundation of life on this planet. Isotopes of organic carbon is an important parameter that is sensitive to change of vegetation and environment and is not affected by the stringent restrictions for fossil preservation, therefore, they can be used for high-resolution reconstruction of palaeoenvironment and are gradually gaining popularity in palaeobotanical and palaeoenvironmental research. Inorganic carbonates in terrestrial environments such as adarce, stalagmite, authigenic carbonate in lacustrine sediment, calcium concretion and authigenic carbonate in soils, and biological carbonate such as shells of mollusks, are important carbon pool, most of which are important subjects of studies for reconstructing palaeoenvironment and paleoclimate. Many biological carbonates are widely distributed and well preserved in geological processes, and current carbon dating technologies could determine the era of formation of these carbonates within a certain accuracy range. Meanwhile, these carbonates are rich in geochemical information such as
elemental and isotopic composition, organic biomarker, and their interactions with environmental factors. Taken together, these characteristics of carbon isotopes serve as fundamental basis for their application in paleoclimatology. Therefore, researchers could study characteristics climatic and environmental development in the past to a certain degree.

2. Fundamental principles
Terrestrial higher plants can be categorized into C3, C4, and CAM plants according to their photosynthetic pathways. C3 plants includes all the macrophanerophytes, most shrubs and herbaceous plants excluding those in the Poaceae family, and psychrophilic plants in the Poaceae and Cyperaceae families. They are generally hygrophilous and chilling tolerant and are dominant species in high latitude and alpine areas [1]. $\delta^{13}C$ of C3 plants ranges between -22 and -35‰ with a mean value of -27‰. In contrast, C4 plants are predominantly philothermal in the Poaceae and Cyperaceae family and are mainly distributed in savanna, temperate grassland, and boskage in semi-desert areas. They can survive heat stress and semi-arid conditions. $\delta^{13}C$ of C4 plants ranges between -10 and -14‰ with a mean value of -13‰ [2]. CAM plants are mainly succulent plants that can tolerate extreme drought stress and are distributed in desert and arid regions, for example, cactus, sedum, and bryophyllum. $\delta^{13}C$ of CAM plants has a wider range relative to C3 and C4 plants with a mean value of -17‰ [3].

Organic matter in terrestrial sediments originates from higher plants. Relative contribution of C3 and C4 plants to biomass of the vegetation and subsequently change of C3/C4 ratio in the vegetation over time can be estimated if composition of $\delta^{13}C$ in organic matter of a certain geological stratum can be obtained. Since C3 and C4 plants represent different ecological conditions, knowing the $\delta^{13}C$ of organic matter in sediments could help reconstruct paleoenvironment [4].

In addition, $\delta^{13}C$ in carbonates of terrestrial sediments can also be used to recover paleoecological and paleoenvironmental conditions. Few protogenic carbonates exist in loess-paleosol [5], thus composition of $\delta^{13}C$ in loess-paleosol sequences predominantly represents composition of $\delta^{13}C$ in authigenic carbonates, which is further determined by composition of $\delta^{13}C$ in soil CO$_2$ that are dominated by relative contribution of C3 and C4 in the vegetation, indicating $\delta^{13}C$ in soil carbonates is also related to relative contribution of C3 and C4 in the vegetation [6].

3. Application of carbon isotopes in loess-paleosol sequences
3.1. Paleobotany
$\delta^{13}C$ of paleosol in Duanjiapo profile varied between -14.6 and -22.0‰, suggesting the vegetation during its formation was comprised of C4 and CAM plants that were mostly herbaceous. Loess in the same profile has a $\delta^{13}C$ value of -22 to -24.9‰, therefore, vegetation during loess deposition could be a mixture of CAM and C3 plants with CAM being the dominant species. C3 plants at the same time were mainly herbaceous as information retrieved from sporopollen studies indicate overwhelming dominance of herbaceous plants. CAM plants can maintain vigorous growth under arid conditions with <500 mm rainfall, but C3 plants usually require >600 mm as well as evenly distributed rainfall across the whole growing season. Therefore, during loess deposition, the climate was more arid and more favorable for CAM plants. At both loess deposition and paleosol formation, the vegetation was mainly herbaceous plants, and few large forests were formed. In contrast, biomass and coverage of vegetation were both low at loess deposition yet high during formation of paleosol [7]. Han et al. (2000) found that vegetation was mainly grassland and lacked forest during formation of paleosol of different stratums in the middle areas of Loess Plateau, while forest may only exist when some well-developed paleosol was formed. Information regarding vegetation is directly recorded in isotopes of soil organic carbon [8]. Li et al. (2003) analyzed Malan loess in Dali area using carbon isotope of intact carbonatite and soil organic matter and indicates that climate in this area was warm and humid and C4 plants were dominant during 40-30 ka, which coincides with the degree of paleosol development at that time as well as slightly warm climate indicated by deep sea oxygen isotope MIS3a [9].
Natural vegetation and landscape at the Chinese Loess Plateau before human activities are still controversial in paleoenvironmental studies. Studies on Holocene soils at a few representative areas using paleopedological methods indicate that vegetation in the Chinese Loess Plateau during Holocene epoch was mainly grassland. When climate factors were optimal during that time, landscape in Guanzhong area, and south of the plateau is mainly meadow prairie and may include some coniferous trees, whereas Luochuan area in the middle of the plateau was typically grassland. Integrated analysis of plant silicate deposit, organic carbon isotope, and sporopollen did not support the existence of lush forest in the Chinese Loess Plateau during Holocene epoch. A systematic analysis on all the paleosol sequences from 2.5 Ma indicate that following 0.85 Ma, the contrast between glacial and interglacial age significantly increased, which may be attributed to intensified strength of winter and summer monsoon.

3.2. Paleoclimatology

Gu et al. (1991) analyzed oxygen isotope in carbonates in loess-paleosol sequences after late pleistocene epoch and found that \( \delta^{18}O \) ranged between -3.9 and -9.0‰ while \( \delta^{13}C \) ranged between -5.4 and -9.9‰, indicating development of paleosol and loess occurred under relatively warm, humid, and cold, dry climate conditions, respectively. This general conclusion proved that oxygen isotope in carbonates in loess-paleosol sequences could be used as indicators for reconstruction or estimation of paleoclimate evolution and compares to other records such as those in terrestrial sediments and deep sea [10].

Chen et al. (1996) composed evolution curve of carbon and oxygen isotope in the past 130 ka in Qishan area. This study found that climate in the middle of the Chinese Loess Plateau at least experienced 8 evident fluctuations. From about 130 to 75 ka was the last interglacial stage in the Chinese Loess Plateau, so the climate was warm and humid and development of paleosol was evident as indicated by widely distributed first stratum of paleosol (S1). According to the analysis of sporopollen, vegetation at that time was forest and grassland with filbert, oak, and wormwood as dominant species. From approximately 75 to 10 ka, the climate conditions were dry and cold, and the accumulation of first stratum of the loess (L1) occurred. During the last glacial stage, relatively warm periods occurred at 60 and 30 ka, respectively, and thin layers of paleosol were observed. Ever since 10 ka until now, the temperature increased and thus entered postglacial stage. The temperature was the highest during 9-0.6 ka and was considered the best stage of Holocene epoch. After that, the temperature declined with increased frequency of fluctuation until now [11].

Ning et al. (2008) determined the correlation between carbon isotopes in different vegetation and mean annual precipitation according to results from development of modern natural ecology in the Chinese Loess Plateau [12], and established the quadratic relationship between \( \delta^{13}C \) of soil organic carbon and annual mean precipitation after integrating known results regarding relative proportion of C4 plants in the Chinese Loess Plateau and mean annual precipitation with this study [13]. Using information of soil organic carbon isotopes recorded in loess-paleosol sequences, the author’s quantitively reconstructed change of mean annual precipitation in Lantian and Weinan areas in eastern Chinese Loess Plateau since 130 ka. In this study, impacts of precipitation on both type of the vegetation and \( \delta^{13}C \) in plant materials were considered, and correlation between \( \delta^{13}C \) of soil organic carbon and mean annual precipitation was established.

Tang et al. (2002) studied the Luochuan profile and demonstrated the evolution of arid (dry and cold) and semiarid (warm and humid) climate conditions and corresponding development of paleosol in the past 20 ka [14].

According to results from isotopic studies in modern soils and precipitation, as well as physiological and isotopic traits of C3 (mainly comprised of macrophanerophytes, shrubs, and psychrophilic herbaceous plants) and C4 (mainly comprised of herbaceous philotherm) plants and their relationship with ecological environment, Han et al. (2000) switched composition of carbon and oxygen isotopes in soil calcium concretion to climate parameters and estimated mean annual temperature, precipitation and vegetation at different stages of paleosol development [8]. They found
that for every 0.3% change in composition of oxygen isotopes in calcium carbonate concretion, mean annual temperature changed 1°C. Mean annual temperature when different stratums of paleosol in the Luochuan area was formed was higher than the present climate, whereas annual precipitation was comparable.

4. Perspectives

4.1. Correlation between carbon isotopes and climate conditions
Relationship between $\delta^{13}C$ and climate conditions is key to interpreting $\delta^{13}C$ in sediments and obtaining reliable paleoenvironmental information [15]. Therefore, future studies should focus more on coefficient of variation between $\delta^{13}C$ in plant materials and climate parameters such as temperature and precipitation, investigate impacts of climate factors (e.g., $\delta^{13}C$ of atmospheric CO$_2$ and change of its concentration) on composition of soil organic carbon isotopes, explore correlation between climate change and composition of carbon isotope using multivariate methodology, and further establish quantitative relationship between $\delta^{13}C$ of organic carbon, plant biomass, and vegetation coverage, which will make the quantitative studies more accurate.

4.2. Composition of carbon isotopes during transformation of plant material to soil organic matter
Transformation of plant materials to soil organic matter is a complicated process as climate and environmental factors determining composition and fractionation of carbon isotope in plant materials are extremely complicated. During deposition and sedimentation, plant residues experience geological and biological process thus further fractionation of carbon isotopes could occur, which may affect the tracking function of carbon isotopes. Meanwhile, fractionation of carbon isotope in plant materials with different photosynthetic pathways may be drastically different during its transformation to soil organic matter [16]. Ecosystem in the Chinese Loess Plateau is a mixture of C3 and C4 vegetation, therefore, fractionation of carbon isotopes during transformation of plant materials to soil organic matter under different ecological conditions should be given priority in paleobotany and paleoclimatology.

4.3. Carbon isotope in modern soils of the Chinese Loess Plateau
Despite of similar source, distribution of precipitation, and seasonal change (e.g. dry and humid season) for monsoon between now and glacial stage in the Chinese Loess Plateau, studies regarding composition of carbon isotopes in modern soils is still lacking and it is difficult to quantitatively estimate paleoenvironmental factors. Therefore, future studies should continue to survey modern ecosystems and clarify the relationships between carbon isotopes in plant materials and climate factors, distribution pattern of modern C4 plants, and relationships between change of C3/C4 ratio in the vegetation and climate and environment [17]. These efforts would offer solid scientific basis for explaining organic carbon isotopic results and obtaining reliable paleoenvironmental information and make the correlations from modern modelling process more accurate.

References
[1] Han, J., A. Wang, and D. Liu. Appearance of C4 plants and global changes. *Earth Science Frontiers*, 2002, 1: 233-243.
[2] Ning, Y. Reviews on quantitatively reconstructing paleoclimate and paleovegetation based on carbon isotope of soil organic matter of Chinese Loess Plateau. *Geological Review*, 2010, 56: 851-857.
[3] Cerling, T.E., and J. Quade. Stable carbon and oxygen isotopes in soil carbonates. In: P.K. Swart, K.C. Lohmann, J. Mckenzie, S. Savin, eds. *Continental Isotopic Indicators of Climate*, Washington, D.C., USA: American Geophysical Union, 1993, 78, 217-231.
[4] Deines, P. The isotopic composition of reduced organic carbon. In: P. Fritz, J.C. Fontes, eds. *Handbook of Environmental Isotope Geochemistry, volume 1: The Terrestrial Environment*. 
Amsterdam, Netherland: Elsevier, 1980, 329-406.

[5] Wen, Q. The geochemistry of loess in China. Beijing, China: Science Press, 1989, 115-145.

[6] Cerling, T.E. The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth and Planetary Science Letters*, 1984, 71: 229-240.

[7] Pang, J. Stable isotope in Chinese Loess Plateau and paleoenvironmental research. *Arid Land Geography*, 1998, 21: 87-95.

[8] Han, J. Oxygen isotopic stratigraphy and pedostratigraphy: their appearance and application. *Quaternary Sciences*, 2000, 20: 203-205.

[9] Li, Y., D. Liu, W. Wu, J. Han, and Y. Hong. Paleoenvironment in Chinese Loess Plateau during MIS3: evidence from Malan loess. *Quaternary Sciences*, 2003, 23: 69-76.

[10] Gu, Z. Carbonate isotopic composition in loess-paleosol sequences and its relationship with change of paleoclimate. *Chinese Science Bulletin*, 1991, 36: 49-52.

[11] Chen, Y., Z. Li, H. Ye, and Y. Wang. Carbon, oxygen isotopic records on climatic changes in the central Loess Plateau since 130 ka B.P. *Marine Geology and Quaternary Geology*, 1996, 16: 17-22.

[12] Ning, Y., W. Liu, and Z. An. A 130-ka reconstruction of precipitation on the Chinese Loess Plateau from organic carbon isotopes. *Paleogeography, Paleoclimatology, Paleoecology*, 2008, 270: 59-63.

[13] An, Z., Y. Huang, W. Liu, Z. Guo, C. Steven, L. Li, P. Warren, Y. Ning, Y. Cai, W. Zhou, B. Lin, Q. Zhang, Y. Cao, X. Qiang, H. Chang, and Z. Wu. Multiple expansions of C4 plant biomass in East Asia since 7 Ma coupled with strengthened monsoon circulation. *Geology*, 2005, 33: 705-708.

[14] Tang, K., and X. He. Revelation of information on genesis of multi paleosol from quaternary loess profile. *Acta Pedologica Sinica*, 2002, 39: 609-617.

[15] Zhao, Y., F. Wu, and Y. Chi. Application of bulk organic carbon isotope composition for paleoenvironmental research. *Journal of Earth Environment*, 2013, 4: 1519-1530.

[16] Si, B., R. Wen, and J. Xiao. Organic carbon isotope of terrestrial plants and the application to paleoenvironmental research. *China Mining Magazine*, 2007, 16: 100-102.

[17] Wang, G. Application of stable carbon isotope carbon for paleoenvironmental research. *Quaternary Sciences*, 2003, 23: 471-484.