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Keywords: biogenic carbonate | calcareous soils | isotopic signature | lithogenic carbonate | Mediterranean soils

ABSTRACT

Studying the soil organic and inorganic carbon (SOC and SIC) dynamics is essential to assess the carbon (C) sequestration potential of calcareous soils. Isotopic signatures ($\delta^{13}C$) are used to assess the C origin of SOC or SIC. However, as measuring SOC and SIC contents, measuring $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$ on a non-pretreated aliquot remains a challenge. Thermal analyses, like the Rock-Eval (RE) analysis, are promising to quantify SOC and SIC in a single analysis, but, to our knowledge, no development was conducted to assess $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$. We coupled a RE device to an isotopic gas analyser (Picarro) to continuously measure $\delta^{13}C_{CO2}$ and approach $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$. We hypothesised that different carbonate mineralogies and/or crystal sizes in SIC involve fluctuations of the $\delta^{13}C_{CO2}$. Two calcareous soils, a lithogenic (calcite) and a biogenic (snail shell) carbonate, and five calcite/shell mixes were analysed with the RE-Picarro setup. Two distinct $\delta^{13}C_{CO2}$ values were obtained before and after 650°C and were consistent with the $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$ obtained by EA-IRMS. The fluctuations of $\delta^{13}C_{CO2}$ above 650°C were higher with calcite/shell mixes than with pure carbonates. A $\delta^{13}C_{CO2}$ fluctuation $> \pm 0.2‰$ could be a pertinent indicator to detect mixes of carbonate with different $\delta^{13}C$ in soils. The RE-Picarro setup is promising to assess SOC and SIC contents, $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$ and detect mixes of carbonate with different origin on a non-pretreated aliquot. Development is needed (i) on more soil and carbonate samples and (ii) to improve the precision and accuracy of the RE-Picarro setup.

1 | Introduction

Soils are the largest terrestrial carbon (C) reservoirs, containing 2000–2100 PgC in their top metre, of which 30% is soil inorganic carbon (SIC, Plaza et al. 2018). Dynamics of soil C, especially soil organic carbon (SOC), have been extensively studied to understand the atmospheric C sequestration potential of soils. Data on calcareous soils, containing both SOC and SIC, are scarce, mainly because of methodological difficulties to distinguish SOC and SIC during C content and stable isotope ($\delta^{13}C$) measurements (Zamanian, Pustovoytov, and Kuzyakov 2016). Therefore, it is essential to devise methods to quantify and characterise both SOC and SIC in calcareous soils.

The $\delta^{13}C$ value is used to assess the C origin of SOC (i.e., C3, C4, eventually CAM plants) or SIC (lithogenic, pedogenic, or biogenic carbonates; Balesdent, Wagner, and Mariotti 1988; Zamanian, Pustovoytov, and Kuzyakov 2016). As for soil C quantification

Summary

- $\delta^{13}C_{CO2}$ can be continuously monitored during thermal analysis by an isotopic gas analyser
- Two distinct $\delta^{13}C_{CO2}$ values are obtained before and after 650°C
- $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$ can be approached on a single non-pretreated aliquot
- $\delta^{13}C_{CO2}$ evolution after 650°C could indicate mixes of carbonate of different $\delta^{13}C$

by Elemental Analysis (EA), soil C isotopic characterisation by Isotope Ratio Mass Spectrometry (EA-IRMS) in calcareous soil requires pretreatments to remove SOC (e.g., by heating at 550°C) or SIC (e.g., by acid fumigation) before $\delta^{13}C$ measurements. Two analyses on two different aliquots are needed to assess both isotopic signatures of SOC ($\delta^{13}C_{SOC}$) and SIC ($\delta^{13}C_{SIC}$). This can lead to discrepancies when comparing results to calculations using the standard isotope dilution equation, SOC and SIC contents, and $\delta^{13}C$ of the bulk soil. Several studies also report losses of organic compounds during acid pretreatments (Schlacher and Connolly 2014) or inappropriate SOC/SIC separation during heating pretreatments (Nayak et al. 2019), both likely affecting isotopic characterisation.

Thermal analyses are increasingly considered to quantify SOC and SIC on a single non-pretreated aliquot, as SOC decomposes at lower temperatures than SIC (Apesteguia, Plante, and Virto 2018; Hazera et al. 2023). For instance, the Rock-Eval (RE) thermal analysis, which involves ramped pyrolysis of the sample followed by ramped oxidation of the residue, has been developed to quantify and characterise SOC (Sebag et al. 2016; Cécillon et al. 2021), as well as different carbonate mineral species (Pillot, Deville, and Prinzhofer 2014; Baudin et al. 2023), and, more recently, to quantify SOC and SIC without using pretreatments (Hazera et al. 2023). Measuring the carbon dioxide isotopic signature ($\delta^{13}C_{CO2}$) on discrete samples of evolved gas collected during thermal analyses, that is, over specific temperature intervals between 300°C and 600°C, was performed to characterise thermal fractions of SOC of non-calcareous soils (Lopez-Capel, Bol, and Manning 2005; Lopez-Capel et al. 2008; Sanderman and Grandy 2020; Stoner et al. 2023) or pure organic and inorganic materials (Manning et al. 2008). However, to our knowledge, no application was conducted on calcareous soils to assess $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$ on a non-pretreated aliquot. This preliminary study is the first one to connect a Rock-Eval and a Picarro. It aims to verify that the $\delta^{13}C_{CO2}$ emitted during RE analysis can be continuously monitored by coupling the device to an isotopic gas analyser (Picarro). We expect different $\delta^{13}C_{CO2}$ values during SOC and SIC decompositions and the $\delta^{13}C_{CO2}$ measured during SIC thermal breakdown to depend on carbonate origin. Kinetics of carbonate thermal breakdown depend on both mineralogy and crystal size of carbonate (Pillot, Deville, and Prinzhofer 2014; Baudin et al. 2023). Thus, we hypothesise that carbonate mixes with different mineralogy and/or crystal size could involve fluctuations in the $\delta^{13}C_{CO2}$ monitored during SIC thermal breakdown, signifying the presence of carbonates with different origin in the soil. Two calcareous soil samples under a C3 vegetation, a lithogenic carbonate sample (calcite), a biogenic carbonate sample (snail shell) and five mixes of the two latter samples were analysed with the RE-Picarro setup.

2 | Materials and Methods

Two calcareous topsoils were collected at a 0–15 cm depth in two vineyard plots (C3 vegetation) in Vergèze, France (43.744 N; 4.221 E). The soils were dried at 40°C and ground (< 200 μm). Soil 1 was a clay loam Arenosol and soil 2 was a silty clay loam Cambisol. The calcite was a natural calcite sample described in Hazera et al. (2023). The snail shells (*Zonites algirus*; Zonitidae) were collected near the soil sites, washed with hydrogen peroxide, and ground (< 200 μm). The shells mainly contain aragonite (Figure S1).

The SOC content, $\delta^{13}C_{SOC}$, SIC content and $\delta^{13}C_{SIC}$ were measured by EA-IRMS after acid fumigation and heating pretreatments as described in Hazera et al. (2023). EA-IRMS was calibrated the Vienna Pee Dee Belemnite international standard (vPDB). SOC content and $\delta^{13}C_{SOC}$ were 9.45 g C kg^{-1} and −26.03‰ for soil 1 and 11.46 g C kg^{-1} and −26.92‰ for soil 2. SIC and $\delta^{13}C_{SIC}$ were 9.09 g C kg^{-1} and −9.18‰ for soil 1 and 52.42 g C kg^{-1} and −2.53‰ for soil 2. Total C contents and isotopic signatures of calcite ($\delta^{13}C_{calcite}$) and shell ($\delta^{13}C_{shell}$) samples were directly measured by EA-IRMS. Calcite C content was 120.79 g C kg^{-1} and $\delta^{13}C_{calcite}$, 2.85‰. Shell C content was 120.72 g C kg^{-1} and $\delta^{13}C_{shell}$, −10.73‰. Five mixes of shell and calcite samples were weighed to contain 10% (noted as 10/90), 25% (25/75), 50% (50/50), 75% (75/25) and 90% (90/10) of shell.

A standard Rock-Eval 6 device (Vinci Technologies, France) was coupled to a Picarro G1101-i isotope analyser. The Rock-Eval 6 device was used in the oxidation mode only, that is, the pyrolysis phase was skipped to avoid the soil samples to be pyrolyzed before oxidation. The gas exhaust of the RE oxidation circuit (after the IR detector) was directly connected to the gas inlet of the Picarro apparatus. The oxidation cycle started with an isotherm of 3 min at 200°C and continued with a temperature ramp of 25°C min^{-1} up to an isotherm of 7 min at 850°C to complete SIC decomposition. The oxidation was performed under synthetic air (80% N_2 and 20% O_2) with a flow of 50 mL/min. The carbon dioxide (CO_2) content and the $\delta^{13}C_{CO2}$ of the gas released during the RE oxidation were continuously monitored by the Picarro device at a measurement interval of 10 s, averaged on 30-s intervals. One aliquot of each soil (75 ± 5 mg) and three aliquots of calcite, shell, and carbonate mix samples (20 ± 1 mg) were analysed with the RE-Picarro set up.

In order to obtain a reliable isotopic signal from the Picarro, we analysed neither isotopic signals at low CO_2 concentrations, nor the ones acquired after the CO_2 emission drop at the end of the analysis. Sudden increases of ≈ 0.5‰ in the isotopic signals at the end of the analysis were observed for all the runs but not included in the study. Thus, the mean and standard deviation of $\delta^{13}C_{CO2}$ signals were calculated on arbitrary operable intervals delimited to exclude the obtained values (i) with $[CO_2] < 2000$ ppm and (ii) during and after the sudden increase of the $\delta^{13}C_{CO2}$ signal at the end of the analysis (Figure 1, Figure S3). The standard deviation of $\delta^{13}C_{CO2}$ signal in the operable interval was qualified as 'fluctuation' to avoid any confusion with the standard deviation

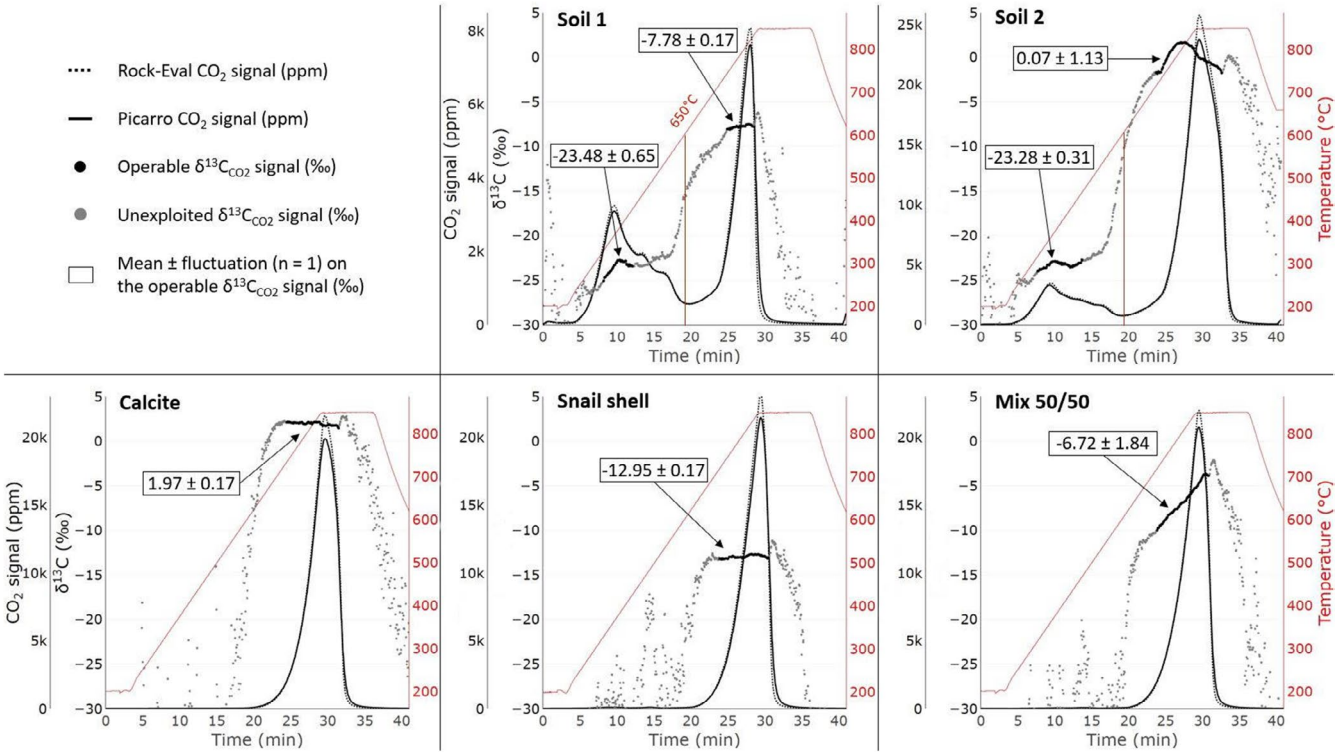

FIGURE 1 | CO_2 signal (ppm) monitored by the Rock-Eval (dotted line) and Picarro (bold line) devices and $\delta^{13}C_{CO2}$ signal (‰) obtained during the analysis of one replicate of soil 1 and 2, calcite, shell, and 50/50 mix samples ($n = 1$). The numbers in the frames refer to the mean and fluctuation of the $\delta^{13}C_{CO2}$ signal in the operable interval (black dots only). Because CO_2 signals monitored by the Rock-Eval and Picarro were very closed, dotted line and bold lines overlapped almost perfectly.

TABLE 1 | Expected $\delta^{13}C_{mix}$ (‰), mean and fluctuation of the $\delta^{13}C_{CO2}$ signal (‰), and calculated shell proportion (%) on the operable interval obtained during the RE-Picarro analyses of the calcite, shell, and carbonate mix samples (mean ± standard deviation, $n = 3$).

		Measured $\delta^{13}C_{CO2}$		
Sample	**Expected $\delta^{13}C_{mix}$ (‰)**	**Mean (‰)**	**Fluctuation (‰)**	**Calculated shell proportion (%)**
Calcite	NA	1.92 ± 0.03	0.13 ± 0.03	NA
Shell	NA	−13.04 ± 0.06	0.15 ± 0.02	NA
10/90	0.42 ± 0.03	−0.25 ± 0.38	1.33 ± 0.19	10 ± 2
25/75	−1.82 ± 0.03	−4.35 ± 1.22	2.93 ± 0.35	32 ± 7
50/50	−5.56 ± 0.03	−6.58 ± 0.48	2.02 ± 0.12	50 ± 4
75/25	−9.30 ± 0.05	−9.60 ± 0.42	0.77 ± 0.03	75 ± 3
90/10	−11.54 ± 0.05	−12.02 ± 0.68	0.55 ± 0.06	93 ± 4

calculated for replicated analyses. The usually temperature limit separating SOC to SIC decomposition during the oxidation phase with RE is fixed at 650°C (e.g., Pillot, Deville, and Prinzhofer 2014; Cécillon et al. 2021; Hazera et al. 2023). Thus, $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$ correspond to the $\delta^{13}C_{CO2}$ signal obtained for soil samples in the operable interval at temperatures below and above 650°C, respectively. $\delta^{13}C_{calcite}$, $\delta^{13}C_{shell}$ and $\delta^{13}C_{mix}$ correspond to the signal obtained at temperatures higher than 650°C for calcite, shell, and carbonate mix samples, respectively. The expected $\delta^{13}C_{mix}$ were calculated using the shell proportion of the mix and the $\delta^{13}C_{calcite}$ and $\delta^{13}C_{shell}$ measured by the RE-Picarro setup and compared to the mean $\delta^{13}C_{mix}$ obtained during the RE-Picarro analysis of the mix (Table 1). The calculated shell proportions (Figure S2) were compared to the expected shell proportion (Table 1).

3 | Results and Discussion

3.1 | Operable Intervals

$\delta^{13}C_{CO2}$ emitted during oxidation can be monitored by coupling a RE device to an isotopic gas analyser (Figure 1). Two operable intervals are obtained below and above 650°C during the

thermal ramped oxidation. Means and fluctuations of $\delta^{13}C_{SOC}$ signal were calculated on 77 and 118 values for soil 1 and 2, respectively. Means and fluctuations of $\delta^{13}C_{SIC}$ signals were calculated on 69 and 172 values for soil 1 and 2, respectively. Means and fluctuations of $\delta^{13}C_{calcite}$, $\delta^{13}C_{shell}$ and $\delta^{13}C_{mix}$ were calculated on 416 ± 13 values. The number of data points in the operable intervals on which mean and fluctuation of $\delta^{13}C_{CO2}$ were calculated depended on the nature of the sample. This number was high for calcite, shells and carbonate mix, probably because of their high C content compared to soils.

3.2 | Distinct $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$ of Soil Samples

As expected, distinct $\delta^{13}C_{CO2}$ values were observed during SOC and SIC decompositions of soil samples (Figure 1). $\delta^{13}C_{SOC}$ means were −23.48‰ and −23.28‰ for soil 1 and 2, respectively. $\delta^{13}C_{SIC}$ means were − 7.78‰ and 0.07‰ for soil 1 and 2. These values differed from the values obtained by EA-IRMS for $\delta^{13}C_{SOC}$ (−26.03‰ and −26.92‰ for the soils 1 and 2) and $\delta^{13}C_{SIC}$ (−9.18‰ and −2.53‰ for the soils 1 and 2). However, these values remained consistent with the literature: around −27‰ for SOC under C3 vegetation (Balesdent, Wagner, and Mariotti 1988), 0‰ ± 2‰ for lithogenic carbonates, and −11‰ ± 2‰ or −18‰ ± 16‰ for pedogenic or biogenic carbonates, respectively (Zamanian, Pustovoytov, and Kuzyakov 2016). Moreover, the shifts in $\delta^{13}C$ values (from 1.4‰ to 3.6‰) observed between EA-IRMS analysis and analysis performed by our coupling setup using a thermal analyser (RE) were fully consistent with those previously observed on IAEA-isotope reference material when coupled with a thermogravimeter (TG), that is, 3.2‰ (Lopez-Capel et al. 2008).

The RE-Picarro setup is a promising way to estimate $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$ on a single non-pretreated aliquot. Discrepancies between $\delta^{13}C$ values obtained by EA-IRMS and RE-Picarro can be also explained by the pretreatments needed for EA-IRMS (Schlacher and Connolly 2014; Nayak et al. 2019) or losses of information due to the short operable $\delta^{13}C_{CO2}$ intervals obtained with the RE-Picarro setup. In the future, development of the RE-Picarro setup should extend the operable intervals by adapting the sample amount (especially for SOC) or by improving the sensibility of the Picarro device. Moreover, the increasing part of the $\delta^{13}C_{CO2}$ signal between the operable $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$ intervals was consistent with an increasing contribution of SIC thermal breakdown to the CO_2 emitted during ramped oxidation and should be investigated in further studies.

3.3 | $\delta^{13}C_{SIC}$ Signal Fluctuation, an Indicator of Carbonate Mixes

$\delta^{13}C_{calcite}$ and $\delta^{13}C_{shell}$ means were in the same range than the EA-IRMS values (Table 1). $\delta^{13}C_{mix}$ means were close to the expected $\delta^{13}C_{mix}$ values except for the 25/75 mix (Table 1). The calculated snail shell proportions were close to the shell proportions of the mixes, except for the 25/75 mix, the mix with the highest standard deviation across the three repetitions (Table 1). $\delta^{13}C_{mix}$ signals increased with temperature, reproducibly within the three repetitions (Figure S3). These results suggested that (i) the $\delta^{13}C_{mix}$ signal was affected by the presence and the proportion of two carbonate mineral species with different $\delta^{13}C$ and (ii) the thermal breakdown of aragonitic snail shells began at lower temperatures than the one of calcite, which is consistent with the literature (Pillot, Deville, and Prinzhofer 2014). The fluctuation of $\delta^{13}C_{CO2}$ signal was different for soil, carbonate, and carbonate mix samples. The fluctuation of $\delta^{13}C_{SIC}$ of soil 1 (0.17‰, Figure 1) was comparable to the mean fluctuation of $\delta^{13}C_{calcite}$ (0.13‰) or $\delta^{13}C_{shell}$ (0.15‰, Table 1). The fluctuation of $\delta^{13}C_{SIC}$ of soil 2 was higher (1.13‰, Figure 1), comparable to that of $\delta^{13}C_{mix}$ (between 0.55‰ and 2.93‰, Table 1) or $\delta^{13}C_{SOC}$ (0.65 and 0.31 for soil 1 and 2, respectively, Figure 1). These results suggested that a high fluctuation of $\delta^{13}C_{CO2}$ signal, that is, a fluctuation > 0.15‰–0.2‰, obtained with pure material in this study, is related to a mix of CO_2 from the oxidation of C forms with different $\delta^{13}C$. Thus, the high fluctuation of $\delta^{13}C_{SIC}$ of soil 2 likely indicated the presence in this soil of a mix of carbonates with different $\delta^{13}C$.

These results confirm that mixes of carbonates with different $\delta^{13}C$ can be detected using the RE-Picarro setup. The degree of fluctuation depends on the characteristics of the operable $\delta^{13}C_{CO2}$ interval used, that is, the threshold values excluding some $\delta^{13}C_{CO2}$ values. With regard to the results of this preliminary study, we suggest that a $\delta^{13}C_{CO2}$ fluctuation > 0.2‰ can be a pertinent indicator to detect such mixes. However, more soil analyses are needed to define with more precision and accuracy this indicator.

4 | Conclusion and Perspectives

These preliminary results confirm that continuous monitoring of $\delta^{13}C_{CO2}$ emitted during ramped oxidation can approach $\delta^{13}C_{SOC}$ and $\delta^{13}C_{SIC}$ in a single analysis. As the SOC and SIC contents can be assessed by RE oxidation (Malou and Sebag 2023), this innovative and easy to handle RE-Picarro setup is promising to assess SOC and SIC contents, $\delta^{13}C_{SOC}$, and $\delta^{13}C_{SIC}$ on a non-pretreated aliquot. In addition, the fluctuation of $\delta^{13}C_{SIC}$ signals appears to be a promising indicator for detecting mixes of carbonate with different $\delta^{13}C$. This initial proof of concept coupling RE and Picarro should be confirmed by accurate and precise $\delta^{13}C$ measurements using certified international or internal standards, for examples the ones used by Lopez-Capel, Bol, and Manning (2005) and Lopez-Capel et al. (2008). Further developments, with more recent versions of Picarro devices and a larger set of calcareous soil samples, could also increase the operable $\delta^{13}C_{CO2}$ interval, for example, limits of the exclusion for values obtained at $[CO_2] < 2000$ ppm, and improve the quantitative and isotopic values obtained by the RE-Picarro set up. Using this new setup with more soil samples, different carbonate mineral species and origins, is promising to explore all the information provided by the $\delta^{13}C_{CO2}$ signal and to investigate the role played by inorganic carbon in soil carbon sequestration, especially in arid and alkaline environments.

Author Contributions

Joséphine Hazera: conceptualization, methodology, writing – original draft, formal analysis. **Isabelle Kowalewski:** formal analysis, conceptualization, writing – review and editing, methodology. **David Sebag:** conceptualization, writing – review and editing. **Eric**

Verrecchia: conceptualization, writing – review and editing. **Herman Ravelojaona:** formal analysis, methodology. **Tiphaine Chevallier:** conceptualization, writing – review and editing, funding acquisition.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.