

Is pedogenic carbonate an important atmospheric CO₂ sink?

LIU ZaiHua

The State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

Received June 25, 2010; accepted November 16, 2010; published online April 13, 2011

Nearly 18 years after the proposal of the weathering-related carbon sink concept (Berner R A. Weathering, plants and the long-term carbon cycle. *Geochim Cosmochim Acta*, 1992, 56: 3225–3231), it is an appropriate timing to re-evaluate its geological context with the updated dataset. Ryskov et al. (Ryskov Ya G, Demkin V A, Oleynik S A, et al. Dynamics of pedogenic carbonate for the last 5000 years and its role as a buffer reservoir for atmospheric carbon dioxide in soils of Russia. *Glob Planet Change*, 2008, 61: 63–69) lately claimed that in the course of soil formation for the last 5000 years the soils of Russia fixed atmospheric carbon dioxide as pedogenic carbonate during the arid periods at a rate of 2.2 kg C/(m² a) in chernozem, 1.13 kg C/(m² a) in dark-chestnut soil, 0.86 kg C/(m² a) in light-chestnut soil, on the basis of carbon isotopic data; however, their interpretations of the data do not appear straightforward nor persuading, and thus their claim is likely misleading. Their interpretations are also contrary to the conclusions drawn by Dart et al. (Dart R C, Barovich K M, Chittleborough D J, et al. Calcium in regolith carbonates of central and southern Australia: Its source and implications for the global carbon cycle. *Palaeogeogr Palaeoclimatol Palaeoecol*, 2007, 249: 322–334) who found that Australian regolith carbonates did not capture any additional CO₂; instead the carbonate was simply being remobilized from one pool to another. Here we raise comments to these explanations on the following two issues: (1) origin of pedogenic carbonate: silicate weathering vs. carbonate weathering, and (2) problems in using carbon isotopic technique to distinguish carbonates formed by silicate weathering and carbonate weathering. It is concluded that pedogenic carbonate may not be an important atmospheric CO₂ sink at all, i.e. carbonate weathering-related pedogenic carbonate does not capture any additional CO₂, while the CO₂ capture in silicate weathering-related pedogenic carbonate is small in short-term time scales due to the slow kinetics of silicate weathering.

pedogenic carbonate, carbonate weathering (carbonate dissolution-reprecipitation), silicate weathering, atmospheric CO₂ sink

Citation: Liu Z H. Is pedogenic carbonate an important atmospheric CO₂ sink? *Chinese Sci Bull*, 2011, 56: 3794–3796, doi: 10.1007/s11434-010-4288-8

Soil carbonate is the third largest C pool in the active global carbon cycle, containing 940 Pg C (1 Pg C=10¹⁵ g of carbon) [1], thus exceeding the amount in the atmosphere (740 Pg C) or in land plants (550 Pg C) [2]. Although carbonate dissolution-precipitation (or carbonate weathering) reactions have been understood for over a century, the role of soil carbonate in carbon sequestration, and in particular pedogenic carbonate, is very complex because its formation involves interdependent linkages among climate, plants, microorganisms, and weathering of silicate and carbonate minerals. An understanding of pedogenic carbonate in carbon

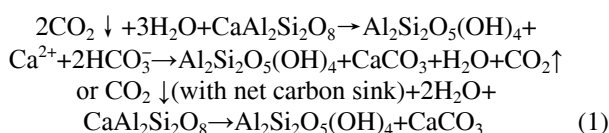
sequestration also requires examination of the system at local to continental scales and at seasonal to millennial time scales.

Ryskov et al. [3] investigated the carbonate deposits in the soils of the Selenga Range and in paleosols buried beneath mounds of various ages on the Russian plain with carbon isotopic technique. They found that all of the soils contained both carbonate remnants inherited from the source rocks and pedogenic carbonates formed during soil formation. The proportions of pedogenic and lithogenic components were calculated from the carbon isotopic composition of soil carbonates. By using radiocarbon dating, they further found that two epochs of carbonate formation

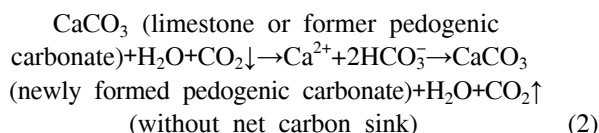
email: liuzaihua@vip.gyig.ac.cn

were clearly manifest in the soils of European Russia. These epochs coincided with the periods of arid climates about 3750 and 2300 years ago. All these seem to be reasonable. However, the other main conclusion of the paper by Ryskov et al. [3], i.e. "In the course of soil formation for the last 5000 years the soils fixed atmospheric carbon dioxide as pedogenic carbonate during the arid periods at a rate of 2.2 kg C/(m² a) in chernozem, 1.13 kg C/(m² a) in dark-chestnut soil, 0.86 kg C/(m² a) in light-chestnut soil", appears misleading because pedogenic carbonates may not capture any additional CO₂; instead the carbonate is simply being remobilised from one pool to another if it is formed by calcite dissolution-precipitation [4,5]. Only by silicate weathering can the thus-formed pedogenic carbonate become a sink of atmospheric CO₂ [6]. Therefore, to understand the origin of pedogenic carbonate is a prerequisite to solve the problem.

Pedogenic carbonate precipitates in the presence of any calcium and bicarbonate ions [7]. The most common source of these ions comes from the weathering byproducts of Ca-silicates and carbonates (e.g. limestone). Weathering of Ca-silicates consumes 1 mol of atmospheric CO₂ for every mol released during the precipitation of pedogenic carbonate [6]. This process sequesters modern atmospheric CO₂ in Ca-silicate-bearing soils, and can be expressed as



This is the theoretical starting point for Ryskov et al. [3] to conclude that the soils sequestered CO₂ from the atmosphere within carbonates and served as an additional sink in the carbon cycle. However, carbonate weathering, or carbonate dissolution-precipitation is an even more important forming mechanism of pedogenic carbonate [4,5,8–11] due to the much quicker kinetics of carbonate dissolution-precipitation (in the order of 10⁻⁶–10⁻⁹ mmol cm⁻² s⁻¹) [12–16], over at least an order of magnitude higher than silicate weathering (in the order of 10⁻¹⁰–10⁻¹⁸ mmol cm⁻² s⁻¹) [5,17–21]. Carbonate dissolution consumes 1 mol of atmospheric CO₂ for every mol dissolved. However, when carbonate reprecipitation as pedogenic carbonate happens 1 mol of CO₂ returns back to the atmosphere for every mol deposited [6]. Therefore, no net atmospheric CO₂ sink exists for this kind of pedogenic carbonate formation. This forming process can be expressed as



According to Ryskov et al.'s data [3] stated in previous section, it is known that the accumulation rate of pedogenic carbonate in soils of Russia was in the order of 10⁻⁷ mmol cm⁻² s⁻¹. This value is much higher than that of silicate

weathering, but just in the range of calcite dissolution-precipitation rate, indicating very likely the carbonate weathering origin of pedogenic carbonate in the soils of Russia. If so, the pedogenic carbonates in the soils of Russia may not capture any additional CO₂.

In open system, like in soil, the isotopic composition of pedogenic carbonate is controlled by the ratio of ¹³C/¹²C of soil CO₂, from which it was formed, and by isotopic fractionation during carbonate precipitation from the soil solution [22–24]. So, it is not possible to use carbon isotopic technique to distinguish the carbonate formed by silicate weathering from that by carbonate weathering, though carbon isotopic technique allows us to discriminate lithogenic from pedogenic carbonates, as Ryskov et al. [3] did. To solve this problem, one may use strontium isotopic technique to separate the calcium from carbonate sources and that from the chemical weathering of silicate minerals [4,5,9–11,24]. For example, Capo and Chadwick [5] investigated the sources of strontium and calcium in a Pleistocene desert soil and calcrete from the USDA-SCS Desert Project area near Las Cruces, NM. They found that strontium isotope values for the labile cations and carbonate from the A, B and K soil horizons had ⁸⁷Sr/⁸⁶Sr values that range from 0.7087 to 0.7093, similar to the values for easily soluble local dust and rain. The parent material, non-calcareous Camp Rice alluvial sediment, had an ⁸⁷Sr/⁸⁶Sr ratio of about 0.7165. Mixing calculations indicated a minimum atmospheric contribution to soil carbonate calcium of ~94%. The variations in ⁸⁷Sr/⁸⁶Sr ratios of soil silicate (0.7131 to 0.7173) were consistent with weathering of volcanogenic sediments and neoformation of clay minerals in the petrocalcic horizon. They further concluded that both the present-day and long-term contribution of calcium from silicate weathering is less than 2% of that supplied from the atmosphere, and confirm that desert soil formation is not a significant sink for atmospheric carbon. Similar conclusions were also made by Chiquet et al. [9] in Central Spain and Hamidi et al. [10] in the Moroccan Middle Atlas. Another important example is the work by Dart et al. [4] who studied the calcium in regolith carbonates of central and southern Australia. They used Sr isotopes to investigate the source of the Ca in regolith carbonates that cover approximately 1.6×10⁶ km² of inland Australia. It was found that ⁸⁷Sr/⁸⁶Sr ratios for nearly all the carbonates were in the range 0.7094 to 0.7211. Their results show that only about 10% of the Ca in regolith carbonates was derived from weathered bedrock, with the remaining component being derived from an external marine source. Therefore, despite the immense area covered, Australian regolith carbonates did not capture any additional CO₂; instead the carbonate was simply being remobilized from one pool (marine) to another (terrestrial) [4].

We have addressed that pedogenic carbonate can be of both silicate-weathering origin and carbonate-weathering origin. If it is carbonate-weathering origin, pedogenic

carbonate does not capture any additional CO₂. If it is silicate-weathering origin, the CO₂ capture in pedogenic carbonate is small in short-term time scales due to the slow kinetics of silicate weathering.

In a word, all lines of evidence presented by Ryskov et al. [3] cannot lead to their conclusion that the soils sequestered large CO₂ from the atmosphere within carbonates and served as an additional important sink in the carbon cycle. Instead, pedogenic carbonates may not capture any additional CO₂; instead the carbonate is simply being remobilised from one pool to another [4,5,9–11].

This work was supported by the Hundred Talents Program of the Chinese Academy of Sciences and the National Natural Science Foundation of China (40872168).

- 1 Eswaran H, Reich P F, Kimble J M, et al. Global carbon stocks. In: Lal R, Kimble J M, Eswaran H, et al., eds. *Global Climate Change and Pedogenic Carbonates*. Boca Raton: Lewis Publishers, 1999. 15–25
- 2 Schlesinger W H. *Biochemistry: An Analysis of Global Change*. 2nd ed. New York: Academic Press, 1997
- 3 Ryskov Ya G, Demkin V A, Oleynik S A, et al. Dynamics of pedogenic carbonate for the last 5000 years and its role as a buffer reservoir for atmospheric carbon dioxide in soils of Russia. *Glob Planet Change*, 2008, 61: 63–69
- 4 Dart R C, Barovich K M, Chittleborough D J, et al. Calcium in regolith carbonates of central and southern Australia: Its source and implications for the global carbon cycle. *Palaeogeogr Palaeoclimatol Palaeoecol*, 2007, 249: 322–334
- 5 Capo R C, Chadwick O A. Sources of strontium and calcium in desert soil and calcrete. *Earth Planet Sci Lett*, 1999, 170: 61–72
- 6 Berner R A. Weathering, plants and the long-term carbon cycle. *Geochim Cosmochim Acta*, 1992, 56: 3225–3231
- 7 Salomons W, Goudie A, Mook W G. Isotopic composition of calcrete deposits from Europe, Africa and India. *Earth Surface Proc Landforms*, 1978, 3: 43–57
- 8 Salomons W, Mook W G. Isotope geochemistry of carbonate dissolution and re-precipitation in soils. *Soil Sci*, 1976, 122: 15–24
- 9 Chiquet A, Michard A, Nahon D, et al. Atmospheric input vs. *in situ* weathering in the genesis of calcretes: An Sr isotope study at Galvez (Central Spain). *Geochim Cosmochim Acta*, 1999, 63: 311–323
- 10 Hamidi E M, Colin F, Michard A, et al. Isotopic tracers of the origin of Ca in a carbonate crust from the Middle Atlas, Morocco. *Chem Geol*, 2001, 176: 93–104
- 11 Van der Hoven S J, Quade J. Tracing spatial and temporal variations in the sources of calcium in pedogenic carbonates in a semiarid environment. *Geoderma*, 2002, 108: 259–276
- 12 Dreybrodt W. *Processes in Karst Systems-Physics, Chemistry, and Geology*. Heidelberg: Springer, 1988
- 13 Liu Z, Svensson U, Dreybrodt W, et al. Hydrodynamic control of inorganic calcite precipitation in Huanglong Ravine, China: Field measurements and theoretical prediction of deposition rates. *Geochim Cosmochim Acta*, 1995, 59: 3087–3097
- 14 Liu Z, Dreybrodt W. Dissolution kinetics of calcium carbonate minerals in H₂O-CO₂ solutions in turbulent flow: The role of the diffusion boundary layer and the slow reaction H₂O+CO₂=H⁺+HCO₃⁻. *Geochim Cosmochim Acta*, 1997, 61: 2879–2889
- 15 Liu Z H, Wolfgang D, Wang H J. A possible important CO₂ sink by the global water cycle. *Chinese Sci Bull*, 2008, 53: 402–407
- 16 Liu Z, Sun H, Lu B, et al. Wet-dry seasonal variations of hydrochemistry and carbonate precipitation rates in a travertine-depositing canal at Baishuitai, Yunnan, SW China: Implications for the formation of biannual laminae in travertine and for climatic reconstruction. *Chem Geol*, 2010, 273: 258–266
- 17 White A F, Brantley S L. *Chemical Weathering Rates of Silicate Minerals: Reviews in Mineralogy*. Washington D C: Mineralogical Society of America, 1995
- 18 White A F, Blum A E, Schulz M S, et al. Chemical weathering rates of a soil chronosequence on granitic alluvium: I. Quantification of mineralogical and surface area changes and calculation of primary silicate reaction rates. *Geochim Cosmochim Acta*, 1996, 60: 2533–2550
- 19 White A F, Bullen T D, Schulz M S, et al. Differential rates of feldspar weathering in granitic regoliths. *Geochim Cosmochim Acta*, 2001, 65: 847–869
- 20 Berg A, Banwart S A. Carbon dioxide mediated dissolution of Ca-feldspar: Implications for silicate weathering. *Chem Geol*, 2000, 163: 25–42
- 21 Hilley G E, Chamberlain C P, Moon S, et al. Competition between erosion and reaction kinetics in controlling silicate-weathering rates. *Earth Planet Sci Lett*, 2010, 293: 191–199
- 22 Deines P, Langmuir D, Harmon R S. Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate waters. *Geochim Cosmochim Acta*, 1974, 38: 1147–1164
- 23 Cerling T E. The stable isotopic composition of modern soil carbonate and its relation to climate. *Earth Planet Sci Lett*, 1984, 71: 229–240
- 24 Quade J, Chivas A R, McCulloch M T. Strontium and carbon isotope tracers and the origins of soil carbonate in South Australia and Victoria. *Palaeogeogr Palaeoclimatol Palaeoecol*, 1995, 113: 103–117

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.