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# Carbon dioxide in scree slope deposits: A pathway from atmosphere to pedogenic carbonate

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## ARTICLE INFO

## ABSTRACT

A continuum of carbon, from atmospheric $CO_2$ to secondary calcium carbonate, has been studied in a soil associated with scree slope deposits in the Jura Mountains of Switzerland. This approach is based on former studies conducted in other environments. This C continuum includes atmospheric $CO_2$, soil organic matter (SOM), soil $CO_2$, dissolved inorganic carbon (DIC) in soil solutions, and secondary pedogenic carbonate. Soil parameters ($pCO_2$, temperature, pH, $C_{min}$ and $C_{org}$ contents), soil solution chemistry, and isotopic compositions of soil $CO_2$, DIC, carbonate and soil organic matter ($\delta^{13}C_{CO_2}$, $\delta^{13}C_{DIC}$, $\delta^{13}C_{car}$ and $\delta^{13}C_{SOM}$ values) have been monitored at different depths (from 20 to 140 cm) over one year. Results demonstrated that the carbon source in secondary carbonate (mainly needle fiber calcite) is related to the dissolved inorganic carbon, which is strongly dependent on soil respiration. The heterotrophic respiration, rather than the limestone parent material, seems to control the pedogenic carbon cycle. The correlation of $\delta^{13}C_{org}$ values with Rock-Eval HI and OI indices demonstrates that, in a soil associated to scree slope deposits, the main process responsible for $^{13}C$-enrichment in SOM is related to bacterial oxidative decarboxylation. Finally, precipitation of secondary calcium carbonate is enhanced by changes in soil $pCO_2$ associated to the convective movement of air masses induced by temperature gradients (heat pump effect) in the highly porous scree slope deposits. The exportation of soil C-leachates from systems such as the one studied in this paper could partially explain the "gap in the European carbon budget" reported by recent studies.

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## 1. Introduction

Soil carbon is the fourth largest pool of C, when including pedogenic carbonates sequestered in sediments and rocks (Retallack, 2007; Lal, 2009). The soil C pool has received increasing attention, since the sustainability of the ocean C sink is being questioned (Le Quéré et al., 2007). In terrestrial environments, C sequestration is almost entirely attributed to soil and plant organic C storage, while the contribution of soil mineral C is generally neglected (Sanderman, 2012), as well as the combined action of carbonate dissolution and the global water cycle (Liu et al., 2010).

Although $CO_2$ transfers at the soil–atmosphere interface have been thoroughly studied (Bond-Lamberty and Thomson, 2010), the $CO_2$ consumption and release through mineral weathering (Szramek et al., 2007; Jin et al., 2009; Liu et al., 2010), as well as the continuum between soil organic matter (SOM) – soil $CO_2$ – dissolved inorganic carbon (DIC) remains poorly documented. Recent studies have emphasized the

importance of the relationships between C dynamics in the soil solution (gas dissolution and weathering) and the soil carbonate formation, as they can play an important role in the sequestration of atmospheric $CO_2$ (Manning, 2008; Ryskov et al., 2008; Renforth et al., 2009; Jin et al., 2009). The link between SOM, soil $CO_2$, and precipitation of secondary carbonates has been described in arid and semi-arid environments for a long time (Cerling, 1984; Cerling et al., 1991; Nordt et al., 1996), but the interactions between those compartments have been less studied in temperate ecosystems. The assessment of the relationships between stable isotopes and soil physicochemical conditions constitutes a conventional tool in the study of processes involved in the terrestrial carbon cycle (Clark and Fritz, 1997; Ehleringer et al., 2000) and the dynamics of soil organic (Wynn et al., 2006; Boström et al., 2007) and inorganic carbon (Aravena et al., 1992; Clark and Fritz, 1997; Jin et al., 2009).

Stable C isotope compositions differ between the various soil compartments. Because of the higher vibrational frequency of the light $^{12}C$ isotope compared to the heavy $^{13}C$ isotope, fractionations occur during physicochemical reactions. For example, $^{12}C$ isotope is favored by the biological system during photosynthesis in order to optimize the energy

expense (Urey, 1947; Park and Epstein, 1960). The stable C isotope signature of SOM, soil $CO_2$, DIC, and pedogenic and lithogenic carbonates differ predictably (Cerling et al., 1991; Clark and Fritz, 1997).

The C content of soil gas in vadose environments is mainly attributed to the $CO_{2(g)}$ source (Cerling, 1984). $CO_{2(g)}$ concentrations in soil pores at any given depth are driven by two main parameters: i) the intensity of biological activity; ii) the diffusion processes that control the transfer of gas mass, inducing the mixing of atmospheric $CO_2$ and soil-respired $CO_2$ in the topsoil and in the lower layers. Previous studies showed that $\delta^{13}C$ values of soil $CO_2$ are higher in the topsoil, due to an enhanced diffusion of $^{12}CO_2$ at the soil–atmosphere interface (Cerling and Wang, 1996). In addition, in most of soils, C isotope composition of soil $CO_{2(g)}$ from the deeper horizons tend to be similar to the $\delta^{13}C$ values of SOM. Furthermore, when rain infiltrates into the soil, it equilibrates with the soil $CO_2$, leading to the diffusion of $CO_{2(g)}$ into the soil solution, a process contributing to the isotopic composition of the DIC species: $CO_{2(aq)}$, $H_2CO_3$, $HCO_3^-$, and $CO_3^{2-}$.

Concentrations of the various carbonate species depend on pH and temperature of the soil solution (Clark and Fritz, 1997). In an open system, the soil solution is only slightly influenced by the dissolution of lithogenic carbonates because soil $CO_{2(g)}$ constitutes an infinitely larger reservoir of carbon (Nordt et al., 1996). The resulting precipitation of pedogenic carbonate from the soil solution ($HCO_3^{-}{}_{(aq)}$) is thus normally in isotopic equilibrium with the soil $CO_{2(g)}$ (in terms of concentrations and C isotope composition) at a given soil depth (e.g., Cerling et al., 1989; Cerling and Wang, 1996; Deutz et al., 2001).

In this study, in order to document C dynamics in the SOM – soil $CO_2$ – DIC continuum, a stable C isotope approach has been chosen. This approach is based on soil parameters ($pCO_2$, temperature, pH, $C_{min}$ $C_{org}$ content), stable isotope compositions of soil organic and inorganic carbon species ($\delta^{13}C_{SOM}$, $\delta^{13}C_{DIC}$ and $\delta^{13}C_{car}$ values), as well as a monitored acquisition of field data. The aim of this study focuses on the following points. i) The continuum between $CO_2$ and pedogenic carbonate (needle fiber calcite — NFC and late calcitic cements — LCC; Millière et al., 2011a) is investigated through the leading processes involved in soil carbon transfers (from $CO_2$ to DIC) in a temperate carbonate soil system. The chosen site is situated in the Swiss Jura Mountains and is associated with scree slope deposits. ii) The second aim is to assess the origin of carbon in both LCC and NFC end-members. iii) In addition, interactions between soil $CO_2$ and DIC will

be documented for a specific soil system, i.e. a carbonate soil developed in coarse cryoclasts. iv) Finally, the $^{13}C$ enrichment of SOM with increasing depth will be discussed. The results of this study show that pedogenic carbonate found in soils from the Swiss Jura Mountains mainly originates from atmospheric $CO_2$ rather than redistribution from the carbonate bedrock through dissolution and reprecipitation processes.

## 2. Field site description

### 2.1. Geographical settings

The study area is located in the central part of the Swiss Jura Mountains, approximately 15 km north of Neuchâtel in western Switzerland (Fig. 1). Cretaceous and Jurassic limestones, in a succession of anticlines and synclines, compose the predominant bedrock of the region. A reference soil in Villiers (47°04′N, 6°59′E, 769 m asl) has been chosen for the monitoring of the various soil compartments (SOM, soil gas, and soil solution) due to its exceptional abundance of secondary carbonate in the deep horizons (Fig. 2; Millière et al., 2011a). The studied soil is situated at the foot slope of an anticline, which is affected by two important overthrusts (Burkhard and Sommaruga, 1998). Kimmeridgian limestone forms the upper part of the slope, whereas its lower part corresponds to glacial tills covering a Portlandian micritic limestone. Scree slope deposits at the foot slope contain frost-shattered fragments of both Jurassic limestones, cryoclasts being covered by the studied soil (Fig. 2), situated at approximately 20 m laterally to a small (<2 m high) quarry front.

The climate in the study area, as in all areas north of the Alps, is influenced by both oceanic (West European) and continental (East European) conditions. The oceanic climate is most prominent in the region of the Swiss Jura where the reference soil of Villiers is situated. The region is exposed to westerly winds bringing warm and wet air masses, with a rainfall often exceeding 1400 mm/year. The climate record in this region reports a mean annual rainfall of 1200 mm, and a mean annual temperature of 6 °C (January $T = -1$ °C; July $T = 18$ °C; MétéoSuisse, 2008). The soil is covered by snow during winter and the beginning of spring. The study area is covered by $C_3$ forest vegetation, dominated by beech trees (*Fagus sylvatica*) and subordinate species such as fir trees (*Abies alba*), and spruce trees (*Picea abies*). The underbrush is poor due to low luminosity caused by the dense foliage of beech trees.
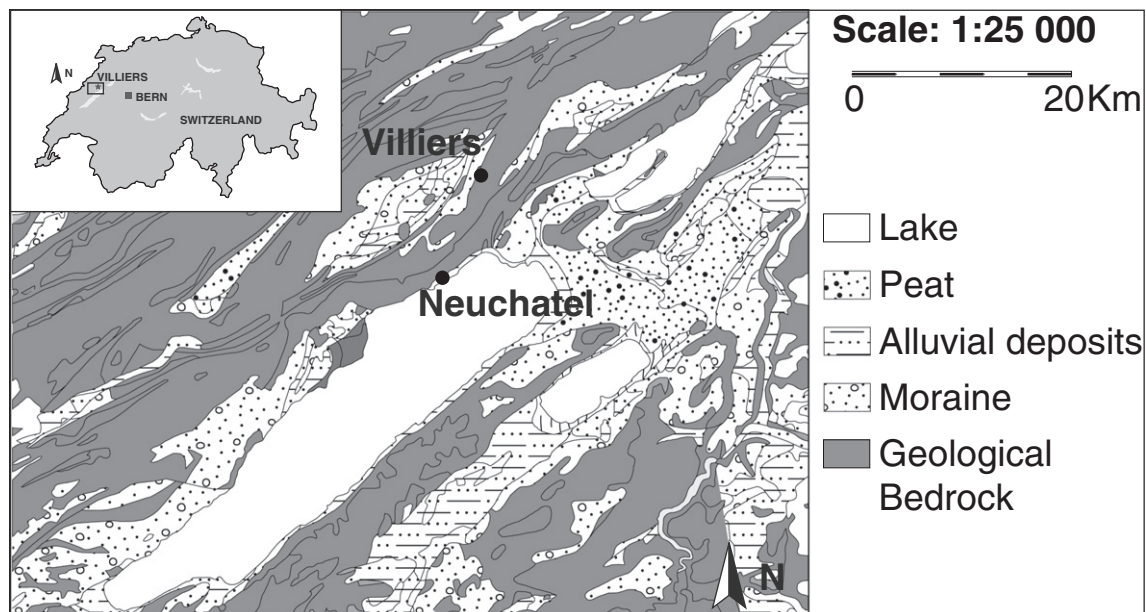


**Fig. 1.** Location of the study area in Switzerland and geological map of the eastern part of the canton of Neuchâtel.