

## Abiotic CO<sub>2</sub> uptake from the atmosphere by semiarid desert

## soil and its partitioning into soil phases

Jiabin Liu<sup>1</sup>, Keyu Fa<sup>1</sup>, Yuqing Zhang<sup>1</sup>, Bin Wu<sup>1</sup>, Shugao Qin<sup>1</sup>, and Xin Jia<sup>1</sup> <sup>1</sup>Yanchi Research Station, School of Soil and Water Conservation, Beijing Forestry University, Beijing, China

摘要:沙漠可表现出强烈的CO<sub>2</sub>通量下降的特性,这就是显著的碳沉降。然而,由于无法 确定通量测量的稳定性和准确的碳固定地点,这种假设受到强烈的挑战。本研究中,我们在 中国北方的毛乌素沙漠中向自然(未杀菌的)土壤中添加<sup>13</sup>CO<sub>2</sub>,并量化固相土壤和气相中 所添加的<sup>13</sup>CO<sub>2</sub>比例。结果显示自然沙漠土壤吸收<sup>13</sup>CO<sub>2</sub>的平均速率为0.28 gm<sup>-2</sup> d<sup>-1</sup>.在 被吸收的<sup>13</sup>CO<sub>2</sub>中,气相中占0.0007%,然而,被吸收的20.0%的<sup>13</sup>CO<sub>2</sub>未被检测到。这 些结果显示未受干扰的沙漠能够从大气中吸收CO<sub>2</sub>,多数被固定的碳被存储在土壤固相中。

Abstract Deserts may show strong downward CO2 fluxes and thus could be a significant carbon sink. However, this hypothesis has been strongly challenged because of the failure to determine both the reliability of flux measurements and the exact location of fixed carbon. In this study, we added <sup>13</sup>CO<sub>2</sub> to natural (unsterilized) soil in the Mu Us Desert in northern China and quantified the partitioning of added 13CO2 into soil solid and vapor phases. Results show that natural desert soil absorbed 13CO2 at a mean rate of 0.28 gm\_2 d\_1. Of the absorbed 13CO2, 7.1% was released over a 48 h period after 13CO2 feeding, 72.8% was stored in the soil solid phase, 0.0007% was found in the vapor phase, while 20.0% of the absorbed 13CO2 was undetected. These results indicate that undisturbed desert soils can absorb CO2 from the atmosphere, with the majority of fixed carbon conserved in the soil solid phase.

【小编注:本文中使用美国LGR公司的CO2同位素分析仪测量δ<sup>13</sup>C和<sup>12</sup>CO2 与 <sup>13</sup>CO2的浓度值,并与LI-COR公司的LI-8100-103土壤呼吸室连用,测量土壤<sup>13</sup>CO2的通量,这是在国内及国际上比较新颖的仪器应用方式,值得借鉴。】

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#### **Key Points:**

- We added <sup>13</sup>CO<sub>2</sub> to natural (unsterilized) desert soil
- Soil absorbed <sup>13</sup>CO<sub>2</sub> at a mean rate of  $0.28 g m^{-1} d^{-1}$
- The majority of fixed carbon was conserved in the soil solid phase

#### Supporting Information:

Tables S1–S3

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## Abiotic CO<sub>2</sub> uptake from the atmosphere by semiarid desert soil and its partitioning into soil phases

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**Abstract** Deserts may show strong downward CO<sub>2</sub> fluxes and thus could be a significant carbon sink. However, this hypothesis has been strongly challenged because of the failure to determine both the reliability of flux measurements and the exact location of fixed carbon. In this study, we added  $^{13}CO_2$  to natural (unsterilized) soil in the Mu Us Desert in northern China and quantified the partitioning of added  $^{13}$ CO<sub>2</sub> into soil solid and vapor phases. Results show that natural desert soil absorbed  $^{13}$ CO<sub>2</sub> at a mean rate of 0.28 g m<sup>-2</sup> d<sup>-1</sup>. Of the absorbed  ${}^{13}$ CO<sub>2</sub>, 7.1% was released over a 48 h period after  ${}^{13}$ CO<sub>2</sub> feeding, 72.8% was stored in the soil solid phase, 0.0007% was found in the vapor phase, while 20.0% of the absorbed <sup>13</sup>CO<sub>2</sub> was undetected. These results indicate that undisturbed desert soils can absorb CO<sub>2</sub> from the atmosphere, with the majority of fixed carbon conserved in the soil solid phase.

#### 1. Introduction

Dry lands, including desert and semiarid ecosystems, cover about 41% of Earth's land surface [Delgado-Baquerizo et al., 2013; Reynolds et al., 2007]. Desert ecosystems have been considered a possible hidden loop in the global carbon cycle [Stone, 2008]. Early studies reported that net ecosystem CO<sub>2</sub> exchange (NEE) in some deserts in North America was similar to that occurring in temperate forests [Hastings et al., 2005; Jasoni et al., 2005; Wohlfahrt et al., 2008], but these results have been strongly debated [Schlesinger et al., 2009]. Carbon accretion in deserts has traditionally been attributed to primary productivity of desert plants or cryptobiotic crusts [Emmerich, 2003]. However, many reported NEE values are significantly higher than local net primary production (NPP) typical of deserts [Chew and Chew, 1965; Whittaker and Niering, 1975]. This discrepancy between NEE and NPP implies that there may be abiotic CO<sub>2</sub> fixation processes other than photosynthesis taking place in desert ecosystems.

With respect to abiotic carbon fixation, it has frequently been observed that alkaline soils can absorb CO<sub>2</sub> from the atmosphere [Ball et al., 2009; Fa et al., 2015; Liu et al., 2015; Ma et al., 2013; Parsons et al., 2004; Xie et al., 2009; Yates et al., 2013]; this may be an overlooked process, which could potentially explain the observed discrepancy. However, this abiotic CO<sub>2</sub> influx has not been completely accepted as a wellvalidated pattern of carbon fixation [Eshel et al., 2007; Schlesinger et al., 2009; Serrano-Ortiz et al., 2010; Walvoord et al., 2005]. Many of these authors have been asked to reconfirm their flux measurements and present a logical answer to the question of where the carbon goes [Schlesinger et al., 2009]. When taking into account the vast areas associated with deserts and semiarid ecosystems, studies of abiotic carbon absorption have been relatively few, suggesting that net CO<sub>2</sub> absorption may only happen occasionally. Furthermore, the downward CO<sub>2</sub> fluxes have been captured both on natural (undisturbed) soils [Ma et al., 2014; Parsons et al., 2004; Yates et al., 2013] and sterilized soils [Fa et al., 2015; Liu et al., 2015; Ma et al., 2013]. These results, indicative of abiotic CO<sub>2</sub> fluxes, need to be reconfirmed, especially for the results from sterilized soils, because sterilization with steam may affect the accuracy of net abiotic carbon absorption [Schlesinger et al., 2009; Stone, 2008]. More importantly, the fate of the absorbed CO<sub>2</sub> in soil is largely unknown and needs to be explicitly examined in order to understand the long-term consequence of abiotic carbon absorption [Ma et al., 2014; Serrano-Ortiz et al., 2010; Stone, 2008]. Whether the absorbed CO<sub>2</sub> in soil is released into the atmosphere again or it is preserved in the soil, long term remains unknown. This information is essential for validating the existence of this abiotic CO<sub>2</sub> absorption process and confirming the stability of absorbed CO<sub>2</sub>. Currently, there is little information on the partitioning of CO<sub>2</sub> in desert soil phases.

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Table 1.	Soil Properties (0-15 cm Depth)
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Soil Property	Value
Bulk density (g cm <sup>-3</sup> )	$1.54 \pm 0.02$
Total porosity (%)	42 ± 3
Soil organic carbon (mg kg $^{-1}$ )	1125.4 ± 126
Soil inorganic carbon (mg kg <sup>-1</sup> )	3775.6 ± 142
pH	$8.60\pm0.06$
Electrical conductivity (dS $m^{-1}$ )	$4.84 \pm 0.42$
$CO_3^{2-}$ (cmol kg <sup>-1</sup> )	$0.04 \pm 0.01$
$HCO_3^{-1}$ (cmol kg <sup>-1</sup> )	$0.45 \pm 0.03$
$CI^{-}$ (cmol kg <sup>-1</sup> )	$0.22 \pm 0.03$
$Mg^{2+}$ (cmol kg <sup>-1</sup> )	$0.48\pm0.04$
$Ca^{2+}$ (cmol kg <sup>-1</sup> )	$5.21 \pm 0.18$
$K^+$ (cmol kg <sup>-1</sup> )	$0.58 \pm 0.05$
$Na^+$ (cmol kg <sup>-1</sup> )	41.23 ± 3.12

In this study, we added <sup>13</sup>CO<sub>2</sub> to natural soil and quantified the partitioning of added <sup>13</sup>CO<sub>2</sub> into soil solid and vapor phases in the Mu Us Desert, northwest China. Our objectives were to test whether natural alkaline desert soils can sequester CO<sub>2</sub> from the atmosphere and reveal the exact location of absorbed carbon.

### 2. Materials and Methods 2.1. Site Description

The study site is located at the Yanchi Research Station, Ningxia Province,

China (37°48'N, 107°22'E), on the southwest edge of the Mu Us Desert. The research site has a temperate continental monsoon climate with 275 mm (1954–2013) mean annual precipitation and 7°C mean annual temperature. Elevation is 1550 m above sea level. Average relative humidity is 51%, and the frost-free period lasts 128 days [Liu et al., 2015]. The soil type is aripsamment; soil properties are given in Table 1. The vegetation at the site is dominated by Artemisia ordosica, Astragalus mongolicum, Salix psammophila, and *Tamarix chinensis* (canopy coverage  $\leq$  30%).

## 2.2. <sup>13</sup>CO<sub>2</sub> Addition and Detection Experiment

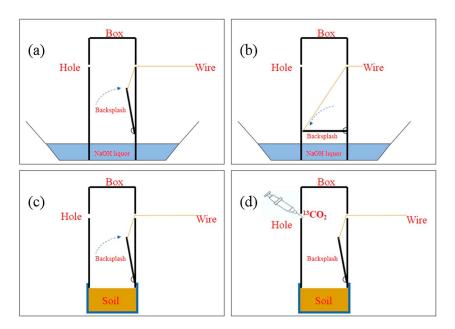
#### 2.2.1. <sup>13</sup>CO<sub>2</sub> Addition

In the study site, a sample plot (100 m  $\times$  100 m) was randomly selected to conduct  ${}^{13}CO_2$  experiments. Six square collars (25 cm long, 25 cm wide, and 20 cm high; no top and bottom) constructed with steel sheets (0.5 cm thick) were inserted into the soil, with 2 cm exposed above the soil surface. The collars were excavated with intact soil; the bottoms were sealed immediately with steel sheets to avoid gas leakage, and the sealed collars with intact soil were backfilled in the original positions to equilibrate them with the surroundings. For the six placed collars, three collars were prepared to be covered with steel boxes and to be added <sup>13</sup>CO<sub>2</sub>. The remaining three collars were not covered with boxes and left untreated; they were used as the control for measuring soil  ${}^{13}$ CO<sub>2</sub> flux and analyzing  $\delta^{13}$ C of soil solid and vapor phases.

Three steel boxes (25 cm long, 25 cm wide, and 70 cm high) with no bottoms were prepared, with each box having a 5 mm diameter hole on its lateral side. One side of a steel square backsplash (24.8 cm long and 24.8 cm wide) was set on the internal side of the box (50 cm away from the top) using a hinge. One side of the backsplash was connected with one end of a soft wire (1 m long), and the other end of the line crossed the hole of the box and was held outside to control the backsplash. The three boxes were immersed in NaOH liquor (5 mol L<sup>-1</sup>) up to 2 cm to eliminate CO<sub>2</sub>, when the backsplashes were pulled up (Figure 1a). Two hours later, the backsplashes were slowly put back down (Figure 1b). The space above the boxes was closed to avoid atmospheric CO<sub>2</sub> invasion during transfer of the boxes to the square collars. After the boxes were placed on three random square collars and pushed 15 cm deep into the soil, the backsplashes were slowly pulled up to allow for the CO<sub>2</sub> exchange between the soil and the head space of the box (Figure 1c). A 150 mL syringe was used to extract 140 mL of gas, which was injected into a carbon dioxide isotope analyzer Model CCIA-EP (912-0003; Los Gatos Research, Mountain View, CA, USA) to measure initial <sup>12</sup>CO<sub>2</sub> concentration. A quantity (10 mL) of <sup>13</sup>CO<sub>2</sub> (concentration: >99.99%) was injected into each box (Figure 1d), and the initial  $^{13}CO_2$  concentration in the box was 295.34  $\mu$ mol mol $^{-1}$ . The hole was immediately sealed with glass cement, when <sup>13</sup>CO<sub>2</sub> injection was completed. After 24 h, 140 mL mixed gas from each box was injected into the Model CCIA-EP to analyze final <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> concentrations.

#### 2.2.2. Soil <sup>13</sup>CO<sub>2</sub> Flux Measurements

Each box was removed from the square collar after gas extraction. A PVC collar (20.3 cm diameter and 20 cm high) was inserted 2 cm into the soil in each of the six square collars. The Model CCIA-EP was connected with a LI-8100-103 chamber (LI-COR Environmental), and the chamber was fitted with a PVC collar to measure the  $^{13}$ CO<sub>2</sub> flux for soil with added  $^{13}$ CO<sub>2</sub> and for the control soil. The  $^{13}$ CO<sub>2</sub> flux was measured for 5 min every 2 h over 48 h.



**Figure 1.** Schematic diagram of <sup>13</sup>CO<sub>2</sub> addition ((a) the original CO<sub>2</sub> in the box was eliminating by NaOH liquor; (b) backsplash was put back down to avoid atmospheric CO<sub>2</sub> invasion during the boxes being transferred; (c) the backsplash was pulled up to keep the inside space of the box through up and down, after the box was placed on collar; and (d) <sup>13</sup>CO<sub>2</sub> was injected into the box placed on collar).

#### 2.2.3. $\delta^{13}\text{C}$ Analyses of Soil Solid and Vapor Phases

After measurement of the soil  ${}^{13}$ CO<sub>2</sub> flux, a 250 mL gas sample was collected from each of the six square collars using a soil gas sampler (DIK-5520-13; Daiki Rika Kogyo, Saitama, Japan); samples were placed in aluminum foil bags. From each aluminum foil bag, 140 mL of gas was extracted using a syringe, with these injected into the Model CCIA-EP to measure  $\delta^{13}$ C for the vapor phase. A 50 g soil sample from each of the six square collars was collected to determine  $\delta^{13}$ C for the solid phase after soil gas sample collection. All the soil samples (both deriving from  ${}^{13}$ CO<sub>2</sub> treated soils and control soils) were treated with 5.25% sodium hypochlorite for 15 days to remove organic matter [*Landi et al.*, 2003] and then dried at 72°C for 8 h. All the soil samples were ground and sieved to <0.075 mm for analysis of  ${}^{13}$ C abundance. The method for determining  $\delta^{13}$ C in the soil solid phase is described in *Nordt et al.* [1998]. The process of adding  ${}^{13}$ CO<sub>2</sub>, for a total of 21 data sets.

#### 2.3. Data Processing and Analysis

The absorbed <sup>13</sup>CO<sub>2</sub> within the square collar was calculated as follows:

$$M = \frac{(C_{\text{final}} - C_{\text{initial}}) \times V_{\text{box}} \times S}{R_t \times 1000}$$
(1)

where *M* is total absorbed <sup>13</sup>CO<sub>2</sub> (mg),  $C_{\text{final}}$  is final <sup>13</sup>CO<sub>2</sub> concentration (µmol mol<sup>-1</sup>),  $C_{\text{initial}}$  is initial <sup>13</sup>CO<sub>2</sub> concentration (µmol mol<sup>-1</sup>),  $V_{\text{box}}$  is the volume of the box exposing above the soil surface (L), *S* is relative molecular mass of <sup>13</sup>CO<sub>2</sub> (g mol<sup>-1</sup>), and  $R_t$  is the molar volume of gas (L mol<sup>-1</sup>).s

Soil <sup>13</sup>CO<sub>2</sub> flux was calculated as follows:

$$Flux = \frac{d^{13}CO_2}{dt} \times \frac{PV}{ART} \times \frac{1 \ L^{13}CO_2}{10^6 \ \mu L^{13}CO_2} \times \frac{13 \ g \ C}{mol^{13}CO_2} \times \frac{3600 \ s}{h}$$
(2)

where  $d^{13}CO_2/dt$  is the slope of change in  ${}^{13}CO_2$  concentration over time ( $\mu LCO_2 Lair^{-1} s^{-1}$ ), *P* is atmospheric pressure (atm), *V* is chamber volume, *T* is air temperature (K), *A* is the collar surface area (0.03245 m<sup>2</sup>), and *R* is the universal gas constant (0.08206 Latm mol<sup>-1</sup> K<sup>-1</sup>). The flux is in units of mg C m<sup>-2</sup> h<sup>-1</sup>. The chamber volume is the sum of the collar volume and the chamber cap volume [*Savage et al.*, 2008].

The <sup>13</sup>CO<sub>2</sub> emitted from soil following addition of <sup>13</sup>CO<sub>2</sub> was calculated as follows:

$$M_{\text{emitted}} = \frac{\sum F_{\text{added}} - \sum F_{\text{control}}}{24 \text{ h}} \times 48 \text{ h}$$
(3)

where  $M_{\text{emitted}}$  is total <sup>13</sup>CO<sub>2</sub> emitted from the soil following addition of <sup>13</sup>CO<sub>2</sub> (mg),  $F_{\text{added}}$  is the <sup>13</sup>CO<sub>2</sub> flux for soil with added <sup>13</sup>CO<sub>2</sub> (C m<sup>-2</sup> h<sup>-1</sup>), and  $F_{\text{control}}$  is the <sup>13</sup>CO<sub>2</sub> flux for the control soil (C m<sup>-2</sup> h<sup>-1</sup>).

The  ${}^{13}CO_2$  absorbed into the soil solid phase within the square collar was calculated as follows:

$$M_{\text{solid}} = C_{\text{SIC}} \times B \times V \times \left[ \frac{(1000 + \delta^{13} C_{\text{added}}) \times R_{\text{st}}}{1000 + (1000 + \delta^{13} C_{\text{added}}) \times R_{\text{st}}} - \frac{(1000 + \delta^{13} C_{\text{control}}) \times R_{\text{st}}}{1000 + (1000 + \delta^{13} C_{\text{control}}) \times R_{\text{st}}} \right] \times 1000 \quad (4)$$

where  $M_{\text{solid}}$  is total <sup>13</sup>CO<sub>2</sub> stored in the soil solid phase,  $C_{\text{SIC}}$  is the SIC content (g kg<sup>-1</sup>), *B* is bulk density (g cm<sup>-3</sup>), *V* is the volume of soil in the square collar (cm<sup>3</sup>),  $\delta^{13}C_{\text{added}}$  is the  $\delta^{13}C$  value for the soil solid phase with added <sup>13</sup>CO<sub>2</sub>, and  $\delta^{13}C_{\text{control}}$  is the  $\delta^{13}C$  value for the soil solid phase in the control.  $R_s = {}^{13}C/{}^{12}C$  and  $R_{\text{st}}$  correspond to the stable isotope ratio in the reference standard [*Friedman and O'Neil*, 1977].

The  ${}^{13}CO_2$  absorbed into the soil vapor phase in the square collar was calculated as per equation (5) below:

$$M_{\text{vapor}} = C_{\text{CO}_2} \times P_{\text{soil}} \times V \times \left[ \frac{(1000 + \delta^{13}\text{C}_{\text{added}}) \times R_{\text{st}}}{1000 + (1000 + \delta^{13}\text{C}_{\text{added}}) \times R_{\text{st}}} - \frac{(1000 + \delta^{13}\text{C}_{\text{control}}) \times R_{\text{st}}}{1000 + (1000 + \delta^{13}\text{C}_{\text{control}}) \times R_{\text{st}}} \right] \times 1000 \quad (5)$$

where  $M_{vapor}$  is total <sup>13</sup>CO<sub>2</sub> stored in the soil vapor phase,  $P_{soil}$  is soil porosity, V is the volume of soil within the square collar (cm<sup>3</sup>),  $\delta^{13}C_{added}$  is the  $\delta^{13}C$  value for soil with added <sup>13</sup>CO<sub>2</sub>, and  $\delta^{13}C_{control}$  is the  $\delta^{13}C$  value for the control soil.

One-way analysis of variance was used to test for differences in  $\delta^{13}$ C for soil solid and vapor phases between soil with added  $^{13}$ CO<sub>2</sub> and the control soil. Descriptive statistics were used to calculate averages and standard deviations of data for each set of replicates. All of the above statistical analyses were conducted in MATLAB 7.11.0 (R2010b; The Mathworks Inc., Natick, MA, USA).

#### 3. Results

#### 3.1. <sup>13</sup>CO<sub>2</sub> Absorption Rate

After  ${}^{13}\text{CO}_2$  was injected into the box, the initial  ${}^{12}\text{CO}_2$  and  ${}^{13}\text{CO}_2$  concentrations in the box were 156.19 µmol mol<sup>-1</sup> and 295.34 µmol mol<sup>-1</sup>, respectively, and total CO<sub>2</sub> concentration ( ${}^{12}\text{CO}_2 + {}^{13}\text{CO}_2$ ) was 454.53 µmol mol<sup>-1</sup>. After 24 h, the final  ${}^{12}\text{CO}_2$  and  ${}^{13}\text{CO}_2$  concentrations in the box were 499.67 µmol mol<sup>-1</sup> and 44.75 µmol mol<sup>-1</sup>, respectively, and  ${}^{13}\text{CO}_2$  had reduced by 250.59 µmol mol<sup>-1</sup>. Natural soil with an area of 625 cm<sup>2</sup> absorbed 17.3 mg  ${}^{13}\text{CO}_2$  d<sup>-1</sup>, corresponding to a  ${}^{13}\text{CO}_2$  absorption rate of 0.28 g m<sup>-2</sup> d<sup>-1</sup>.

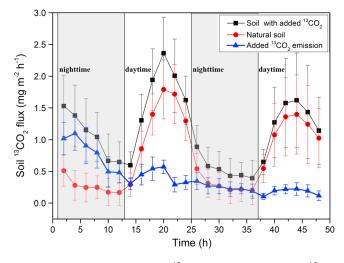
#### 3.2. Emission of Absorbed <sup>13</sup>CO<sub>2</sub>

The emission rate of added  ${}^{13}$ CO<sub>2</sub> decreased from 1.0183 mg m<sup>-2</sup> h<sup>-1</sup> after 1 h to 0.2 mg m<sup>-2</sup> h<sup>-1</sup> after 36 h and further to 0.1 mg m<sup>-2</sup> h<sup>-1</sup> after 48 h (Figure 2). Over 48 h,  ${}^{13}$ CO<sub>2</sub> emitted from the square collar totaled 1.2308 mg, accounting for 7.1% of absorbed  ${}^{13}$ CO<sub>2</sub> (17.3 mg).

#### 3.3. Partitioning of Absorbed <sup>13</sup>CO<sub>2</sub> Into Soil Vapor and Solid Phases

 $\delta^{13}$ C for the soil solid phase with added  ${}^{13}$ CO<sub>2</sub> was -1.9% (Figure 3a), significantly greater than for the control soil (n = 21, p < 0.05). The percentage of  ${}^{13}$ C in soil inorganic carbon (SIC) was 1.1091% for soil with added  ${}^{13}$ CO<sub>2</sub> and 1.1036% for control soil. SIC content was 3775.6 mg kg<sup>-1</sup>;  ${}^{13}$ C in the square collar totaled 0.7349 g for soil with added  ${}^{13}$ CO<sub>2</sub> and 0.7313 g for control soil. Added  ${}^{13}$ C stored in the soil solid phase in the square collar was therefore 3.6411 mg (12.6038 mg  ${}^{13}$ CO<sub>2</sub>), accounting for 72.8% (Figure 4) of absorbed  ${}^{13}$ CO<sub>2</sub> (17.3 mg).

The  $\delta^{13}$ C for the soil vapor phase with added  ${}^{13}$ CO<sub>2</sub> was -7.8% (Figure 3b), significantly greater than for the control soil (n = 21, p < 0.05). The percentage of  ${}^{13}$ C of total CO<sub>2</sub> ( ${}^{12}$ CO<sub>2</sub> +  ${}^{13}$ CO<sub>2</sub>) was 1.1027% for soil with added  ${}^{13}$ CO<sub>2</sub> and 1.0998% for the control soil. The total CO<sub>2</sub> ( ${}^{12}$ CO<sub>2</sub> +  ${}^{13}$ CO<sub>2</sub>) concentration was 473 µmol mol<sup>-1</sup>, and  ${}^{13}$ C in the square collar was 48.4072 µg for soil with added  ${}^{13}$ CO<sub>2</sub> and 48.2817 µg for the control soil. Added  ${}^{13}$ CO<sub>2</sub> stored in the soil vapor phase was therefore 0.1254 µg, accounting for



**Figure 2.** Temporal variations in soil <sup>13</sup>CO<sub>2</sub> fluxes of soil with added <sup>13</sup>CO<sub>2</sub> and natural soil within 48 h after addition of <sup>13</sup>CO<sub>2</sub> (mean ± standard deviation (SD), n = 21). Added <sup>13</sup>CO<sub>2</sub> emission is the difference between soil with added <sup>13</sup>CO<sub>2</sub> and natural soil. The shadow and white areas in the figure represented the nighttime and the daytime, respectively.

0.0007% (Figure 4) of absorbed  ${}^{13}CO_2$  (17.3 mg). It should be noted that 20.0% of the absorbed  ${}^{13}CO_2$  was not detected in our study.

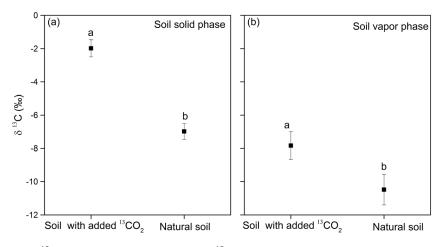
## 4. Discussion 4.1. Abiotic CO<sub>2</sub> Absorption by Natural Desert Soil

Natural soil from our study site sequestered CO<sub>2</sub> at a rate of  $0.28 \text{ g m}^{-2} \text{ d}^{-1}$ . Similar negative net CO<sub>2</sub> exchange rates were found in northern China [*Xie et al.*, 2009] and North America [*Yates et al.*, 2013] between sterilized alkaline soils and the atmosphere. Net CO<sub>2</sub> absorption was detected both on natural and sterilized soil, indicating that CO<sub>2</sub> absorption is an actual function of alkaline soils. The <sup>13</sup>CO<sub>2</sub> absorption rate in this study was lower than those reported previously

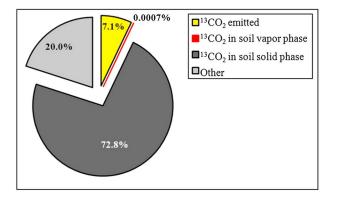
[Xie et al., 2009; Yates et al., 2013], likely as a result of differences in soil property (i.e., pH and electrical conductivity) among study sites. Additionally, the box used in this study was closed and not large enough to supply sufficient  ${}^{13}CO_2$ , which may have also decreased the carbon absorption rate. A higher box was not used in this study, because  ${}^{13}CO_2$  may accumulate at the bottom of the box and elevate the  ${}^{13}CO_2$  concentration on surface soils. Future research may be able to include a design with a height allowing a sufficient supply of  ${}^{13}CO_2$  without increasing  ${}^{13}CO_2$  concentration at the bottom.

#### 4.2. Location of the Absorbed Carbon

After <sup>13</sup>CO<sub>2</sub> was added, the majority of <sup>13</sup>CO<sub>2</sub> was observed in the soil solid phase (Figure 4). Even if some of the added <sup>13</sup>CO<sub>2</sub> may initially adhere to soil particle surfaces, this was cleared prior to measurement of  $\delta^{13}$ C. Soil was immersed in sodium hypochlorite liquor to eliminate organic carbon, and this alkaline liquor can sequester <sup>13</sup>CO<sub>2</sub> on the soil particle surface. In addition, the higher  $\delta^{13}$ C observed in soil with added <sup>13</sup>CO<sub>2</sub> could not have been due to carbonate recrystallization, because recrystallization of carbonates is a very slow process (occurring over centuries or millennia) [*Ryskov et al.*, 2008]. On a short time scale, the quantity of recrystallized carbonate would be very small and could only be detected with <sup>14</sup>C labeling [*Gocke et al.*, 2010, 2011; *Gocke and Kuzyakov*, 2011]. Ruling out surface adhesion of CO<sub>2</sub> onto soil minerals and carbonate



**Figure 3.** (a and b) <sup>13</sup>C abundance (‰) in soil with added <sup>13</sup>CO<sub>2</sub> and natural soil (mean ± SD, n = 21, p < 0.05).



recrystallization, we speculate that the absorbed carbon may become part of newly formed matter and be conserved in certain minerals (quartz, calcite, plagioclase, and potash feldspar) of the solid phase. This could be the subject of future studies. The <sup>13</sup>CO<sub>2</sub> stored in the solid phase should be relatively stable. Since added <sup>13</sup>CO<sub>2</sub> was still preserved in the soil solid phase after immersion in sodium hypochlorite liquor and drying, this implies that it could not be easily removed with variations in soil water or temperature. The results of soil <sup>13</sup>CO<sub>2</sub> fluxes following <sup>13</sup>CO<sub>2</sub> addition also sug-

**Figure 4.** Distribution of adsorbed  ${}^{13}CO_2$  in the soil phases. (Other represents added  ${}^{13}CO_2$  that was not accounted for in our study.)

gest that the <sup>13</sup>CO<sub>2</sub> conserved in the solid phase may be stable (Figure 4). Although the intensity of <sup>13</sup>CO<sub>2</sub> emissions was initially large, it decreased to 0.1 mg m<sup>-2</sup> h<sup>-1</sup> after 48 h and subsequently declined further (Figure 2). Within the initial 48 h after <sup>13</sup>CO<sub>2</sub> addition, emitted CO<sub>2</sub> only accounted for 7.1% of absorbed <sup>13</sup>CO<sub>2</sub>. After 48 h, the <sup>13</sup>CO<sub>2</sub> emission rate was too low to induce substantial erosion of added <sup>13</sup>CO<sub>2</sub> over a long period. The partitioning of absorbed CO<sub>2</sub> into soil solid and vapor phases in our study therefore indicated that the exact location of absorbed carbon should be in the soil solid phase and that abiotic carbon sequestration is a nontrivial process within the carbon cycle of desert ecosystems.

The result that the majority of absorbed  ${}^{13}CO_2$  was fixed in the soil solid phase may help to improve understanding of the mechanism of abiotic CO<sub>2</sub> absorption. Most previous studies found that soil absorbed a substantial amount of atmospheric CO<sub>2</sub> at night, while acting as a weak CO<sub>2</sub> source during the day [*Liu et al.*, 2015; *Ma et al.*, 2013; *Parsons et al.*, 2004; *Xie et al.*, 2009; *Yates et al.*, 2013]. The phenomenon can be interpreted as dissolution and exsolution of CO<sub>2</sub>, modified by temperature [*Liu et al.*, 2015; *Ma et al.*, 2013; *Shanhun et al.*, 2012]. Synthesizing our results and the literatures, the mechanism of abiotic CO<sub>2</sub> absorption can be inferred and described as follows: Atmospheric CO<sub>2</sub> enters the soil and dissolves in soil water, and most of the dissolved CO<sub>2</sub> returns to the atmosphere when the temperature increases. The remaining dissolved CO<sub>2</sub> reacts with some matters in the soil and is stored in the soil solid phase. Even though it remains unknown how CO<sub>2</sub> is sequestered in the solid phase, our finding that the majority of dissolved CO<sub>2</sub> was fixed in the solid phase at least verifies that such a process indeed occurs. We further estimate that the 20.0% of absorbed  ${}^{13}CO_2$  that remained undetected (Figure 4) was conserved in soil water, which may be confirmed in future studies.

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#### References

Ball, B. A., R. A. Virginia, J. E. Barrett, A. N. Parsons, and D. H. Wall (2009), Interactions between physical and biotic factors influence CO<sub>2</sub> flux in Antarctic dry valley soils, *Soil Biol. Biochem.*, *41*, 1510–1517.

Chew, R. H., and A. E. Chew (1965), The primary productivity of a desert-shrub (*Larreatridentata*) community, *Ecol. Monogr.*, *35*, 355–375. Delgado-Baquerizo, M., et al. (2013), Decoupling of soil nutrient cycles as a function of aridity in global drylands, *Nature*, *502*, 672–676. Emmerich, E. W. (2003), Carbon dioxide fluxes in a semiarid environment with high carbonate soils, *Agric. Forest Meteorol.*, *116*, 91–102. Eshel, G., P. Fine, and M. J. Singer (2007), Total soil carbon and water quality: An implication for carbon sequestration, *Soil Sci. Soc. Am. J.*, *71*, 397–405. Fa, K., J. Liu, Y. Zhang, B. Wu, S. Qin, W. Feng, and Z. Lai (2015), CO<sub>2</sub> absorption of sandy soil induced by rainfall pulses in a desert ecosystem,

Hydrol. Process., 29, 2043–2051.
 Friedman, I., and J. R. O'Neil (1977), Compilation of stable isotope fractionation factors of geochemical interest, in *Data of Geochemistry*, edited by M. Fleischer, pp. 1–12, USGPO, Wash.

Gocke, M., and Y. Kuzyakov (2011), Effect of temperature and rhizosphere processes on pedogenic carbonate recrystallization: Relevance for paleoenvironmental applications, *Geoderma*, 166, 57–65.

Gocke, M., K. Pustovoytov, and Y. Kuzyakov (2010), Carbonate recrystallization in root-free soil and rhizosphere of Triticumaestivum and Loliumperenne estimated by <sup>14</sup>C labeling, *Biogeochemistry*, *103*, 209–222.

Gocke, M., K. Pustovoytov, and Y. Kuzyakov (2011), Pedogenic carbonate recrystallization assessed by isotopic labelling: A comparison of <sup>13</sup>C and <sup>14</sup>C tracers, *J. Plant Nutr. Soil Sci.*, *174*, 809–817.

Hastings, S. J., W. C. Oechel, and A. Muhlia-Melo (2005), Diurnal, seasonal and annual variation in net ecosystem CO<sub>2</sub> exchange of a desert shrub community (*Sarcocaulescent*) in Baja California, Mexico, *Global Change Biol.*, 11, 927–939.

Jasoni, R. L., S. D. Smith, and J. A. Arnone (2005), Net ecosystem CO<sub>2</sub> exchange in Mojave Desert shrublands during the eighth year of exposure to elevated CO<sub>2</sub>, *Global Change Biol.*, 11, 749–756.

Landi, A., A. R. Mermut, and D. W. Anderson (2003), Origin and rate of pedogenic carbonate accumulation in Saskatchewan soils, Canada, Geoderma, 117, 143–156.

Liu, J., W. Feng, Y. Zhang, X. Jia, B. Wu, S. Qin, K. Fa, and Z. Lai (2015), Abiotic CO<sub>2</sub> exchange between soil and atmosphere and its response to temperature, *Environ. Earth Sci.*, 73, 2463–2471.

Ma, J., Z. Y. Wang, B. A. Stevenson, X. J. Zheng, and Y. Li (2013), An inorganic CO<sub>2</sub> diffusion and dissolution process explains negative CO<sub>2</sub> fluxes in saline/alkaline soils, *Sci. Rep.*, *3*, 20–25.

Ma, J., R. Liu, L. S. Tang, Z. D. Lan, and Y. Li (2014), A downward CO<sub>2</sub> flux seems to have nowhere to go, *Biogeosciences*, *11*, 6251–6262.
Nordt, L. C., C. T. Hallmark, L. P. Wilding, and T. W. Boutton (1998), Quantifying pedogenic carbonate accumulations using stable carbon isotopes. *Geoderma*, *82*, 115–136.

Parsons, A. N., J. E. Barrett, D. H. Wall, and R. A. Virginia (2004), Soil carbon dioxide flux in Antarctic dry valley ecosystems, *Ecosystems*, *7*, 286–295.

Reynolds, J. F., et al. (2007), Global desertification: Building a science for dryland development, Science, 316, 847–851.

Ryskov, Y. G., V. A. Demkin, S. A. Oleynik, and E. A. Ryskova (2008), Dynamics of pedogenic carbonate for the last 5000 years and its role as a buffer reservoir for atmospheric carbon dioxide in soils of Russia, *Global Planet. Change*, *61*, 63–69.

Savage, K., E. A. Davidson, and A. D. Richardson (2008), A conceptual and practical approach to data quality and analysis procedures for high-frequency soil respiration measurements, *Funct. Ecol.*, 22, 1000–1007.

Schlesinger, W. H., J. Belnap, and G. Marion (2009), On carbon sequestration in desert ecosystems, Global Change Biol., 15, 1488–1490.

Serrano-Ortiz, P., M. Roland, S. Sanchez-Moral, I. A. Janssens, F. Domingo, Y. Goddéris, and A. S. Kowalski (2010), Hidden, abiotic CO<sub>2</sub> flows and gaseous reservoirs in the terrestrial carbon cycle: Review and perspectives, *Agric. For. Meteorol.*, *150*, 321–329.

Shanhun, F. L., P. C. Almond, T. J. Clough, and C. M. J. Smith (2012), Abiotic processes dominate CO<sub>2</sub> fluxes in Antarctic soils, *Soil Biol. Biochem.*, 53, 99–111.

Stone, R. (2008), Have desert researchers discovered a hidden loop in the carbon cycle?, Science, 320, 1409–1410.

Walvoord, M. A., R. G. Striegl, D. E. Prudic, and D. A. Stonestrom (2005), CO<sub>2</sub> dynamics in the Amargosa Desert: Fluxes and isotopic speciation in a deep unsaturated zone, *Water Resour. Res.*, 41, W02006, doi:10.1029/2004WR003599.

Whittaker, R. H., and W. A. Niering (1975), Vegetation of the Santa Catalina Mountains, Arizona. V: Biomass, production, and diversity along the elevation gradient, *Ecology*, *56*, 771–790.

Wohlfahrt, G., L. F. Fenstermaker, and J. A. Arnone (2008), Large annual net ecosystem CO<sub>2</sub> uptake of a Mojave Desert ecosystem, *Global Change Biol.*, 14, 1475–1487.

Xie, J. X., Y. Li, C. X. Zhai, C. H. Li, and Z. D. Lan (2009), CO<sub>2</sub> absorption by alkaline soils and its implication to the global carbon cycle, *Environ*. *Geol.*, 56, 953–961.

Yates, E. L., A. M. Detweiler, L. T. Iraci, B. M. Bebout, C. P. McKay, K. Schiro, E. J. Sheffner, C. A. Kelley, J. M. Tadić, and M. Loewenstein (2013), Assessing the role of alkaline soils on the carbon cycle at a playa site, *Environ. Earth Sci.*, 70, 1047–1056.