Adjustments of the Rock-Eval® thermal analysis for SOC and SIC quantifications

Joséphine, HAZERA [1,3], David, SEBAG [1], Isabelle, KOWALEWSKI [1], Herman, RAVELOJAONA [1], Eric, VERRECCHIA [2], Tiphaine, CHEVALLIER [3]

(1) IFP Energies Nouvelles, Earth sciences and environmental technologies division, Rueil-Malmaison, France

(2) University of Lausanne, Institute of Earth Surface Dynamics, Lausanne, Swiss

(3) Eco&Sols, IRD, CIRAD, INRAE, L'institut Agro, University of Montpellier, Montpellier, France

Abstract:
The standard method to quantify soil organic and inorganic carbon (SOC & SIC) separately in calcareous soils relies on pretreatments (decarbonatation or decarbonation) and calculation of the difference between the C contents measured by Elemental Analysis (EA) on the bulk and the pretreated aliquot (ISO, 1995; Bispo et al., 2017). This procedure leads to i) analytical bias due to pretreatment (*e.g.,* acid pretreatment which is supposed to destroy all the SIC without damaging the SOC), ii) measurement deviation associated with the heterogeneity of the bulk and pretreated aliquots and iii) cumulative errors associated with the calculation (Chatterjee et al., 2009; Schlacher and Connolly, 2014; Nayak et al., 2019). The Rock-Eval® (RE) thermal analysis provides a technical solution to quantify both SOC and SIC with a single analysis on a non-pretreated aliquot (Behar et al., 2001). During the RE analysis, two standard parameters, TOC (for total organic content) and MinC (for mineral carbon), which estimate the organic C and inorganic C contents respectively, are calculated from the carbonaceous effluents emitted by the ramped pyrolysis of the aliquot followed by the oxidation of the residue. The RE analysis was initially developed in the 1970s by IFPEN to study oil bearing rocks. Since the 2000s, the RE analysis has been applied on soil samples and statistical corrections of the TOC parameter have been proposed to improve its estimation of the SOC content assessed by EA (Disnar et al., 2003; Sebag et al., 2022a; 2022b). Thus the RE has been increasingly used to quantify and characterize SOC (Sebag et al., 2016; Soucémarianadin et al., 2018; Malou et al., 2020; Cécillon et al., 2021). However, few applications have focused on SIC quantification and no adjustments of the RE standard analysis cycle have been investigated. This study aims at adjusting the RE standard analysis protocol to quantify SOC and SIC without using statistical corrections. For this aim, a panel of 30 soil samples of southern France and northern Tunisia with a wide range of SOC and SIC contents was analyzed by RE. The results were compared to SOC and SIC quantifications by EA after decarbonatation and decarbonation respectively. First, the total carbon content estimated by RE (TOC + MinC) systematically underestimated the total carbon content estimated by EA for samples with high SIC contents. The higher the SIC amount in the RE crucible, the more the MinC parameter underestimated the SIC content. The oxidation thermograms of crucibles containing more than 4 mg of SIC showed a sudden drop of the CO_2 signal at the end of the analysis suggesting an incomplete thermal breakdown of the carbonates. Thus, the last oxidation isotherm was extended to achieve the SIC thermal breakdown (Hazera et al., 2023, in prep). Secondly, the pyrolysis thermograms showed that, after 550°C, a part of thermoresistant SOC and a part of SIC decomposed simultaneously. To avoid the fluxes mixing and the use of statistical corrections, the pyrolysis phase was stopped at the onset of SIC decomposition to drag all SIC signal during the oxidation phase only. The
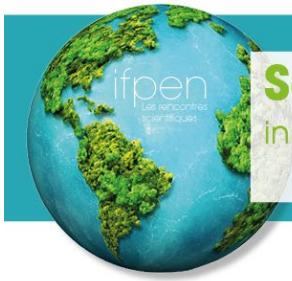
parameters obtained with this cycle of analysis are strongly related to those obtained with the standard cycle and the statistical corrections. Finally, the new cycle of RE analysis (extended oxidation and low temperature pyrolysis) improved the SOC and SIC content estimations by the TOC and MinC parameters on a single aliquot of calcareous sample and without using statistical corrections.

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