Adjustments of the Rock-Eval® thermal analysis for soil organic and inorganic carbon quantification

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Abstract. Quantifying both soil organic and inorganic carbon (SOC & SIC) is essential to understand carbon (C) dynamics and to assess the atmospheric C sequestration potential in calcareous soils. The procedures usually used to quantify SOC and SIC involve pretreatments (decarbonation, decarbonatation) and calculation of the difference between C contents estimated by elemental analysis on raw and pretreated aliquots. These procedures lead to analytical bias associated to pretreatments, measurement deviations associated to the sample heterogeneity, and cumulative errors associated to calculations. The Rock-Eval® analysis is a ramped thermal analysis, used in soil sciences since the 2000s, consisting in a pyrolysis of the sample followed by an oxidation of the residue. A single Rock-Eval® analysis on a non-pretreated aliquot provides two parameters estimating the organic (TOC) and inorganic (MinC) C contents of the sample. Nevertheless, the Rock-Eval® protocol has been standardized in the 70s by *IFP Energies Nouvelles* for studying oil bearing rocks and is, thus, not perfectly suited for soil study. Previous studies suggested statistical corrections of the standard parameters to improve their estimations of C contents assessed by elemental analysis but only few of them focused on the estimation of inorganic C content using the MinC parameter. Moreover, none of them suggested adjustments of the standard Rock-Eval® protocol. This study proposes to adapt this protocol to optimize SOC and SIC quantifications in soil samples. Comparisons between SOC and SIC quantifications by elemental analysis and by Rock-Eval®, with and without statistical corrections of the standard TOC and MinC parameters, were carried out on 30 agricultural topsoils with a wide range of SOC and SIC contents. The results show that the standard Rock-Eval® protocol properly estimates SOC contents once the TOC parameter is corrected. However, it cannot achieve a complete thermal breakdown of SIC amounts > 4 mg leading to an underestimation of high SIC contents by the MinC parameter, even after correcting it. Thus, the final oxidation isotherm is extended to 7 min to complete the thermal breakdown of SIC before the end of the analysis.

1 Introduction

The carbon (C) cycle is particularly at work in the pedosphere, which is at the interface between life and mineral matter. Indeed, the world's first soil meter contain 2'000 to 2'200 PgC on average with 70% of Soil Organic Carbon (SOC) and 30% of Soil Inorganic Carbon (SIC, Batjes, 1996; Plaza et al., 2018). Stocks and dynamics of SOC and SIC strongly affect soil functions and atmospheric C sequestration (Virto et al., 2022; Zamanian and Kuzyakov, 2022; Sharififar et al., 2023). Furthermore, quantifying the changes in SIC is also a challenge to follow the weathering processes of parent materials in critical zone studies (Martin et al., 2021). Thus, study of soil C is essential to address scientific, societal, and economic issues related to food security, climate change and, to a larger extent, to C fluxes in Earth's critical zone.

Although most of the studies focus on SOC, SIC plays a fundamental role inasmuch as calcareous soils represents 30% to 50% of world's soils (Chen and Barak, 1982; Zamanian et al., 2018). The SIC can act as a sink of atmospheric C (Bughio et al., 2016; Cailleau et al., 2011; Gao et al., 2017; Vicca et al., 2022) and improves SOC stability *via* the calcium ion associated to carbonate (Rowley et al., 2018; Shabtai et al., 2023); nevertheless, SIC can also act as a source of atmospheric C (Chevallier et al., 2016; Cardinael et al., 2019; Zamanian et al., 2021). Subsequently, it is essential to clearly identify and quantify soil C forms, in terms of SOC and SIC, to understand the different processes of C dynamics and to assess the atmospheric C sequestration potential in calcareous soils.

Elemental Analysis (EA) is often considered as the reference test for soil C quantification (ISO, 1995b; Bispo et al., 2017; Chatterjee et al., 2009). However, as EA consists into a flash combustion of the sample, it cannot quantify separately SOC and SIC when applied to a calcareous soil sample. Therefore, the Total C (TC) must be first quantified by EA on one aliquot and the SOC (or the SIC) on a second aliquot. The SIC (or the SOC) content not measured by EA is then calculated using the difference: SIC= TC-SOC (or SOC= TC-SIC). The SOC quantification can be performed by EA on an aliquot previously decarbonated by acid fumigation (Harris et al., 2001), or by wet oxidation method (ISO, 1998; Bispo et al., 2017). The SIC quantification can be performed by EA on an aliquot previously heating at 550°C to remove the SOC (Bertrand et al., 2007), or by the Scheibler or the calcimetry method (ISO, 1995a; Bispo et al., 2017).

Unfortunately, removing SIC or SOC without any modification of the other C form remains a methodological issue. Some studies reported a possible measurement bias due to incomplete decarbonatation and/or organic matter alteration after acid fumigation (Schlacher and Connolly, 2014; Apesteguia et al., 2018). Others did not find a consensus on the ignition temperature nor on the exposure time to complete the organic matter combustion without carbonate alteration after soil heating around 550°C (Nayak et al., 2019; Chatterjee et al., 2009). Alternatively, the wet oxidation method quantifies SOC without pretreatments thanks to organic matter digestion. However, the recovery percentage of this digestion depends on soil type, depth, and mineralogy. Consequently, correction factors are needed to estimate the SOC content, but can lead to over- or under-estimations (Nayak et al., 2019; Chatterjee et al., 2009). In addition of errors related to the pretreatments or measurements, quantifying SOC and SIC on two aliquots can also generate analytical deviations associated to the heterogeneity of the sample. Moreover, these pretreatments and specific methods for SOC and SIC quantifications are time consuming, require handling chemicals (acid fumigation, wet combustion, calcimetry) and even produce chemical wastes (wet combustion).

Thermal analyses monitor physicochemical properties of a sample while it is progressively heated in an reductive (pyrolysis) or oxidative (oxidation) atmosphere (Plante et al., 2009; Lever et al., 2014). Thermograms measure a property against time and temperature and provide a rapid characterization of C associations in the sample, based on a single aliquot. Yet, most of the thermal methods used in soil science, such as thermogravimetry, differential thermal analysis or differential scanning calorimetry, study organic compounds (Plante et al., 2009). The ramped combustion was a promising method to measure SOC and SIC on a single aliquot (Bisutti et al., 2007; Vuong et al., 2016; Apesteguia et al., 2018), but remains poorly tested. To our knowledge, none of the thermal methods is standardized to quantify SOC and SIC, unlike the Rock-Eval® (RE) thermal analysis that provides two standardized parameters estimating the organic and inorganic C contents of a sample (TOC and MinC, respectively). The RE analysis consists in a pyrolysis of the sample followed by an oxidation of the residue. Temperature boundaries are used to distinguish the signals released by the pyrolytic cracking and oxidative combustion of organic C from the signals released by the inorganic C thermal breakdown. The TOC and MinC parameters are then calculated by integrating these signals between these temperature boundaries. The temperature boundaries were initially set for the study of oil bearing rocks (Behar et al., 2001).

The RE thermal analysis has been progressively developed and used in soil science mostly to quantify SOC with the TOC parameter (Disnar et al., 2003; Saenger et al., 2013), and to characterize SOC stability through several indexes directly calculated from the signals (Sebag et al., 2016; Soucémarianadin et al., 2018; Malou et al., 2020) or statistically predicted with a machine-learning model (Cécillon et al., 2021). To quantify SOC, Disnar et al. (2003) corrected the underestimation of the SOC content by the TOC parameter comparatively to EA carried out on non-calcareous soils. No application was dedicated to SIC quantification, only some studies have focused on inorganic C quantification in sediments (Pillot et al., 2014; Baudin et al., 2015; Wattripont et al., 2019). Recently, Sebag et al. (2022a; 2022b) used relations between the TOC and the MinC parameters assessed in calcareous and non-calcareous soils to correct their estimations of the SOC and SIC contents, respectively (SOTHIS – SOil characterization by THermal analysIS – correction). All these approaches rely on post hoc statistical corrections of the standardized TOC and MinC parameters to quantify SOC and SIC, without changing the standard analysis protocol of the RE method.

This study proposes to adapt the RE thermal analysis protocol, by adjusting the aliquot weights and the standard analysis cycle, to optimize the quantification of SOC and SIC in soil samples. Comparisons between SOC and SIC quantifications by EA (after decarbonatation, noted EA_{HCl}, and after decarbonation, noted $EA_{550°C}$, respectively) and by RE (with and without statistical corrections of the standard TOC and MinC parameters) were carried out on 30 agricultural topsoils with a wide range of SOC and SIC contents and on three geostandard materials and a calcite sample.

2 Material and methods

2.1 Material

Thirty agricultural topsoils were selected among the soil library of the Eco&Sols lab in Montpellier. These 30 soils were selected to have a wide range of SOC and SIC contents and soil types (Table 1). These 30 soils were collected at a depth of 0-10 or 0-15 cm in Mediterranean agricultural settings of southern France and northern Tunisia (Table 1). Among these 30 soils, four were considered non-calcareous: three with a SIC content assessed by Elemental Analysis after decarbonation (EA$_{550°C}$) lower than 0.1 gC.kg^{-1}soil (Table 1) and one with a SIC content lower than the EA analytical error (< 2.0 gC.kg^{-1}soil, Table 1). These four non-calcareous soils have been analysed by EA and Rock-Eval® (Supplementary Materials, SM 1) just as the other soils. All soil samples have been dried at 40°C, sieved at 2 mm, and milled at 200 µm mesh before analysis.

As the most common carbonate mineral in soils is calcite, a sample of calcite was analysed by X-Ray Diffraction (XRD, SM 2), EA (SM 3), and RE (SM 4) to check its purity. The positions of the X-ray diffraction maximum (SM 2) corresponded to those of the reference sample *PDF 04-008-0788* of the International Centre for Diffraction Data. Thus, the calcite sample used in this study is composed by only one crystallized solid and corresponds to calcite. The estimations of the TC content of this sample were very close to hypothetic stoichiometric TC content of pure calcite (120 gC.kg^{-1}soil, M(C)/M(CaCO$_3$), SM 3). Moreover, the RE thermograms (SM 4) corresponded to those obtained for pure calcite (Lafargue et al., 1998; Pillot et al., 2014).

To check the accuracy of our results, three natural geostandard materials were selected based on the availability of their TC content assessment: two soil standards (*ERMCC690* from the European Commission – Joint Research Centre and *ISE850* from the WEPAL International Soil-analytical Exchange Program) and one Norwegian Geochemical Standard of rock (*SR1*).

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Table 1: Description of the 30 agricultural topsoils. The WRB qualifiers were added to the soil type when available. The depth is in cm. The TC (gC.kg^{-1}soil) were assessed by EA and the SOC and SIC contents (gC.kg^{-1}soil) were assessed by EA after decarbonatation (EA$_{HCl}$) and decarbonation (EA$_{550°C}$), respectively.

City	Country	Land use	Soil type	Depth	Texture	pH	TC	SOC	SIC
Aigues-Mortes	France	Vineyard	Arenosol	0-15	Sand	8.22	38.7	10.7	26.5
Aigues-Mortes	France	Vineyard	Arenosol	0-15	Sand	8.58	31.8	6.6	24.5
Montagnac	France	Vineyard	Calcisol	0-15	Clay	8.21	108.1	24.0	90.4
Montagnac	France	Vineyard	Calcisol	0-15	Loam	8.20	60.9	16.1	46.2
Montagnac	France	Vineyard	Calcisol	0-15	Silty loam clay	8.27	45.4	14.9	31.3
Montagnac	France	Vineyard	Calcisol	0-15	Clay loam	8.49	79.2	11.8	69.3
Vergèze	France	Vineyard	Cambisol	0-15	Clay loam	8.10	17.8	9.4	9.1
Vergèze	France	Vineyard	Cambisol	0-15	Silty clay loam	8.18	62.7	11.4	52.4
Vergèze	France	Vineyard	Cambisol	0-15	Clay loam	8.12	34.6	17.0	18.1
Jonquières-Saint-Vincent	France	Vineyard	Rhodic Luvisol	0-15	Loam	7.78	35.9	42.3	3.1
Jonquières-Saint-Vincent	France	Vineyard	Rhodic Luvisol	0-15	Loam	7.44	14.1	14.3	0.1
Saint-Victor la Coste	France	Vineyard	Calcisol	0-15	Sandy loam	8.15	44.9	12.0	31.8
Terrats	France	Vineyard	Luvisol or Cambisol	0-15	Loam	5.76	5.6	5.7	0.1
Terrats	France	Vineyard	Luvisol or Cambisol	0-15	Loam	8.17	13.1	10.0	3.2
Restinclières	France	Agroforestry	Alluvial Fluvisol	0-10	Loam	7.99	86.2	22.6	69.4
Restinclières	France	Agroforestry	Alluvial Fluvisol	0-10	Loam	8.32	78.4	13.2	69.7
Restinclières	France	Agroforestry	Alluvial Fluvisol	0-10	Loam	8.42	76.7	9.0	70.9
Restinclières	France	Agroforestry	Alluvial Fluvisol	0-10	Loam	8.19	74.3	8.8	68.8
Manouba	Tunisia	Annual crops	Epileptic Cambisol (calcaric)	0-10	Silt loam	8.01	22.0	1.7	19.1
Nabeul	Tunisia	Orchard	Epileptic Cambisol (calcaric)	0-10	Sandy clay loam	8.51	8.0	6.4	0.0
Sfax	Tunisia	Orchard	Calcaric Cambisol (chromic)	0-10	Sandy loam	8.90	19.4	1.8	15.4
Fahs	Tunisia	Orchard	Cambisol (calcaric)	0-10	Clay loam	8.48	46.9	7.6	39.1
Kairouan	Tunisia	Annual crops	Epileptic Cambisol (calcaric)	0-10	Clay loam	9.32	38.1	5.5	30.3

Kairouan	Tunisia	Grazing land	Mixing of Cambisol and Leptosol	0-10	Clay	8.32	29.2	15.7	11.6
Siliana	Tunisia	Grazing land	Calcaric Cambisol (vertic)	0-10	Clay	7.97	3.4	3.0	1.7
Siliana	Tunisia	Forest	Epileptic Cambisol (calcaric)	0-10	Silt loam	8.18	176.7	123.1	73.5
Siliana	Tunisia	Annual crops	Leptic Vertisol or calcaric Cambisol (vertic)	0-10	Clay	8.37	71.8	12.6	64.6
Siliana	Tunisia	Annual crops	Cambisol (calcaric)	0-10	Silt loam	8.14	127.0	38.9	97.2
Siliana	Tunisia	Orchard	Epileptic Cambisol (calcaric)	0-10	Silty clay loam	8.39	107.0	15.5	97.5
Siliana	Tunisia	Orchard	Calcaric Cambisol (vertic)	0-10	Clay loam	8.33	93.5	20.1	79.2

2.2 Measurements

2.2.1 Elemental analysis

C contents were estimated for the 30 agricultural topsoils, the three geostandard materials and the calcite sample with an elemental analyser (Carlo Erba NA 2000) without any pretreatment for TC (noted: EA), after an HCl decarbonatation to remove SIC from the sample for SOC measurement (noted: EA_{HCl}) and after a 550°C heating pretreatment to remove SOC from the sample for SIC measurement (noted: $EA_{550°C}$). Decarbonatation pretreatment was performed by acid fumigation on the aliquots dedicated to the SOC content estimation. The Ag-foil capsules were filled with 30±5 mg of soil and 50 µL of demineralized water and placed in a vacuum desiccator with a 100 mL-beaker of concentrated HCl (37%) during 8h. The capsules were then dried at 60 °C for 48h before being closed and analysed with the elemental analyser (Harris et al., 2001; Cardinael et al., 2015). Decarbonation pretreatment was performed by heating the aliquots dedicated to the SIC content estimation. The capsules were filled with 30±5 mg of soil and placed in a muffle furnace at 550°C during 6h (Bertrand et al., 2007). The capsules were then closed and analysed with the elemental analyser.

2.2.2 Rock-Eval® thermal analysis

Standard cycle of Rock-Eval® analysis

The Rock-Eval® (RE) method is a ramped thermal analysis performed by a RE-6 device consisting in a pyrolysis furnace and an oxidation furnace. The analyses were carried out on the standard RE-6 device of *IFP Energies Nouvelles* (IFPEN) laboratory using the "Basic" method (Behar et al., 2001; Baudin et al., 2022). The steel crucibles were filled with different sample amounts depending on the sample (see *2.3 Experimental design*) and analysed with the standard cycle consisting in two phases: a pyrolysis of the sample under an inert nitrogen atmosphere (purity = 99.999%) and an oxidation of the residue under pure air (purity = 99.999%). The pyrolysis starts with an isotherm of 3 min at 200°C and continues with a temperature ramp of 25°C.min^{-1} up to an isotherm of 3 min at 650°C. The oxidation starts with an isotherm of 3 min at 200°C and continues with a temperature ramp of 25°C.min^{-1} up to an isotherm of 3 min at 850°C. The analysis takes about an hour per sample.

The amounts of hydrocarbon compounds (HC), carbon monoxide (CO) and carbon dioxide (CO_2) emitted by the sample during the heating are continuously monitored by two detectors: the Flame Ionization Detector (FID) measures the HC released during the pyrolysis; the InfraRed (IR) detector measures four signals: the CO and the CO_2 released during the pyrolysis and the oxidation phases. Therefore, the RE analysis results in five thermograms plotting the effluent amount emitted by the sample as a function of time and temperature.

Calculation of the standard parameters
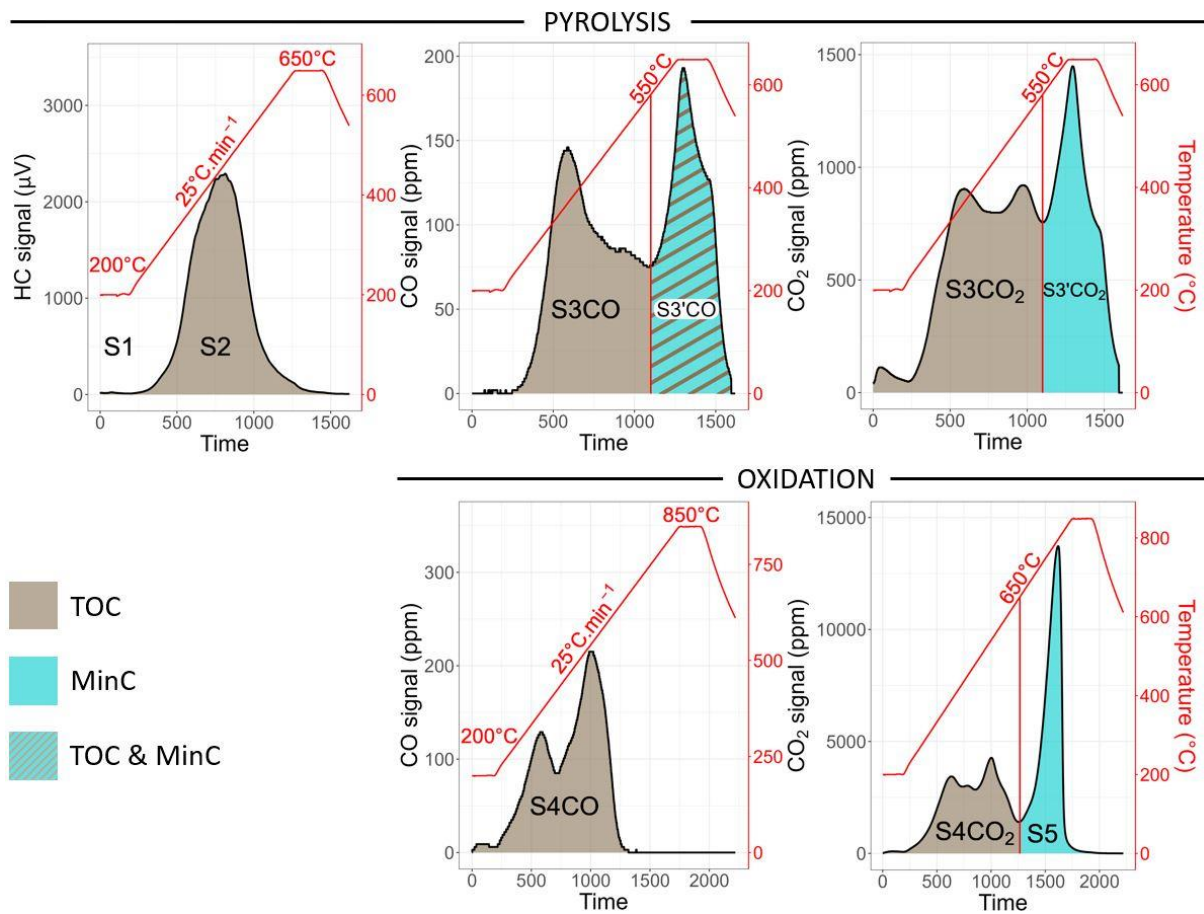
Figure 1: Example of the 5 thermograms and 9 curves (S1, S2, S3CO, S3'CO, S3CO$_2$, S3'CO$_2$, S4CO, S4CO$_2$ and S5) obtained during the Rock-Eval® analysis of a calcareous agricultural topsoil with a SOC content of 15.68 gC.kg^{-1}soil and a SIC content of 11.61 gC.kg^{-1}soil. The brown areas correspond to the curves formed by the pyrolytic cracking and the oxidative combustion of SOC and are integrated in the TOC parameter calculation. The blue areas correspond to the curves formed by the SIC thermal breakdown and are integrated in the MinC parameter calculation. The blue area with brown stripes corresponds to the curve formed by the SOC pyrolytic cracking and the SIC thermal breakdown and is integrated in both TOC and MinC parameters calculation. FID: Flame Ionization Detector; IR: InfraRed.

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Table 2: Temperature span for curve integration and associated conversion factor for TOC and MinC calculations

	PYROLYSIS						OXYDATION		
	HC		CO		CO_2		CO	CO_2	
	S1	S2	S3CO	S3'CO	S3CO_2	S3'CO_2	S4CO	S4CO_2	S5
Temperature span (°C)	0-200	200-650	0-550	550-650	0-550	550-650	0-850	0-650	650-850
Conversion factor*	0.83	0.83	12/28	12/28	12/44	12/44	12/28	12/44	12/44
Associated parameter	TOC	TOC	TOC	TOC; MinC	TOC	MinC	TOC	TOC	MinC

170 *from mg of HC, CO, or CO_2 to mgC

The five thermograms are divided into nine curves usually called "peaks" according to temperature boundaries: S1 and S2 curves refer to the HC effluents released during pyrolysis, S3CO, S3'CO, S3CO_2 (also called S3, Baudin et al., 2022), and S3'CO_2 (also called S3', Baudin et al., 2022) curves to the CO and CO_2 released during pyrolysis, and S4CO, S4CO_2, and S5 curves to the CO and CO_2 released during oxidation (Figure 1, Table 2).

175 The SOC pyrolytic cracking and oxidative combustion occur at lower temperature than the SIC pyrolytic and oxidative thermal breakdown. Thus, the S1, S2, S3CO, half of the S3'CO, the S3CO_2, S4CO and S4CO_2 curves correspond to the SOC cracking and combustion whereas the other half of the S3'CO, the S3'CO_2 and the S5 curves correspond to the SIC thermal breakdown (Figure 1, Table 2). The SIC thermal breakdown releases only CO_2 ($CaCO_3 \overset{\Delta}{\rightarrow} CaO + CO_2$). However, half of the S3'CO curve is attributed to SIC thermal breakdown

180 because the CO_2 released by the SIC thermal breakdown reacts with the residual organic C to produce two molecules of CO (Boudouard's reaction: $CO_2 + C \rightarrow 2CO$, Lafargue et al., 1998). These curves are integrated between their temperature boundaries to estimate the amounts of HC, CO, or CO_2 released by the SOC cracking and combustion and the SIC thermal breakdown (Figure 1, Table 2). The choice of these temperature boundaries is critical to correctly quantify SOC and SIC. Behar et al. (2001) set the temperature boundaries between the

185 S3CO and S3'CO curves and S4CO_2 and S5 curves to the local minimum of the CO pyrolysis and the CO_2 oxidation thermograms, respectively, sample by sample for rock studies. During soil analyses, these local minima usually occur at 550°C and 650°C, respectively (Figure 1, SM 1, and SM 4). Thus, in this study, the boundaries between the S3CO and S3'CO curves and S4CO_2 and S5 curves were fixed for all the samples at 550°C and 650°C, respectively (Figure 1, Table 2). Regarding the boundary between the S3CO_2 and S3'CO_2

190 curves, Lafargue et al. (1998) set the temperature at 400°C for rock studies because the siderite and magnesite thermal breakdown starts at 400°C. When the most common carbonate mineral is calcite, operators usually shift this boundary to the local minimum of the CO_2 pyrolysis thermogram sample by sample. In this study, the thermograms did not show any of the specific curves of siderite, magnesite, or dolomite. Moreover, the thermograms obtained with the calcite sample showed that the calcite pyrolytic thermal breakdown starts at

195 550°C (SM 4). Thus, in this study, the boundary between the S3CO_2 and S3'CO_2 curves was shifted to 550°C for all the samples (Figure 1, Table 2).

The integrations of the curves are expressed in mg of HC, CO, or CO_2 depending on the thermogram. These integrations are multiplied by the ratio of the C molar mass (12) to the CO or CO_2 molar mass (28 or 44 respectively, Table 2) to convert CO and CO_2 amounts in mgC. On the other hand, HC refers to molecules made

200 of C and hydrogen atoms exclusively (e.g., C_nH_{2n+2} for alkane derivatives). The HC released during the RE

pyrolysis contain about 83% of organic C on average (Espitalié et al., 1985). Thus, the HC amount is multiplied by 0.83 to be converted in mgC. Once converted, the curve integrations corresponding to SOC cracking and combustion and SIC thermal breakdown are summed to calculate the standard TOC and MinC parameters, respectively, as described in the Eq. (1) and (2) (Disnar et al., 2003).

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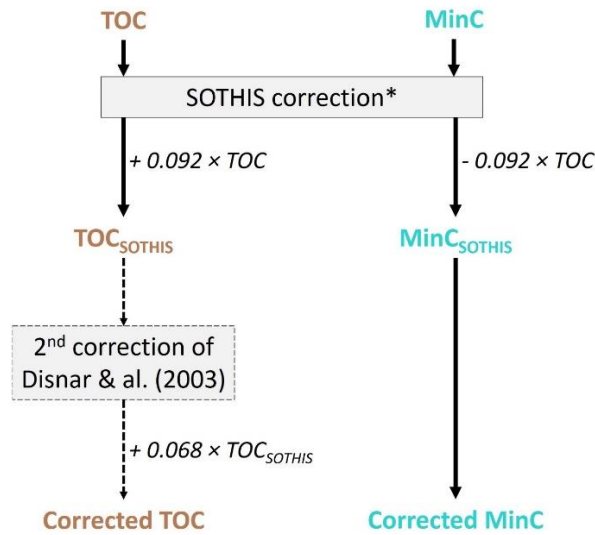$$TOC = S1 + S2 + S3CO + \frac{1}{2}S3'CO + S3CO_2 + S4CO + S4CO_2 \tag{1}$$

$$MinC = \frac{1}{2}S3'CO + S3'CO_2 + S5 \tag{2}$$

The calibration of all the RE devices and the quality of the RE analyses are routinely checked by the operator with the so-called *160 000* standard. The *160 000* standard is a clayey rock with an organic C content of 3.28 gC.kg^{-1}soil and an inorganic C content of 3.26 gC.kg^{-1}soil. Two *160 000* standards are analysed at the

210 beginning and the end of each sample set, as well as every ten samples. The values obtained for each curve, the TOC and the MinC parameters and a few other indicators are compared with the reference values of the *160 000* standard.

Corrections of the standard parameters

215 Up to now, Disnar et al. (2003) were the first to propose corrections for a better SOC quantification in soil samples. On a wide panel of non-calcareous soils, Disnar et al. (2003) estimated that the TOC parameter underestimates by 9.2% the SOC content appraised by EA. Moreover, for soils with organic matter enriched in poorly degraded organic compounds and litter debris, they suggested to add a supplementary correction of 6.8% on the previously corrected TOC parameter.

220 Sebag et al. (2022a; 2022b) demonstrated that, in calcareous and non-calcareous soils, a part of the MinC parameter corresponds to thermoresistant organic matters (SM 1) and thus must be subtracted from the MinC parameter and added to the TOC parameter for calcareous soils. This correction named SOTHIS for SOil characterization by THermal analysIS has been statistically evaluated between 4% and 12% of the TOC parameter and depends on the content of thermoresistant organic matters in the soil samples (Sebag et al., 2022a;

225 2022b). When the uncorrected MinC parameter is lower than 2.0 gC.kg^{-1}soil, the sample is considered non-calcareous. The signals associated to the MinC parameter (SM 1) are then integrated in the correction of the TOC parameter and the corrected MinC parameter is set to 0.

Figure 2: Corrections of the TOC and MinC parameters for calcareous soils. *The first correction proposed by Disnar et al. (2003) is assumed to correspond to the SOTHIS correction with a 9.2% coefficient.

In this study, it is assumed that the first correction proposed by Disnar et al. (2003) *i.e.*, the missing 9.2% of the TOC parameter, corresponds to thermoresistant organic matters comprised in the MinC parameter as proposed by the SOTHIS correction. Consequently, for the calcareous soils of this study, 9.2% of the TOC parameter are systematically added to the TOC and subtracted from the MinC (Figure 2), as notified by the SOTHIS correction. For non-calcareous soils, the MinC is added to the TOC parameter and set to 0. As the studied soils have been collected in agricultural topsoils (soil depth < 15 cm), they contain organic matter enriched in poorly degraded organic compounds and litter debris. Thus, in this study, the TOC parameter corrected using SOTHIS is also corrected with the second correction of Disnar et al. (2003) *i.e.,* by adding 6.8% of the corrected TOC (Figure 2). The corrected TOC and corrected MinC parameters are finally calculated as described by Eq. (3) and (4) for calcareous soils.

$$Corrected\ TOC = 1.17\ \times TOC \tag{3}$$

$$Corrected\ MinC = MinC - 0.092\ \times TOC \tag{4}$$

For non-calcareous soils, the corrected TOC and MinC parameters are calculated as described by Eq. (5) et (6).

$$Corrected\ TOC = (TOC + MinC)\ \times 0.068 \tag{5}$$

$$Corrected\ MinC = 0 \tag{6}$$

Results of the corrected parameters are systematically compared with the uncorrected standard parameters. Corrections were applied on the results obtained from soil sample. Because the geostandard *SR1* and the calcite samples are rock and mineral samples, respectively, the parameters obtained with these samples were not corrected.
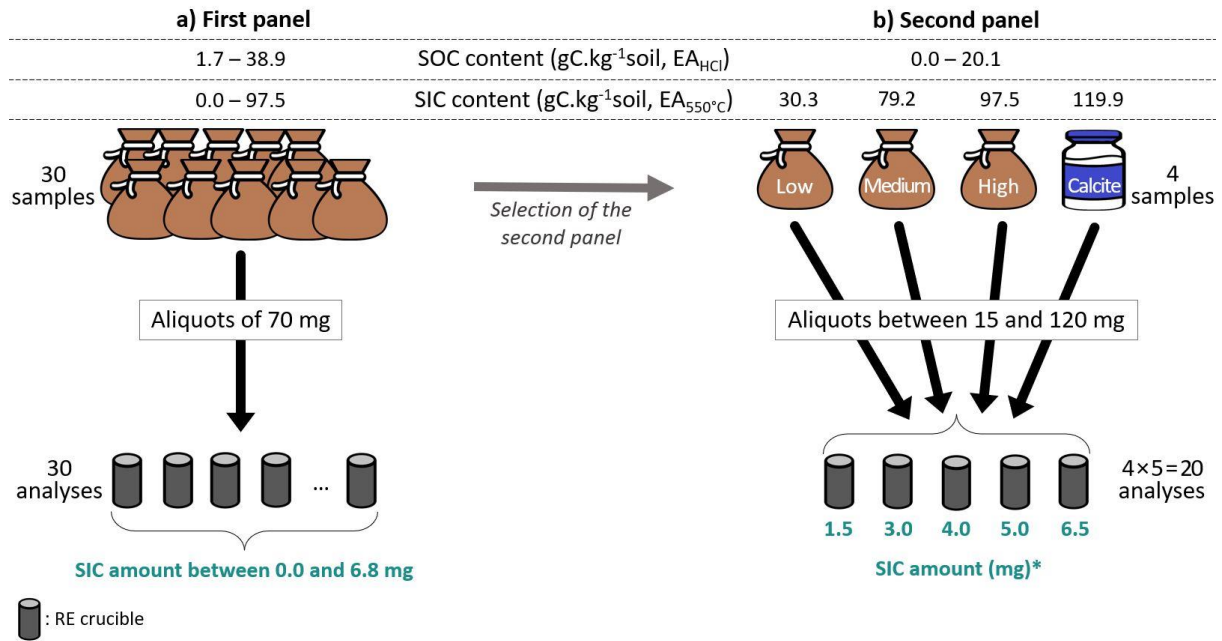
2.3 Experimental design

Figure 3: Settings of the two soil panels and their associated RE analyses. a) The first soil panel is composed of 30 soils. For each soil, a RE analysis was carried out on one aliquot of 70 mg. b) The second soil panel is composed of four samples: three soils chosen among the 30 soils with low, medium, and high SIC contents, and the calcite sample.
For each sample, five RE analyses were carried out on five aliquots between 15 and 120 mg *i.e.*, on five chosen SIC amounts in the five RE crucibles (from 1.5 to 6.5 mg of SIC). * For the sample with the lower SIC content, the five chosen SIC amounts were 1.5, 2.5, 3.0, 3.5 and 4.0 mg of SIC.

Two soil panels designed from the 30 soils and the calcite sample were studied with different RE experimental conditions (Figure 3).

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In the first soil panel, which includes the 30 soils, the SOC content ranges from 1.7 to 38.9 gC.kg^{-1}soil (EA$_{HCl}$) and the SIC content from 0.0 to 97.5 gC.kg^{-1}soil (EA$_{550°C}$, Figure 3, Table 1). The RE analyses were carried out on one aliquot of 70±1 mg for each sample. Thus, the SIC amounts in each RE crucible were comprised between 0.0 and 6.8 mg of SIC (Figure 3). For each sample of the first panel, the SOC and SIC contents were measured
one time by EA$_{HCl}$ and EA$_{550°C}$, respectively, and one time by RE.

Regarding the second panel, three soil samples were selected from the 30 soils based on their SIC content. The calcite sample was also added to this second panel. The SOC content of the three soil samples ranged from 0.0 to 20.1 gC.kg^{-1}soil (EA$_{HCl}$) and their SIC content from a low (30.3 gC.kg^{-1}soil, EA$_{550°C}$) to a high content (97.5 gC.kg^{-1}soil, EA$_{550°C}$). The TC content of the calcite sample, assumed to be only SIC, was 120.87 ± 0.29 gC.kg^{-1}soil (EA, Figure 3). The RE analyses were carried out on five aliquots between 15 and 120 mg for each sample
in order to analyse five chosen SIC amounts. These five SIC amounts corresponded to different sample charges in the RE crucibles and were 1.5, 3.0, 4.0, 5.0 and 6.5 mg of SIC for the medium (79.2 gC.kg^{-1}soil) and high SIC content soils (97.5 gC.kg^{-1}soil) and the calcite sample (Figure 3). The five RE crucibles of the medium SIC content soil and the calcite sample were replicated three times. For the low SIC content soil (30.3 gC.kg^{-1}soil),
the five SIC amounts in the RE crucibles were 1.5, 2.5, 3.0, 3.5 and 4.0 mg of SIC because the maximal amount of matter in the RE crucibles is 120 mg. In order to compare the RE results, sand was added and mixed with the

samples to complete the initial loading in each RE crucible to 120 mg. The calcite sample and the medium SIC content soil (79.2 gC.kg^{-1}soil) were also analysed with standard cycles of analysis with an extended final oxidation isotherm from 3 min to 5 or 7 min. For each sample of the second panel, the SOC and SIC contents were measured one time by EA$_{HCl}$ and EA$_{550°C}$, respectively, and five time by RE but on different sample amount in the RE crucible each time.

To evaluate the precision and the accuracy of the RE method, the TC, SOC and SIC contents of the three geostandard materials and the calcite sample were measured by EA and RE on four aliquots (SM 3). These samples were analysed with a RE analysis cycle with an extended final oxidation isotherm of 7 min.

2.4 Data analysis

The uncorrected and corrected TOC parameters were compared to the EA$_{HCl}$ values. The uncorrected and the corrected MinC parameters were compared to the EA$_{550°C}$ values. The corrected MinC parameter is also compared to the SIC content estimated as the difference between the TC and the SOC contents estimated by EA (noted: EA$_{TC-SOC}$).

For the first panel, the normality of the distribution of the parameters (uncorrected and corrected TOC and MinC, EA$_{HCl}$ and EA$_{550°C}$) was tested with a Shapiro-Wilk's test (H0: the distribution is normal, function shapiro.test of the statistical R software) with a confidence interval of 95%. Then, the significance of the differences between the RE parameter and the EA value (paired variables) were tested with a Student test (H0: $\mu_{RE} = \mu_{EA}$, function t.test of the statistical R software) for parametric variables or a Wilcoxon test (H0: $\mu_{RE} = \mu_{EA}$, function wilcox.test of the statistical R software) for non-parametric variables with a confidence interval of 95%.

Least squares regressions between SOC content estimations by EA$_{HCl}$ *vs* uncorrected TOC or corrected TOC and between SIC content estimations by EA$_{550°C}$ or EA$_{TC-SOC}$ *vs* uncorrected MinC or corrected MinC were tested with the lm function (Fitting Linear Models) of the statistical R software on non-replicated values. This function tests the overall significance of the regression with a Fisher test (H0: the regression slope and the intercept are not significantly different from zero, the relationship between the two variables is not significant): if the p-value (P) is < 0.01 or < 0.05, the regression is significant with a confidence interval of 99% or 95%, respectively. If the intercept was not significantly different from 0 with a confidence interval of 99%, the regressions were performed without intercept. The goodness of fit of regression is assessed by the coefficient of determination R^2 given by the lm function: the closer the R^2 is to 1, the higher the proportion of variance explained by the regression. The significance of difference of the regression slope from 1 was tested with a Student test (H0: $\mu_{SLOPE} = 1$).

The grey area in the graphs corresponds to the analytical error of the two methods (EA and RE). To build this area, a relative error of 5% was applied to the x-axis (EA) according to the norm ISO (1995b). For the TOC and the MinC parameters, a relative error of 2% and 1.7%, respectively, was applied on the y-axis (RE). These relative error values come from an IFPEN study of intern repeatability conducted on five replicates of five soils (data not shown). These relative errors are consistent with Behar et al. (2001) measurements on rock and kerogen samples.

3 Results & discussion

3.1 Comparison between the estimations of SOC and SIC contents of the 30 soils (first panel) measured by RE and EA
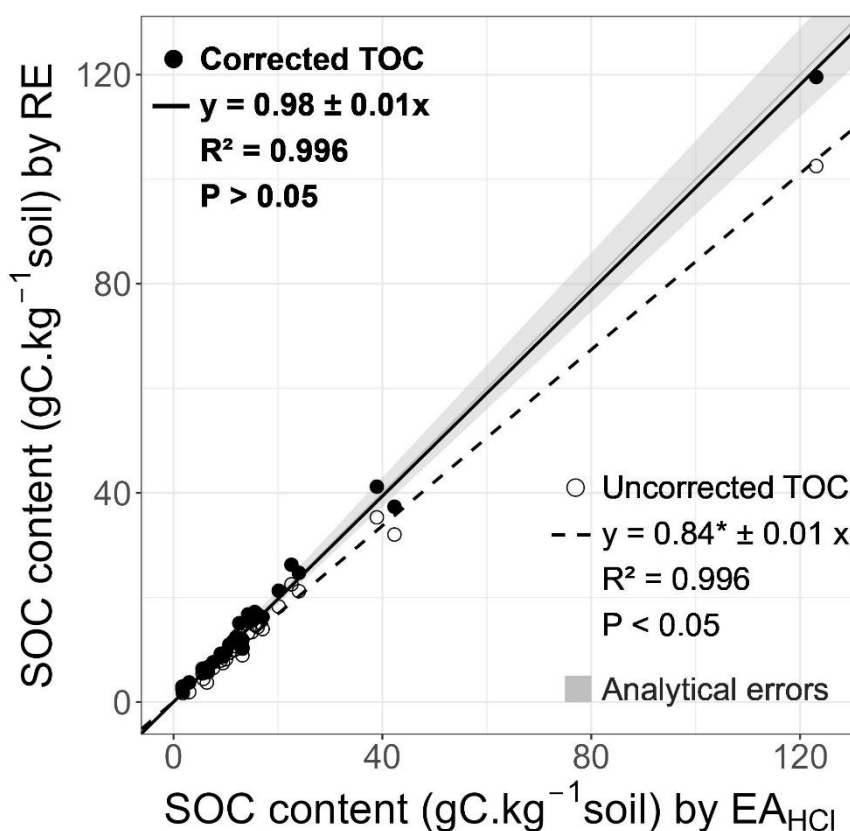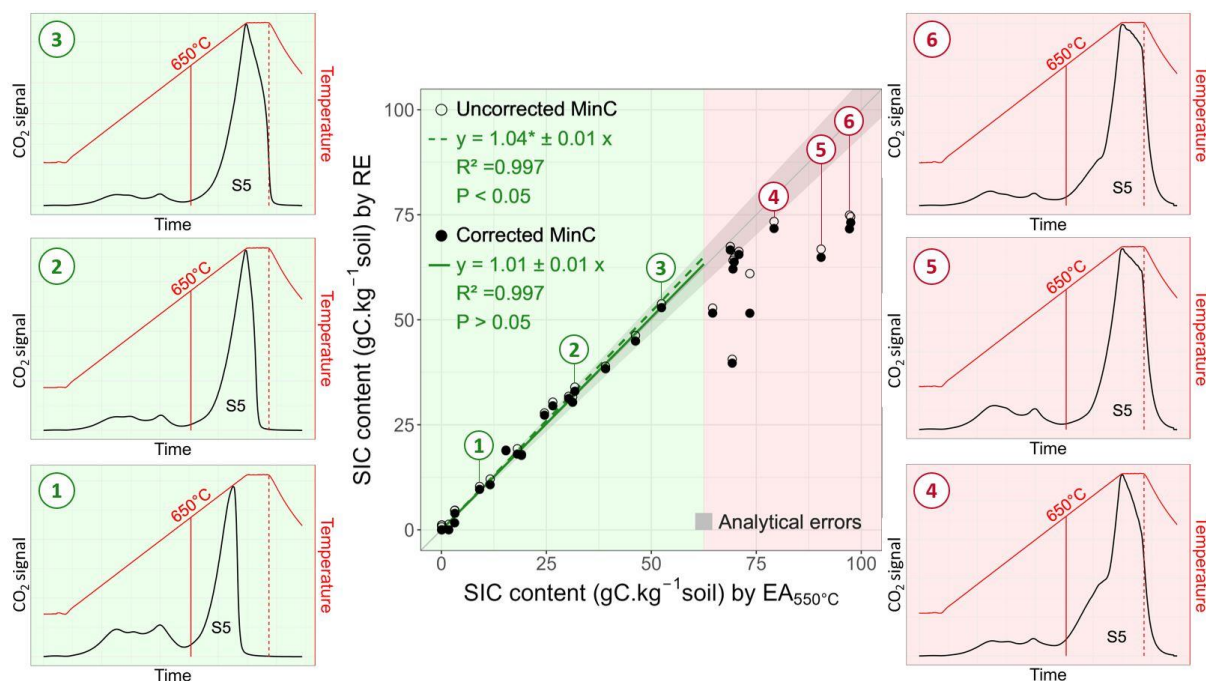

Figure 4: Plot of the SOC content estimated by the uncorrected and the corrected TOC parameters of the RE analysis on one aliquot *vs* the SOC content estimated by EA$_{HCl}$ on one aliquot for the 30 soils of the first panel. The linear regressions *corrected TOC vs EA$_{HCl}$* (bold line) and *uncorrected TOC vs EA$_{HCl}$* (dashed line) are provided with their coefficient of determination (R^2). For both regressions, the slopes were significantly different from 0 (p-value (P) < 0.001) but not the intercepts (P > 0.01). *The slope of the regression was significantly different from 1 (P < 0.05). The grey area, centred on the grey line $y = x$, represents the analytical error of the two methods.

The estimations of the SOC contents by RE and by EA$_{HCl}$ in the first panel are related ($R^2 = 0.996$, $P < 0.001$, Figure 4). The SOC contents estimated by the uncorrected TOC parameter significantly differ from those estimated by EA$_{HCl}$ (Wilcoxon test: $P < 0.05$) while the SOC contents estimated by the corrected TOC parameter do not significantly differ from those estimated by EA$_{HCl}$ (Wilcoxon test: $P > 0.05$). Moreover, the slope of the regression line between the SOC contents estimated by EA$_{HCl}$ and by the uncorrected TOC parameter is significantly different from 1 (0.84 ± 0.01, Figure 4, Student test: $P < 0.05$) while the slope of the regression line *corrected TOC vs EA$_{HCl}$* does not significantly differ from 1 (0.98 ± 0.01, Figure 4, Student test: $P > 0.05$). Thus, for these 30 agricultural topsoils, the RE estimations of the SOC content by the corrected TOC parameter, either with Eq. (3) for the calcareous soil samples or with the Eq. (5) for the non-calcareous soils, are similar to the SOC content estimations by EA$_{HCl}$.

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Figure 5: Plot of the SIC content estimated by the uncorrected and the corrected MinC parameter on one aliquot *vs* the SIC content estimated by EA$_{550°C}$ on one aliquot for the 30 soils of the first panel. The coloured areas in green and red refer to SIC contents estimated by EA$_{550°C}$ lower (n = 19) and higher (n = 11) than 62.50 gC.kg^{-1}soil, respectively. The linear regressions *corrected MinC vs EA$_{550°C}$* (green bold line) and *MinC vs EA$_{550°C}$* (green dashed line) correspond only to SIC contents < 62.50 gC.kg^{-1}soil. For both regressions, the slopes were significantly different from 0 (P < 0.001) but not the intercepts (P > 0.01). *The slope of the regression was significantly different from 1 (P < 0.05). The oxidation thermograms presented on both sides of the plot are examples of the S4CO$_2$ and S5 curves obtained for six soils of the first panel: three with SIC contents < 62.50 gC.kg^{-1}soil (N° 1-3) and three with SIC contents > 62.50 gC.kg^{-1}soil (N° 4-6). The grey area, centred on the grey line y = x, represents the analytical error of the two methods.

For the non-calcareous soils, the uncorrected MinC parameter averages 1.07 ± 0.26 gC.kg^{-1}soil. Surprisingly, for the whole first panel, the SIC contents estimated by the uncorrected MinC parameter are not significantly different from those estimated by EA$_{550°C}$ (Wilcoxon test: n = 30, P > 0.05) while the SIC contents estimated by the corrected MinC parameter do significantly differ from those estimated by EA$_{550°C}$ (Wilcoxon test: n = 30, P < 0.05).

However, the distribution of the points around the y = x line differs according to the SIC content. For SIC contents lower than a value around 62.50 gC.kg^{-1}soil, data plot mostly above the line y = x with a sparse dispersion. For SIC contents higher than a value around 62.50 gC.kg^{-1}soil, data plot mostly below the line y = x with a higher dispersion (Figure 5). For SIC contents < 62.50 gC.kg^{-1}soil, the estimations by the corrected MinC parameter do not significantly differ from those by EA$_{550°C}$ (Student test: n = 19, P > 0.05) while the SIC contents estimated by the uncorrected MinC parameter significantly differ from those by EA$_{550°C}$ (Student test: n = 19, P < 0.05). Moreover, for SIC contents < 62.50 gC.kg^{-1}soil, the slope of the regression line *corrected MinC vs EA$_{550°C}$* is not significantly different from 1 (1.01 ± 0.01, Figure 5, Student test: P > 0.05) while the slope of the regression line *uncorrected MinC vs EA$_{550°C}$* is significantly different from 1 (1.04 ± 0.01, Figure 5, Student test: P < 0.05). Since the correction decreases the value of the MinC parameter (Figure 2), correcting the MinC parameter reduces its overestimation when SIC contents < 62.50 gC.kg^{-1}soil, but increases its

underestimation when SIC contents > 62.50 gC.kg^{-1}soil. Thus, for these 30 agricultural topsoils, the correction applied to the MinC parameter (Eq. (4) for calcareous soils, and Eq. (6) for non-calcareous soils) improves its estimation only when SIC contents are lower than a value around 62.50 gC.kg^{-1}soil.

Table 3: Average contribution (%, mean ± standard deviation) of each curve integration to the TOC and MinC parameters for the 26 calcareous soils of the first panel.

	S1	S2	S3CO	S3'CO		S3CO$_2$	S3'CO$_2$	S4CO	S4CO$_2$	S5
Parameter	TOC	TOC	TOC	TOC	MinC	TOC	MinC	TOC	TOC	MinC
Contribution (%)	0.1 ± 0.1	13 ± 5	2 ± 0.3	1 ± 1	1 ± 2	17 ± 9	9 ± 9	2 ± 1	62 ± 7	90 ± 10

The oxidative thermal breakdown of SIC occurs at temperatures > 650°C and forms the S5 curve (Figure 5), whose integration provides the main contributor to the MinC parameter (about 90%, Table 3). The S5 curves of the samples with SIC contents > 62.50 gC.kg^{-1}soil drop sharply at the end of the final oxidation isotherm, unlike the S5 curves of the samples with SIC contents < 62.50 gC.kg^{-1}soil (Figure 5). This sharp drop is likely related to a stop in the thermal breakdown of SIC due to the temperature decrease at the end of the final oxidation isotherm. Thus, the underestimation of SIC contents > 62.50 gC.kg^{-1}soil by the MinC parameter is probably caused by an incomplete thermal breakdown of a too large amount of SIC in the RE crucibles, estimated above 4.4 mg of SIC for 70 ± 1 mg of sample in the RE crucible.

3.2 Effect of the SIC amount in the RE crucible on the SIC content estimated by RE on the 4 samples of the second panel
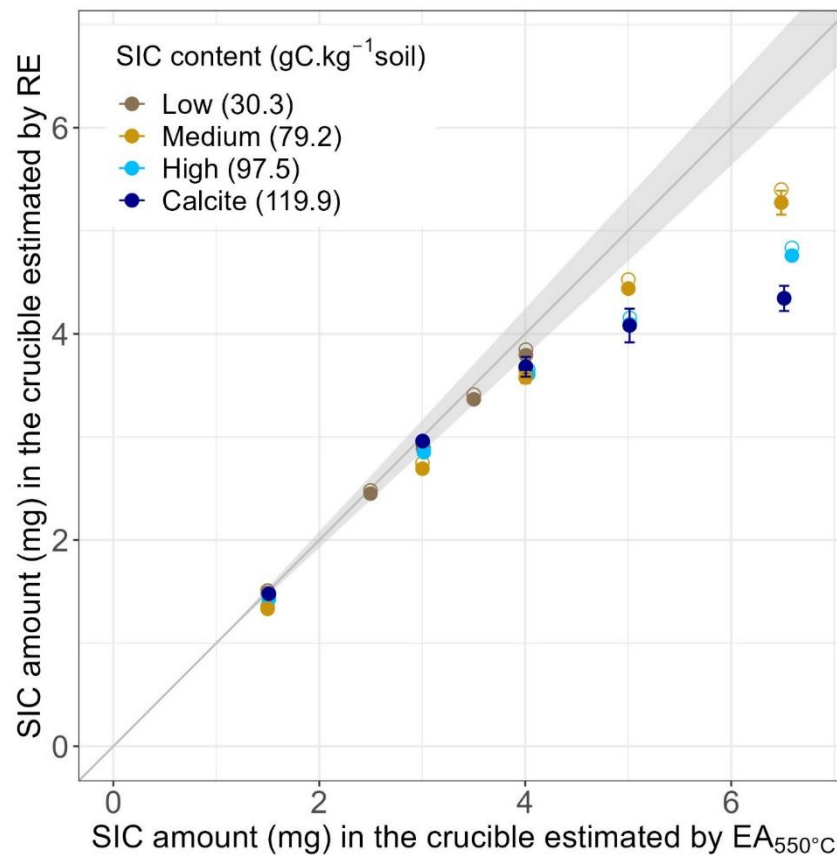
Figure 6: Plot of the SIC amount in the crucible estimated by the uncorrected (hollow point) and the corrected (full point) MinC parameter on one aliquot for the low and high SIC content soils and on five aliquots for the medium SIC content and the calcite samples *vs* the SIC amount in the crucible estimated by EA$_{550°C}$ on one aliquot for the four samples of the second panel. The grey area, centred on the grey line *y = x*, represents the analytical error of the two
methods.

Analysis of the second panel with increasing SIC amounts in the RE crucibles shows that the MinC and the corrected MinC parameters properly estimate SIC amounts < 4 mg (Figure 6). For SIC amounts in the RE crucible > 4 mg, the higher the SIC amount, the more the MinC parameter underestimates it (Figure 6). These results are consistent with the assumption that the underestimation of high SIC contents by the MinC parameter
is due to an incomplete thermal breakdown of the SIC amount in the RE crucible.

In addition to the SIC amount (mg) in the crucible, the SIC content (gC.kg^{-1}soil) of the sample seems also affect the SIC thermal breakdown during the RE analysis. The higher the SIC content (gC.kg^{-1}soil) in the sample, the more the MinC parameter underestimates the SIC amount (mg) in the RE crucible (Figure 6). This result can be explained by the SIC content and/or by different SIC forms within the samples. Pillot et al. (2014) assumed that
the mineral size has an effect on its thermal destabilization, especially for calcite: the smaller the calcite mineral, the easier it is to destabilize it, explaining the faster breakdown of chalk compared to marble. Thus, the quality of SIC seems to affect its thermal breakdown. The higher probability to contain bigger SIC crystals hard to decompose in the soil with a high SIC content or in the calcite sample than in the soil with a medium SIC content likely explain the observed results.

395   The RE standard cycle analysis cannot accurately estimate the SIC content when the SIC amount in the crucible is higher than 4 mg. This is especially valuable for soils with a high SIC content. To solve this problem, two solutions are proposed: i) when the SIC content is known, the standard cycle of analysis can be used by limiting the SIC amount in the crucible at 4 mg; ii) when the SIC content is unknown, the RE standard cycle of analysis can be customized by extending the final oxidation isotherm.

400   *3.3 Adaptation of the RE standard cycle of analysis*
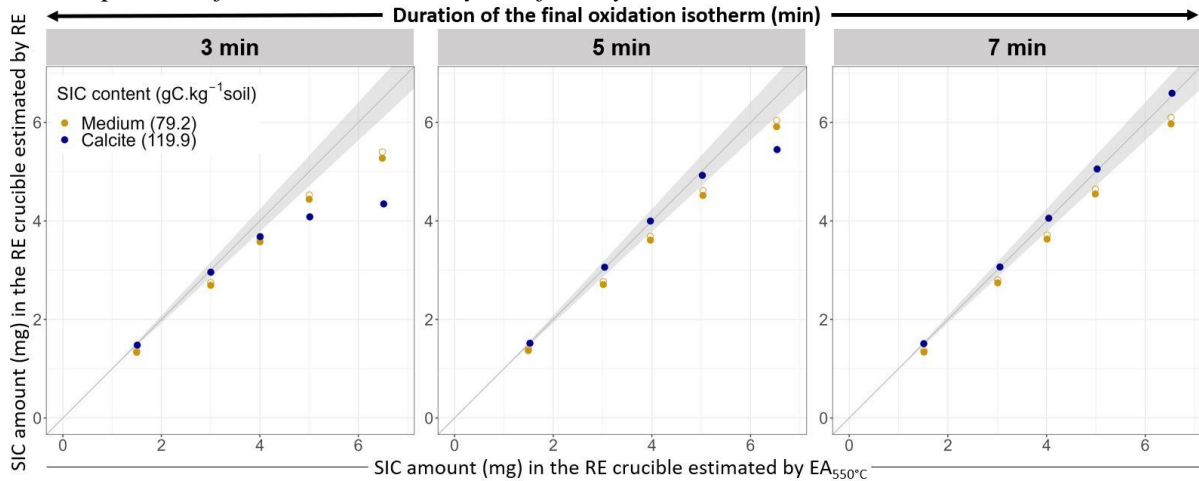
Figure 7: Plots of the SIC amount in the crucible estimated by the uncorrected (hollow point) and the corrected (full point) MinC parameter *vs* the SIC amount in the crucible estimated by EA$_{550°C}$ on one aliquot for the soil with a medium SIC content and the calcite sample. Three cycles with different durations of the final oxidation isotherm (3, 5
405 **and 7min) have been applied. The grey area, centred on the grey line *y* = *x*, represents the analytical error of the two methods.**

    To provide enough time for SIC thermal breakdown during the oxidation phase, two options are possible: extending the time or raising the maximal temperature during the oxidation phase. Because raising the maximal temperature of oxidation up to 850°C requires a RE7 device and most labs still use a RE6 device, we have
410 preferred to test the extension of the oxidation time to 7 min.

    The SIC amounts in the crucibles with calcite are properly estimated by the MinC parameter with a final oxidation isotherm of 7 min (Figure 7). Unlike the results with calcite, a systematic error is observed for the estimation of the SIC amount of the soil with a medium SIC content, even with a final oxidation isotherm of 7 min (Figure 7). This error seems to be proportional to the quantity of sample in the crucible, as it increases with
415 the SIC amount in the crucible (Figure 7). Thus, it is suggested that this error can propagate on the five SIC amounts calculated from the single EA$_{550°C}$ measurement on the soil with a medium SIC content. Heating the soil sample at 550°C may have resulted in an incomplete combustion of thermoresistant organic matters leading to an overestimation of its SIC content by EA$_{550°C}$ (Nayak et al., 2019; Chatterjee et al., 2009). Thus, this error can be related to the pretreatment performed on the soil before the SIC content estimation by EA$_{550°C}$ rather than from
420 the RE analyses. Indeed, the SIC amount estimated by EA as the difference between the TC and SOC amounts after decarbonatation (EA$_{TC-SOC}$, Figure 8) should be less overestimated than the SIC amount estimated by EA after heating at 550°C (EA$_{550°C}$, Figure 8).
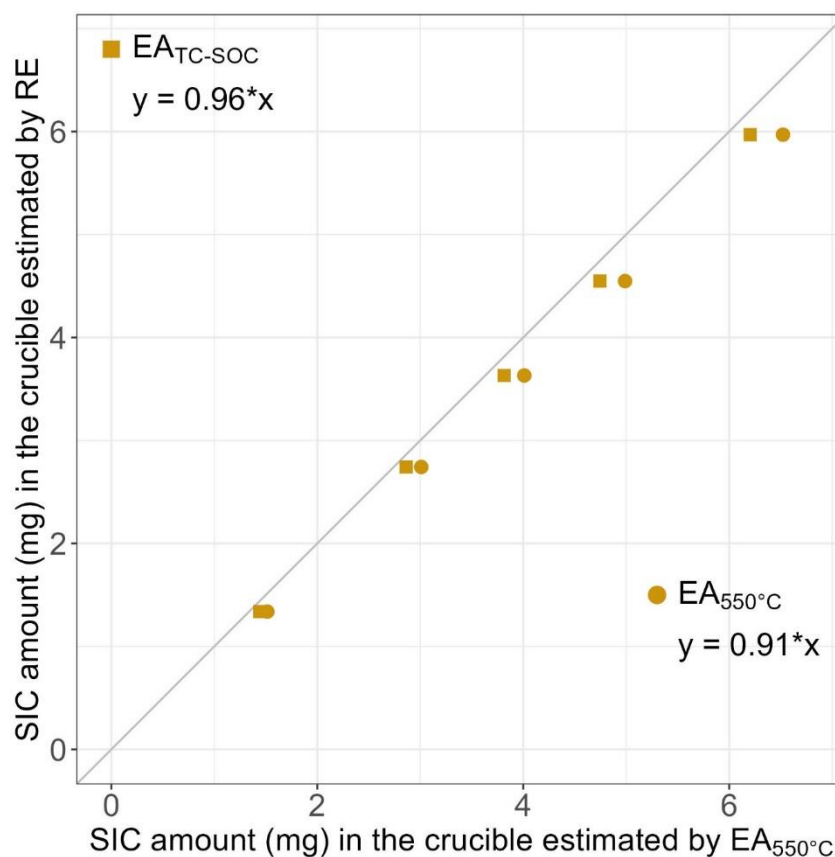
Figure 8: Plot of the SIC amount in the crucible estimated by the corrected MinC parameter *vs* the SIC amount in the crucible estimated by EA$_{550°C}$ (point) and by EA$_{TC-SOC}$ *i.e.*, the difference between the TC and the SOC (square) on one aliquot for the soil with a medium SIC content. The grey area, centred on the grey line *y = x*, represents the analytical error of the two methods.

The slope of the regression line between the SIC amount in the crucible estimated by RE and by EA is closer to 1 with the EA$_{TC-SOC}$ (0.96) value than with the EA$_{550°C}$ value (0.91, Figure 8). This result confirm that the systematic error observed in Figure 7 for the soil with a medium SIC content is probably due to an incomplete combustion of the organic matter during the heating pretreatment before the SIC content estimation by EA$_{550°C}$. These results have been observed on one calcareous soil only and, thus, cannot be generalized for all calcareous soils.

The results obtained for the four EA and RE (with a 7 min final oxidation isotherm) analyses on the three geostandard materials and the calcite samples are presented in SM 3. For the three geostandard materials, the relative errors for the TOC, MinC and TOC+MinC parameters were comprised between 0.13% and 5.88%, 0.83% and 2.44% and, 0.35% and 1.92%, respectively. These relative errors are equivalent to the ones of EA: between 0.22% and 5.02% for organic C content, between 1.57% and 23.80% for the inorganic C content and between 1.12% and 2.44% for the total C content. These relative errors of EA are closed to the 5% given by the norm (ISO, 1995b) for TC. On these samples, the precision of the RE method is comparable or better for inorganic content, than the precision of the EA method. As for EA, the estimations of the total C content by RE were closed to the informative values given for the three geostandard materials and the hypothetic stoichiometric value of the calcite sample. Thus, the RE method gives accurate estimation of total C content and similar values

and precision for SOC and SIC contents than EA_{HCl} and $EA_{550°C}$, respectively, without any soil sample pretreatment.

4 Conclusion

The RE thermal analysis is a promising tool to measure precisely and accurately both SOC and SIC contents with a single analysis on a single calcareous soil aliquot. To accurately estimate the SOC and SIC contents with the RE, the standard TOC and MinC parameters must be statistically corrected and the RE standard cycle needs to be adjusted. The RE standard cycle of analysis properly estimates SOC contents in calcareous and non-calcareous soils once the TOC parameter is corrected. However, the standard cycle of analysis cannot achieve a complete thermal breakdown of SIC amounts in the RE crucible > 4 mg. This boundary leads to an underestimation of high SIC contents by the MinC parameter even after correcting it. The final oxidation isotherm must be extended to at least 7 min to complete the thermal breakdown of SIC before the end of the analysis.

These results have been obtained on 26 calcareous and 4 non-calcareous agricultural topsoils. The 26 calcareous agricultural topsoils contained calcite as main carbonate mineral. Thus, these results need to be repeated with other calcareous soils and on other carbonate mineral type with different thermal breakdown behaviour as siderite, magnesite and, dolomite for instance. In this study, the RE method has been compared with the pretreated EA values to compare two methods based on the measure of the gases emitted by the sample oxidation (EA) or the sample pyrolysis and oxidation (RE). Comparison with other C quantification methods could be interesting to perform as MinC parameter *vs* calcimetry or TOC parameter *vs* loss on ignition method for instance. The TOC and MinC parameters still need to be statistically corrected (Disnar et al. (2003) and SOTHIS corrections, Figure 2) even with the adaptation of the oxidation phase. To be independent of statistical corrections, which could depend on the SOC and SIC forms in the analysed soil, further study should focus on the distinction between the signals from the pyrolytic cracking and oxidative combustion of SOC and the signals from the SIC pyrolytic and oxidative thermal breakdown. These methodological adjustments would improve the organic and inorganic C quantifications in soils and surficial deposits and contribute to better understand C content changes in the Earth's critical zone.

Data availability

The data set and the R-script used for this article can be assessed upon request to Joséphine Hazera.

Declaration of competing interests

The authors declare that they have no conflict of interest.

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