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® thermal analysis, used in soil sciences since the 2000s, provides two parameters estimating the organic (TOC) and inorganic (MinC) C contents of a non-pretreated aliquot with a single analysis. 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 a soil panel 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

35   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.

40   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).

45   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

50   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

55   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

60   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

65   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

70   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 (Apesteguia et al., 2018), but

remains poorly tested. To our knowledge, none of the thermal methods is standardized to quantify SOC and SIC,
75 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 distinction between the organic C
cracking and the inorganic C thermal breakdown signals is based on fixed temperature limits 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 characterize SOC
80 (Disnar et al., 2003; Sebag et al., 2016; Malou et al., 2020; Cécillon et al., 2021). Indeed, Disnar et al. (2003)
corrected the underestimation of the SOC content by the TOC parameter comparatively to EA carried out on non-
calcareous soils. Some studies have focused on inorganic C quantification in sediments (Pillot et al., 2014; Baudin
et al., 2015; Wattripont et al., 2019), but no application was dedicated to SIC quantification. Recently, Sebag et al.
(2022a; 2022b) used relations between the TOC and the MinC parameters assessed in calcareous and non-
85 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, 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
90 quantifications by EA and by RE, with and without statistical corrections of the standardized TOC and MinC
parameters, were carried out on a soil panel with a wide range of SOC and SIC contents.

2 Material and methods

2.1 Material

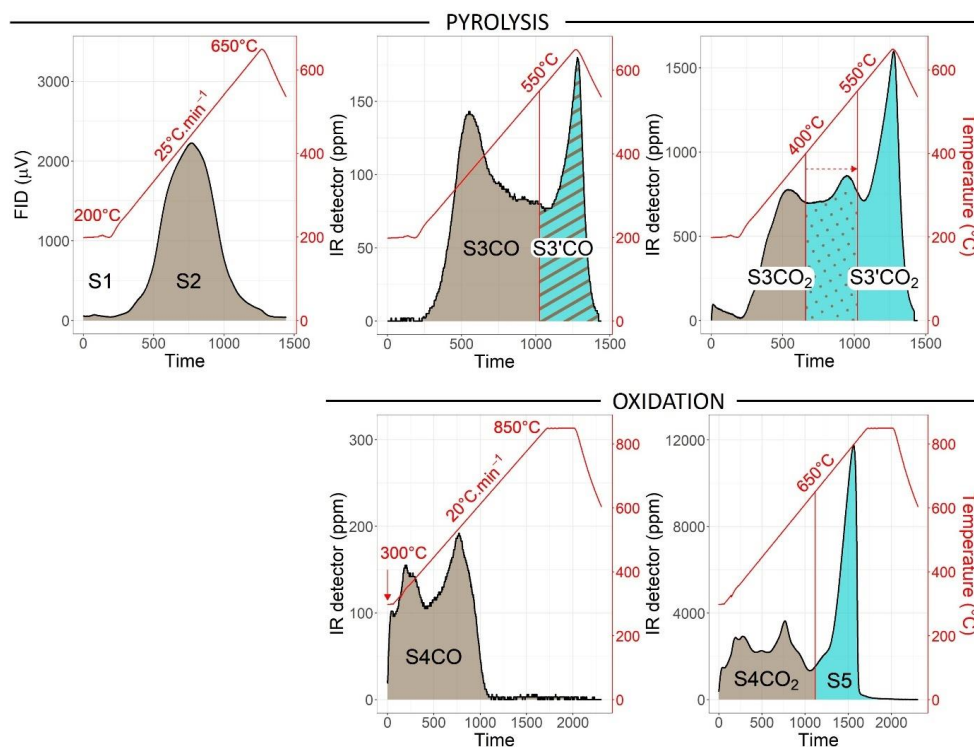
Twenty-four soils were selected among the soil library of the Eco&Sols lab in Montpellier. These 24 soils were
95 collected at a depth of 0-10 or 0-15 cm in Mediterranean agricultural settings of southern France and northern
Tunisia. These soils have been dried, sieved at 2 mm, and milled at 200 µm mesh. A sample of natural calcite was
also selected.

2.2 Measurements

2.2.1 Elemental analysis

100 C contents were estimated for each of the 25 samples with an elemental analyser (Carlo Erba NA 2000) without
any pretreatment for TC, after decarbonatation or decarbonation for SOC and SIC, respectively. Decarbonatation
pretreatment was performed by a 6h acid fumigation on the aliquot dedicated to the SOC content estimation
(Harris et al., 2001). Decarbonation pretreatment was performed by a 6h heating at 550°C on the aliquot dedicated
to the SIC content estimation (Bertrand et al., 2007). Each C content (TC, SOC or SIC) was measured on one
105 aliquot of 23±5 mg, without any replicate for the 24 soils. The TC content of the natural calcite was measured on
three replicates of 13±1 mg.

2.2.2 Rock-Eval® thermal analysis

Standard cycle of Rock-Eval® analysis

110 **Figure 1: Principle of the Rock-Eval® analysis. The thermograms were obtained during the analysis of a soil with a SOC content of 15.7 gC.kg-1soil and a SIC content of 11.6 gC.kg-1soil with the Rock-Eval 6 standard device at the University of Lausanne.**

The RE method is a ramped thermal analysis and a trademark registered by *IFP Energies Nouvelles* (IFPEN). The analyses were carried out using two standard RE6 devices: one at IFPEN laboratory and one at the University of
115 Lausanne (Unil). The "Bulk Rock" method (Lafargue et al., 1998; Baudin et al., 2022) and the standard cycle adapted to soils were applied for this study. Briefly, the standard cycle consists into two phases: a pyrolysis of the sample under an inert nitrogen atmosphere and an oxidation of the residue under pure air (Figure 1). 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 0 or 3 min (Unil and IFPEN devices, respectively) at 650°C (Figure 1). The oxidation starts with an isotherm
120 of 3 min at 200°C or 300°C (IFPEN and Unil devices, respectively) and continues with a temperature ramp of 20°C.min^{-1} or 25°C.min^{-1} (Unil and IFPEN devices, respectively) up to an isotherm of 3 or 5 min (IFPEN and Unil devices, respectively) at 850°C (Figure 1). The minor differences between the standard cycles of the two devices do not affect the parameters calculations.

The amounts of hydrocarbon compounds (HC), carbon monoxide (CO) and carbon dioxide (CO2) emitted by the
125 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 specific 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 (Figure 1).

130 *Calculation of the standard parameters*

Table 1: 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

*from mg of HC, CO, or CO2 to mgC

The five obtained thermograms are divided into nine curves usually called "peaks": S1 and S2 curves refer to the HC effluents released during pyrolysis, S3CO, S3'CO, S3CO$_2$, and S3'CO$_2$ curves to the CO and CO_2 released

135 during pyrolysis, and S4CO, S4CO$_2$, and S5 curves to the CO and CO_2 released during oxidation (Figure 1, Table 1). These curves are integrated between fixed temperature boundaries to estimate the amounts of HC, CO, or CO_2 released during each specific phase of the cycle. Behar et al. (2001) set the temperature boundaries between the 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. In this study, these boundaries were fixed for all the

140 samples at 550°C and 650°C, respectively (Figure 1, Table 1). Regarding the boundary between the S3CO$_2$ and S3'CO$_2$ curves, Behar et al. (2001) set the temperature at 400°C; but operators usually shift this boundary to the local minimum of the CO_2 pyrolysis thermogram, sample by sample. In this study, the boundary for all the samples was shifted to 550°C to be consistent with the one used for the decarbonation pretreatment (Figure 1, Table 1).

The integrations of the curves are expressed in mg of HC, CO, or CO_2 depending on the thermogram. These

145 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 1) to convert CO and CO_2 amounts in mgC. On the other hand, HC refers to molecules made 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. Each curve integration corresponds to a part of SOC or SIC degradation and is

150 thus integrated to the TOC or the MinC standard parameter as described in the equations (1) and (2) (Disnar et al., 2003). The S3'CO integration is divided between the TOC and the MinC parameters because the CO_2 released by the inorganic C thermal breakdown can react with the residual C to produce two molecules of CO (Boudouard's reaction, Lafargue et al., 1998).

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

155
$$MinC = \frac{1}{2}S3'CO + S3'CO_2 + S5 \qquad (2)$$

Correction of the standard parameters

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

160   organic compounds and litter debris, they suggested to add a supplementary correction of 6.8% on the previously corrected TOC parameter (Figure 2).

Sebag et al. (2022a; 2022b) demonstrated that, in calcareous and non-calcareous soils, a part of the MinC parameter corresponds to thermoresistant organic matters and thus must be subtracted from the MinC parameter and added to the TOC parameter. This correction named SOTHIS for SOil characterization by Thermal AnalysIS has been

165   statistically evaluated between 4% and 12% of the TOC parameter and depends on the content of thermoresistant organic matters in the soil samples.

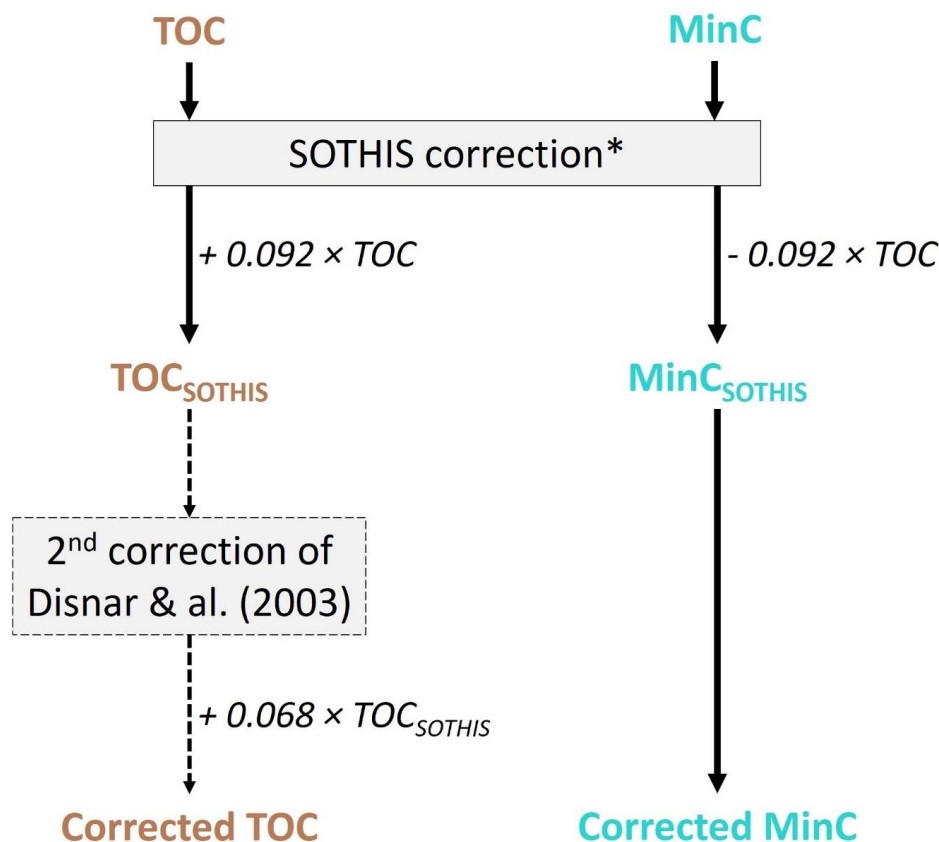



Figure 2: Corrections of the TOC and MinC parameters. *The first correction proposed by Disnar et al. (2003) is
170   **assumed to correspond to the SOTHIS correction with a 9.2% coefficient.**

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, in 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. 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).

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

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

Results of the corrected parameters are systematically compared with the uncorrected standard parameters.

2.3 Experimental design

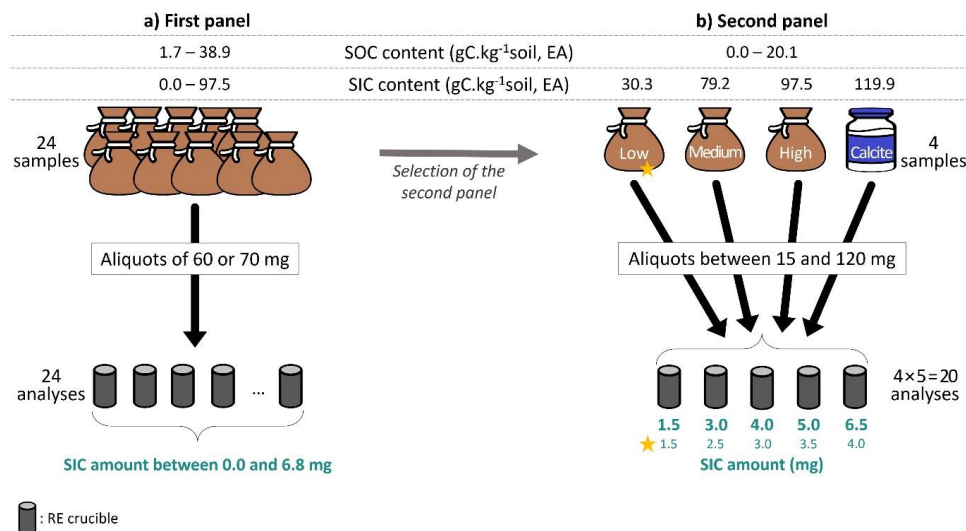



Figure 3: Settings of the two soil panels and their associated RE analyses. a) The first soil panel is composed of 24 soils. For each soil, a RE analysis was carried out on one aliquot between 60 and 70 mg i.e., with a SIC amount in the RE crucible directly driven by the SIC content of the soil, not with a chosen value. b) The second soil panel is composed of four samples (three soils chosen among the 24 soils and a natural 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.

Two soil panels designed from the 24 soils and the natural calcite sample were studied with different RE experimental conditions (Figure 3).

In the first soil panel, which includes the 24 soils, the SOC content ranges from 1.7 to 38.9 gC.kg^{-1}soil (after decarbonatation and EA measurement) and the SIC content from 0.0 to 97.5 gC.kg^{-1}soil (after decarbonation and EA measurement, Figure 3). The RE analyses were carried out on one aliquot between 60 and 70 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).

195 The RE analyses were performed on a standard RE6 device at Unil with its standard cycle of analysis. For each sample of the first panel, the SOC and SIC contents were measured one time by EA and one time by RE.

Regarding the second panel, three soil samples were selected from the 24 soils based on their SIC content. The sample of natural calcite 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 (after decarbonatation and EA measurement) and their SIC content from a low (30.3

200 gC.kg^{-1}soil) to a high content (97.5 gC.kg^{-1}soil, after decarbonation and EA measurement). The TC content of the natural calcite, assumed to be only SIC, was 119.9 ± 0.3 gC.kg^{-1}soil (without pretreatment before EA measurement, Figure 3). The RE analyses were carried out on five aliquots between 15 and 120 mg for each sample in order to analyze 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

205 content soils (97.5 gC.kg-1soil) and the natural calcite (Figure 3). The five RE crucibles of the medium SIC content soil and the natural calcite 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. For the second panel, the RE analyses were performed

210 on the standard RE6 device at IFPEN with its standard cycle of analysis. The natural calcite and the medium SIC content soil (79.2 gC.kg^{-1}soil) were also analyzed 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 and five time by RE on different sample amount in the RE crucible each time.

2.4 Data analysis

215 Linear regressions of estimations of SOC and SIC contents obtained by EA vs TOC, corrected TOC, MinC, or corrected MinC parameters obtained using RE, were tested with the lm function (Fitting Linear Models) of the statistical R software. This function tests the overall significance of the regression with a Fisher test (H0: the coefficient *i.e.*, the regression slope, is not significantly different from zero, the relationship between the two variables is not significant): if the p-value is < 0.001, the regression is significant with a confidence interval of

220 99%. 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 TOC and corrected TOC parameters were compared to the EA values obtained after decarbonatation. The MinC and the corrected MinC parameters were compared to the EA values obtained after decarbonation in order to compare two thermal methods using 550°C as the temperature boundary. The corrected MinC parameter is also

225 compared to the SIC content estimated as the difference between the TC and the SOC contents estimated by EA.

The significance of the difference between the slopes of the two compared linear models (EA vs TOC or MinC and EA vs corrected TOC or corrected MinC) was tested by testing the significance of the difference between the uncorrected and the corrected parameters. First, the normality of the parameter distribution was tested with a Shapiro-Wilk's test (function shapiro.test of the statistical R software) with a confidence interval of 99%. Then,

230 the significance of the differences between the uncorrected and the corrected parameters (paired variables) were tested with a Student test (function t.test of the statistical R software) or a Wilcoxon (function wilcox.test of the statistical R software) test with a confidence interval of 99% for parametric or non-parametric variables, respectively.

The grey area in the graphs corresponds to the analytical error between the two methods. To build this area, a

235 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 errors

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

240 **3.1 Comparison between the estimations of SOC and SIC contents of the 24 soils (first panel) measured by**

RE and EA

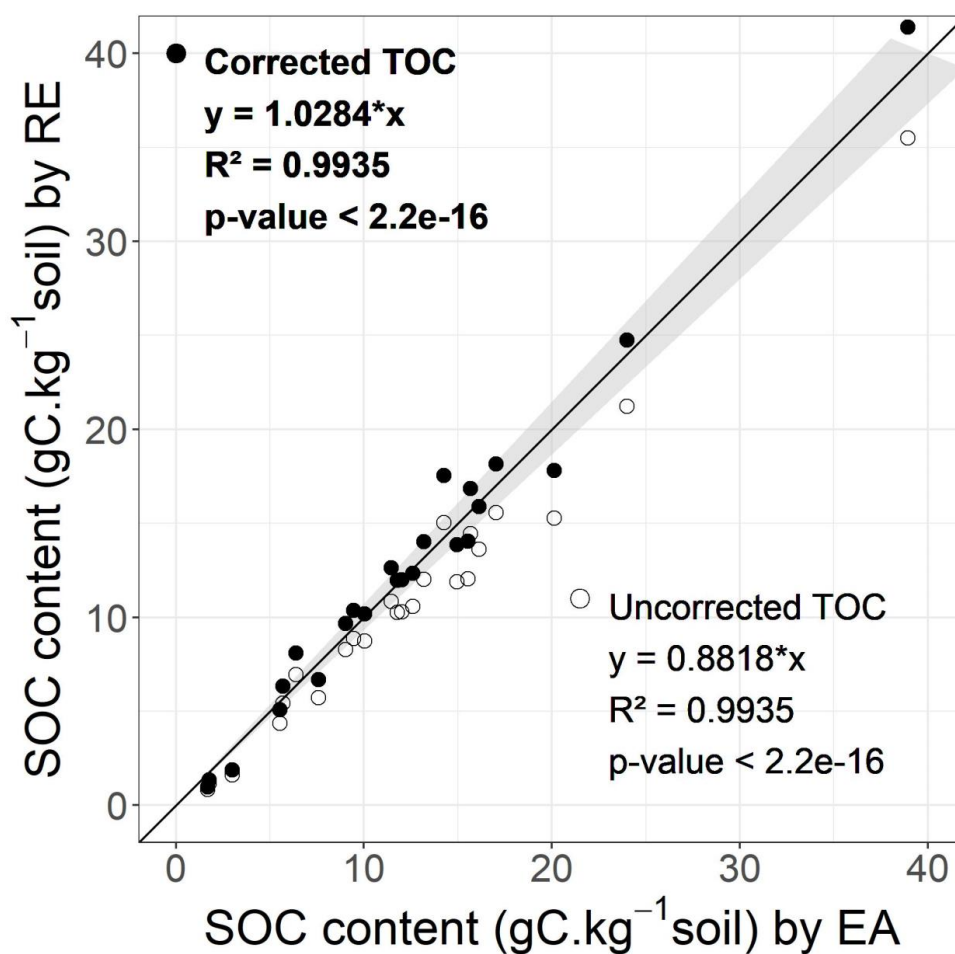



Figure 4: Plot of the SOC content estimated by the uncorrected (hollow point) and the corrected (full point) TOC

parameters vs the SOC content estimated by EA after decarbonatation for the 24 soils of the first panel. The grey area

245 **represents the measurement error of the two methods. The equation of the linear regression is provided with its coefficient of determination and its p-value.**

The estimations of the SOC contents measured by RE and EA in the first panel are correlated ($R^2 = 0.9935$, $p < 2.2 \cdot 10^{-16}$, Figure 4). The slope of the regression line between the SOC contents estimated by EA and RE is statistically closer to 1 with the corrected TOC parameter (1.03) than with the uncorrected TOC parameter (0.88,

250 Wilcoxon test: p-value = $1.192 \cdot 10^{-7}$, Figure 4). Thus, the correction applied to the TOC parameter leads to an estimation closer to the SOC content estimated by EA after decarbonatation for calcareous soils.

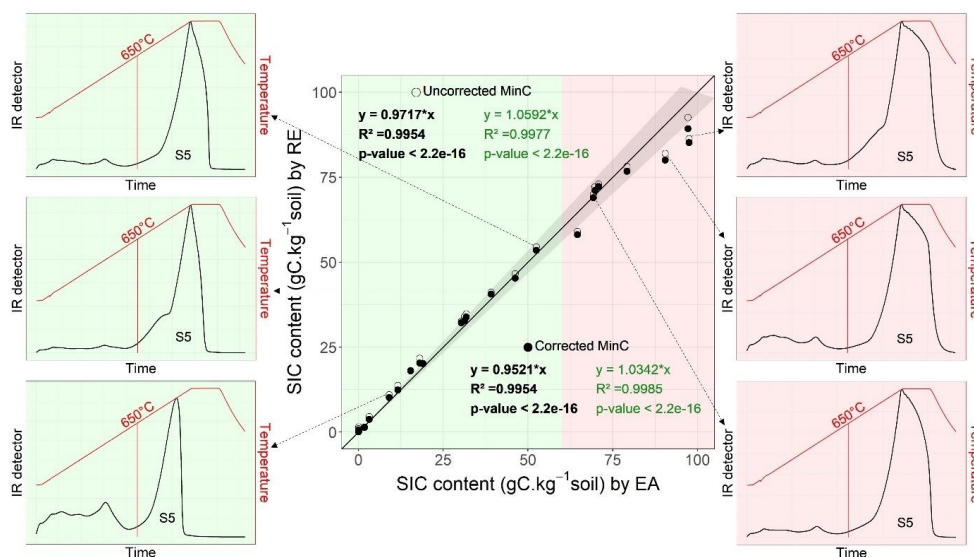



Figure 5: Plot of the SIC content estimated by the uncorrected (hollow point) and the corrected (full point) MinC parameter vs the SIC content estimated by EA after decarbonation for the first panel. The colored areas in green and

255 **red refer to SIC contents estimated by EA lower and higher than 60 gC.kg-1soil, respectively. The grey area represents the measurement error of the two methods. On both sides of the plot, the S4CO2 and S5 peaks were obtained during the oxidation phase of RE analyses of six soils (as examples). The equations of the linear regressions are provided with their coefficient of determination and their p-value.**

As for SOC, the estimations of the SIC content appraised by RE are correlated with the estimations of the SIC

260 content assessed with EA ($R^2 = 0.9954$, $p < 2.2 \cdot 10^{-16}$, Figure 5). Surprisingly, the slope of the regression line between the SIC content estimated by EA and by RE is statistically closer to 1 with the uncorrected MinC parameter (0.97) than with the corrected MinC parameter (0.95, Wilcoxon test: p-value = $1.192 \cdot 10^{-7}$, Figure 5). However, for both regressions (with the uncorrected MinC and the corrected MinC parameters), the distribution of the residues differs according to the SIC content. For SIC contents lower than a value around 60 gC.kg^{-1}soil,

265 data plot mostly above the line y=x with a sparse dispersion. For SIC contents higher than a value around 60 gC.kg^{-1}soil, data plot mostly below the line y=x with a higher dispersion (Figure 5). The slope of the regression line between the SIC contents < 60 gC.kg^{-1}soil estimated by EA and by RE is statistically closer to 1 with the corrected MinC parameter (1.03) than with the uncorrected MinC parameter (1.06, Student test: p-value = $6.004 \cdot 10^{-6}$, Figure 5). Since the correction decreases the value of the MinC parameter (Figure 2), correcting the MinC parameter

270 reduces its overestimation of SIC contents < 60 gC.kg^{-1}soil, but increases its underestimation of SIC contents > 60 gC.kg^{-1}soil. Thus, the correction applied to the MinC parameter improves its estimation of SIC contents estimated by EA after decarbonation only when they are lower than a value around 60 gC.kg^{-1}soil.

Table 2: Average contribution (mean ± standard deviation) of each curve integration to the TOC and MinC parameters for the 24 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 (%)	0.5 ± 0.2	13 ± 3	2 ± 0.6	1 ± 0.2	1 ± 1	6 ± 1	12 ± 20	3 ± 1	74 ± 4	87 ± 22

275

The thermal breakdown of SIC into CO$_2$ occurs at temperatures > 650°C under oxidative conditions (Table 2). The SIC thermal breakdown forms the S5 curve (Figure 5), whose integration provides the main contributor to the MinC parameter (Table 2). The higher the SIC content, the more distorted the S5 curve (Figure 5). Moreover, when SIC contents are higher than a value around 60 gC.kg^{-1}soil, the S5 curve drops sharply at the end of the final

280 oxidation isotherm (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 $>$ 60 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 (between 3.6 and 4.2 mg of SIC in these cases).

3.2 Effect of the SIC amount in the RE crucible on the SIC content estimated by RE on the 4 samples of the

285   **second panel**

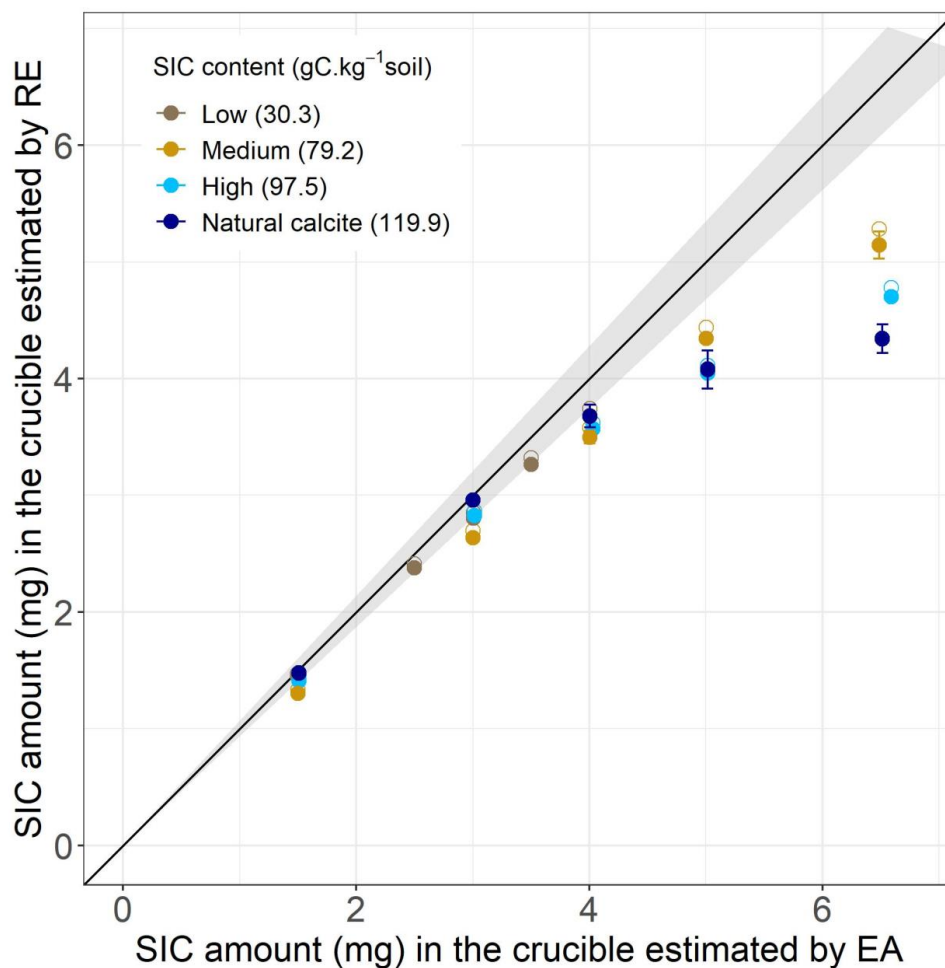



Figure 6: Plot of the SIC amount in the crucible estimated by the uncorrected (hollow point) and the corrected (full point) MinC parameter vs the one estimated by EA after decarbonation. The grey area represents the measurement error of the two methods. The error bars stand for the three replicates performed with the five crucibles of the soil with

290   **a medium SIC content and with the natural calcite.**

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). The corrected and uncorrected MinC parameters are close, and even equal for the natural calcite, because SOC contents in the second panel are very low. For SIC amounts in the RE crucible > 4 mg, the higher the SIC amount, the more the MinC parameter

295   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 300 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 natural calcite than in the soil with a medium SIC content 305 likely explain the observed results.

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 310 can be customized by extending the final oxidation isotherm.

3.3 Adaptation of the RE standard cycle of analysis

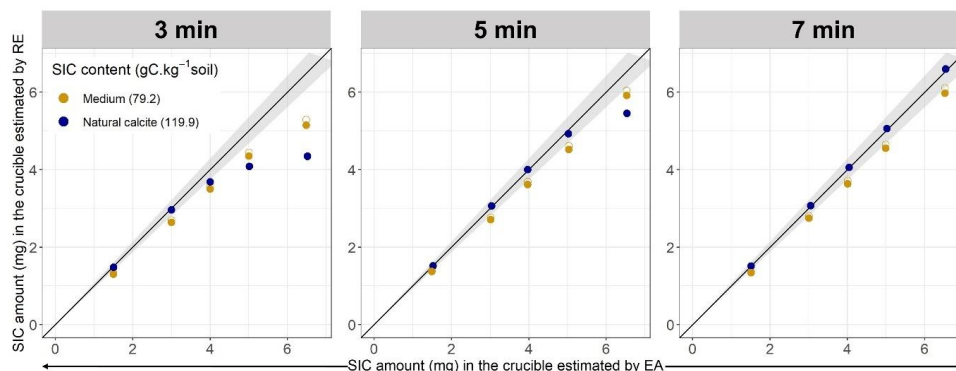



Figure 7: Plots of the SIC amount in the crucible estimated by the uncorrected (hollow point) and the corrected (full point) RE MinC parameter vs the SIC amount in the crucible estimated using EA after decarbonation. Three cycles
315 **with different durations of the final oxidation isotherm step (3, 5 and 7min) have been applied. The grey area represents the measurement error of the two methods.**

The SIC amounts in the crucibles of natural calcite are properly estimated by the MinC parameter with a final oxidation isotherm of 7 min (Figure 7).

Unlike the natural calcite, a systematic error is observed for the estimation of the SIC amount of the soil with a 320 medium SIC content, even with a final oxidation isotherm of 7 min (Figures 6 and 7). This error seems to be proportional to the quantity of sample in the crucible, as it increases with the SIC amount in the crucible (Figures 6 and 7). Thus, it is suggested that this error can propagate on the five SIC amounts calculated from the single EA 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 325 (Nayak et al., 2019; Chatterjee et al., 2009). Thus, this error can be related to a measurement bias originating from

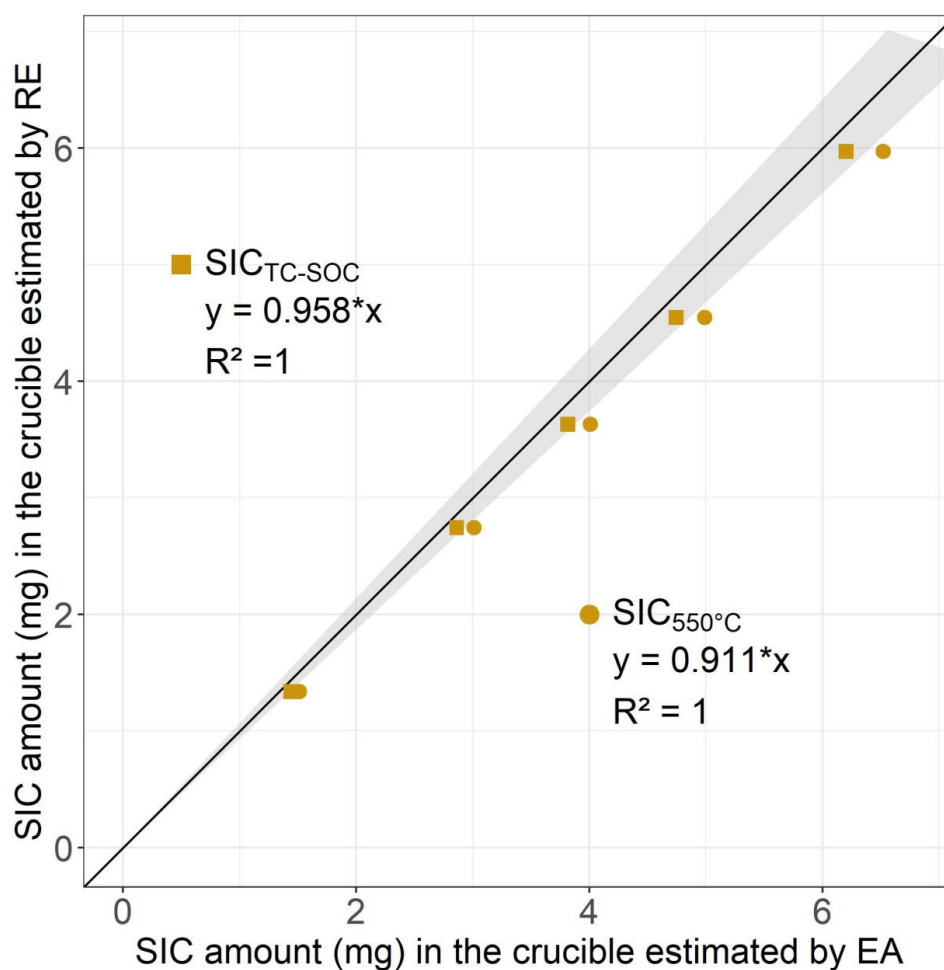
the pretreatment performed on the soil before the SIC content estimation by EA rather than from the RE analyses. Thus, the SIC amount estimated by EA as the difference between the TC and SOC amounts after decarbonatation (SIC_{TC-SOC}, Figure 8) should be less overestimated than the SIC amount estimated by EA after heating at 550°C ($SIC_{550°C}$, Figure 8).

330

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 after decarbonation (SIC550°C, point) and via the difference between the TC and the SOC (SICTC-SOC, square) for the soil with a medium SIC content. The grey area represents the measurement error of the two methods. Linear regression equations are provided with the coefficient of determination.

335   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 SIC_{TC-SOC} (0.96) value than with the $SIC_{550°C}$ value (0.91, Student test: p-value = 0.009247, Figure 8). This result confirm that the systematic error observed in Figure 6 and 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.

340 To provide enough time for SIC thermal breakdown during the oxidation phase, the maximal temperature could have been raised. However, raising the maximal temperature during the oxidation phase *i.e.*, up to 850°C, requires a RE7 device, and most labs still use a RE6 device.

4 Conclusion

The RE thermal analysis is a promising tool to measure both SOC and SIC contents with a single analysis on a
345 single aliquot of a calcareous soil. 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 soils once the TOC parameter is corrected. However, the standard cycle of analysis cannot achieve a complete thermal breakdown of SIC amounts > 4 mg. This boundary leads to an underestimation of high SIC contents by the MinC parameter even
350 after correcting it. Thus, 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. However, when the SIC content is known, the standard cycle of analysis can be used by limiting the SIC amount in the crucible to 4 mg of SIC.

These results need to be repeated with other calcareous soils. The TOC and MinC parameters still need to be statistically corrected even with the adaptation of the oxidation phase. To be independent of statistical corrections,
355 which could depend on the SOC and SIC forms in the analyzed soil, further study should focus on the distinction between the signals from the cracking of organic matter and the ones from the SIC thermal breakdown.

In conclusion, 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

360 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.

Author contributions

JH, DS, TC, and IK designed the experiment. JH and HR performed the measurements. JH, DS, IK, EV, and HR
365 analyzed the data. JH wrote the manuscript. DS, IK, TC and EV reviewed and edited the manuscript.

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