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Identification and Quantification of Carbonate Species Using Rock-Eval Pyrolysis

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Résumé — Détermination et quantification des carbonates par pyrolyse Rock-Eval — Cet article présente une nouvelle méthode fiable et rapide pour caractériser et quantifier les carbonates dans tout type d'échantillon solide. La méthode est basée sur la quantification du flux de CO₂ émis lors de la décomposition thermique progressive des carbonates au cours d'un chauffage programmé. Les différents pics de déstabilisation permettent la détermination des différents types de carbonates présents dans l'échantillon analysé. La quantification de chaque pic donne les proportions respectives de ces différents types de carbonate présents dans l'échantillon. La procédure qui a été choisie dans ce travail utilise un pyrolyseur Rock-Eval 6 standard en mode oxydation. Des profils caractéristiques d'échantillons de références sont présentés pour les carbonates naturels les plus courants. Cette méthode devrait permettre différents types d'application dans des disciplines diverses et dans des domaines à la fois académiques et industriels.

Abstract — Identification and Quantification of Carbonate Species Using Rock-Eval Pyrolysis — This paper presents a new reliable and rapid method to characterise and quantify carbonates in solid samples based on monitoring the CO₂ flux emitted by progressive thermal decomposition of carbonates during a programmed heating. The different peaks of destabilisation allow determining the different types of carbonates present in the analysed sample. The quantification of each peak gives the respective proportions of these different types of carbonates in the sample. In addition to the chosen procedure presented in this paper, using a standard Rock-Eval 6 pyrolyser, calibration characteristic profiles are also presented for the most common carbonates in nature. This method should allow different types of application for different disciplines, either academic or industrial.

INTRODUCTION

The characterisation and quantification of carbonates in solids is required by a wide range of activities. In geoscience, identification of carbonates is instrumental for carbonate geology (including sedimentology, metallogeny and diagenesis), for petroleum geoscience (in order to characterise source rocks, reservoirs and seals) and for underground storage of acid gases such as CO₂ or H₂S (in order to assess the impact of these gases on the pre-existing carbonates, if any, of the

receiving reservoir). Carbonate analysis and quantification is also useful in soil science for characterisation and subsequent agricultural purposes. It is also useful in various additional industrial domains including iron smelting, cement and lime manufacture, production of ceramic glazes, drilling industries (quality of the cements) and building (quality of the construction rocks).

Semi-quantitative determination of carbonates can commonly be done using classical optical methods (such as

an optic microprobe on thin sections) or X-ray diffraction (Diebold *et al.*, 1963; Gavish and Friedman, 1973; Weber, 1968; Roselle, 1982; Martinez and Plana, 1987; Hillier *et al.*, 2001; Al Jaroudi *et al.*, 2007) or by a group of different analytical methods (such as Scanning Electron Microscope, electron microprobe, infrared or Raman spectroscopy, chemical analysis, etc.). Nevertheless, the real quantification of carbonates, especially in the case of mixing of different carbonates in the same sample, is not such an easy task and, to date, only a few methods allowing one to directly quantify the carbonate content in samples of rocks or other solid materials are available. Classical methods of calcimetry by acid attack and gravimetry or measurement of the released CO₂ (Scheibler method, ÖNORM, 1999), or else Fourier Transform InfraRed (FT-IR) (Legodi *et al.*, 2001; Bosch *et al.*, 2002; Boke *et al.*, 2004; Vagenas *et al.*, 2003; Tatzber *et al.*, 2007) spectroscopy can be used in the case of occurrence of a single carbonate family in the sample, especially calcium carbonate, but the quantification in cases of mixing of different carbonates requires relatively time-consuming studies such as thermogravimetry (Cebulak *et al.*, 2003; Siewert, 2004; Villain *et al.*, 2007), SEM mapping or microprobe mapping, or whole-rock analyses with processing of the results. Methods based on X-ray diffraction allow a good determination of the different types of carbonates but these methods allow only a semi-quantitative estimate of the proportions of the different carbonates.

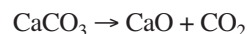
However, all these methods mentioned above require a relatively long chain of data acquisition and processing and some of them need expensive devices. To the best of the authors' knowledge, to date, there is no available method to quickly determine and directly quantify the entire family of carbonates in solid samples. In this paper, we present a simple and rapid method for determination and quantification of the carbonates in solid samples which is based on the thermal decomposition of the different carbonates during a programmed heating and on the monitoring of the released CO₂ during the decomposition.

Using the Rock-Eval[®] pyrolyser, previous published works have already shown how it is possible to quantify the amount of calcium carbonates provided that the carbonates present in the samples are only calcium carbonates (Lafargue *et al.*, 1998). This method is thus not applicable when we are

dealing with other carbonates (such as dolomite, siderite, magnesite and other carbonates less common in nature). The aim of this paper is to complete this approach using Rock-Eval pyrolysis techniques to allow the characterisation and quantification of the different types of carbonates in any types of solid samples and in a relatively short time (about 30 minutes with the chosen procedure).

1 METHOD PRINCIPLES

This method[®] (Pillot *et al.*, 2011), which allows characterising and quantifying carbonates in powder of all types of solid samples (rocks, soils, cements, etc.) with relatively small samples (from 10 mg to 300 mg, preferentially > 40 mg), consists of measuring the CO₂ emitted by a sample when it is thermally decomposed during a monitored heating. For instance, the thermal destabilisation of calcite (CaCO₃) produces the following reaction:



Because the different families of carbonates are destabilised at different temperatures, it is possible to deduce their nature according to their decomposition temperature and because carbonates emit CO₂ during their destabilisation, it is possible to quantify the amount of carbonate initially present in the sample after a complete thermal decomposition. It is also possible to distinguish carbonates and organic matter, because when carbonates are thermally decomposed with a flux of air (input of oxygen), they do not produce CO, whereas oxidation of organic matter produces CO and CO₂ by combustion in the presence of oxygen.

For this study, we used a classical Rock-Eval 6[®] (Lafargue *et al.*, 1998) to develop a systematic analytical procedure. The method is based on a combustion of the sample using specifically the oxidation cycle of the Rock-Eval 6. A prior pyrolysis as is done in a standard run is not mandatory but it provides complementary useful information about the organic matter present in the samples. For the determination and quantification of the carbonates using the oxidation mode, the samples are heated according to a programmed temperature ramp in an oven flushed with a continuous flux of air (carrier gas to the analysers). This allows a thermal

TABLE 1

Typical values for the temperature peak of the different carbonates *versus* the weight of the samples

Weight (mg)	Azurite	Malachite	Siderite	Rhodochrosite	Magnesite	Dolomite peak1	Dolomite peak2	Aragonite	Chalk	Marble
5	416		515	652	602		765	762	776	780
10	413	382	516	650	613		790	788	801	805
20	408	388	516	647	622	797	817	819	835	837
40		393	519	647	631	822	831	838	850	850

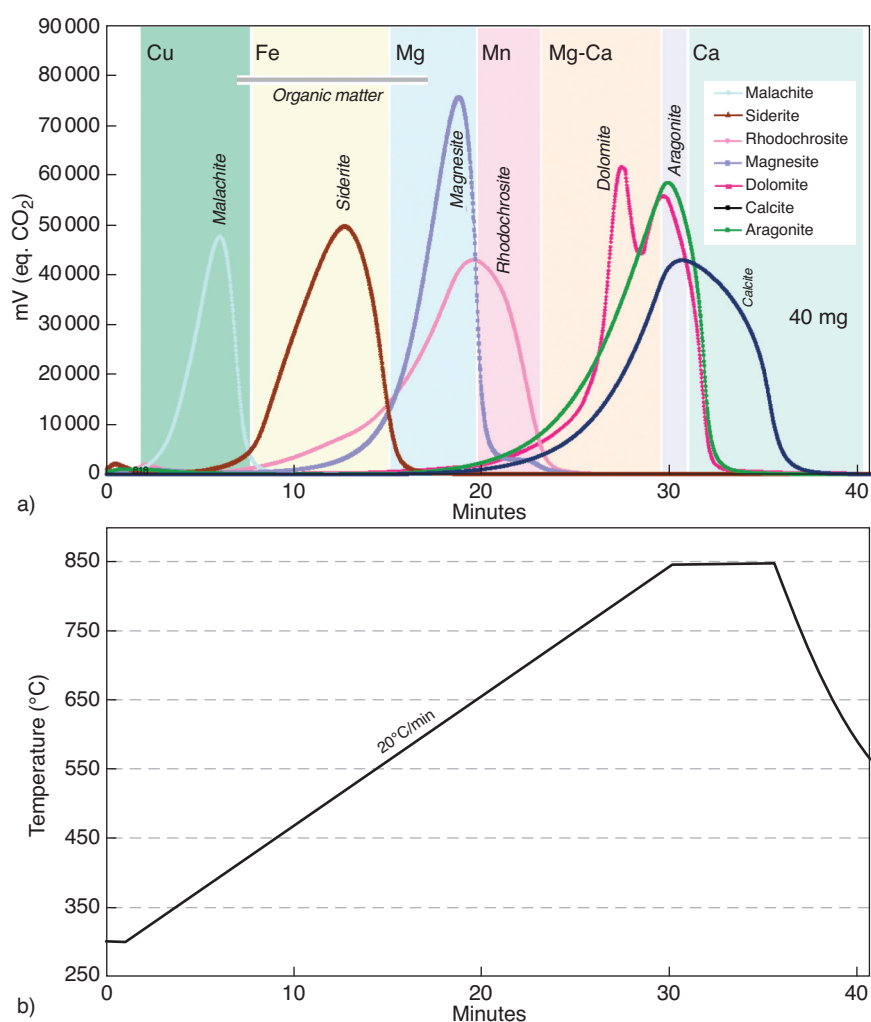


Figure 1

Examples of characteristic peaks a) obtained with 40 mg of different pure mineral standards (malachite, siderite, magnesite, rhodochrosite, dolomite, aragonite, calcite), b) with a heating ramp of 20°C/min between 300 and 850°C.

decomposition of the carbonates which is monitored by analysing the produced gas with an analyser (infrared spectrometer) giving a continuous measurement of the amount of CO₂ as a function of temperature and time. The oxidation oven heats the samples in the range 300°C to 850°C with a preset temperature programme. The Rock-Eval 6 device is limited to 850°C but heating at slightly higher values would be very useful, especially for the study of calcite because this mineral is destroyed at the upper limit of the temperature capability of the Rock-Eval 6 (*Fig. 3c, d*). With the new version of the Rock-Eval (7), it will be possible to heat up to 1 200°C and so this specific problem concerning calcium carbonates will be resolved. However, even with the Rock-Eval 6, calcite is fully destroyed after the run and so the quantification is correct. It is

just the temperature value of the peak which is imposed by the temperature at the end of the heating ramp. In all the experiments shown here, we chose a constant standard temperature ramp of 20°C per minute in order to be able to reliably compare the different results.

2 CHARACTERISATION OF CARBONATES

2.1 Procedure

During heating, carbonates destabilise and give a characteristic profile of CO₂ depending on the temperature of thermal destabilisation of the different carbonate minerals. For each individual carbonate mineral, the pattern of CO₂ shows one or

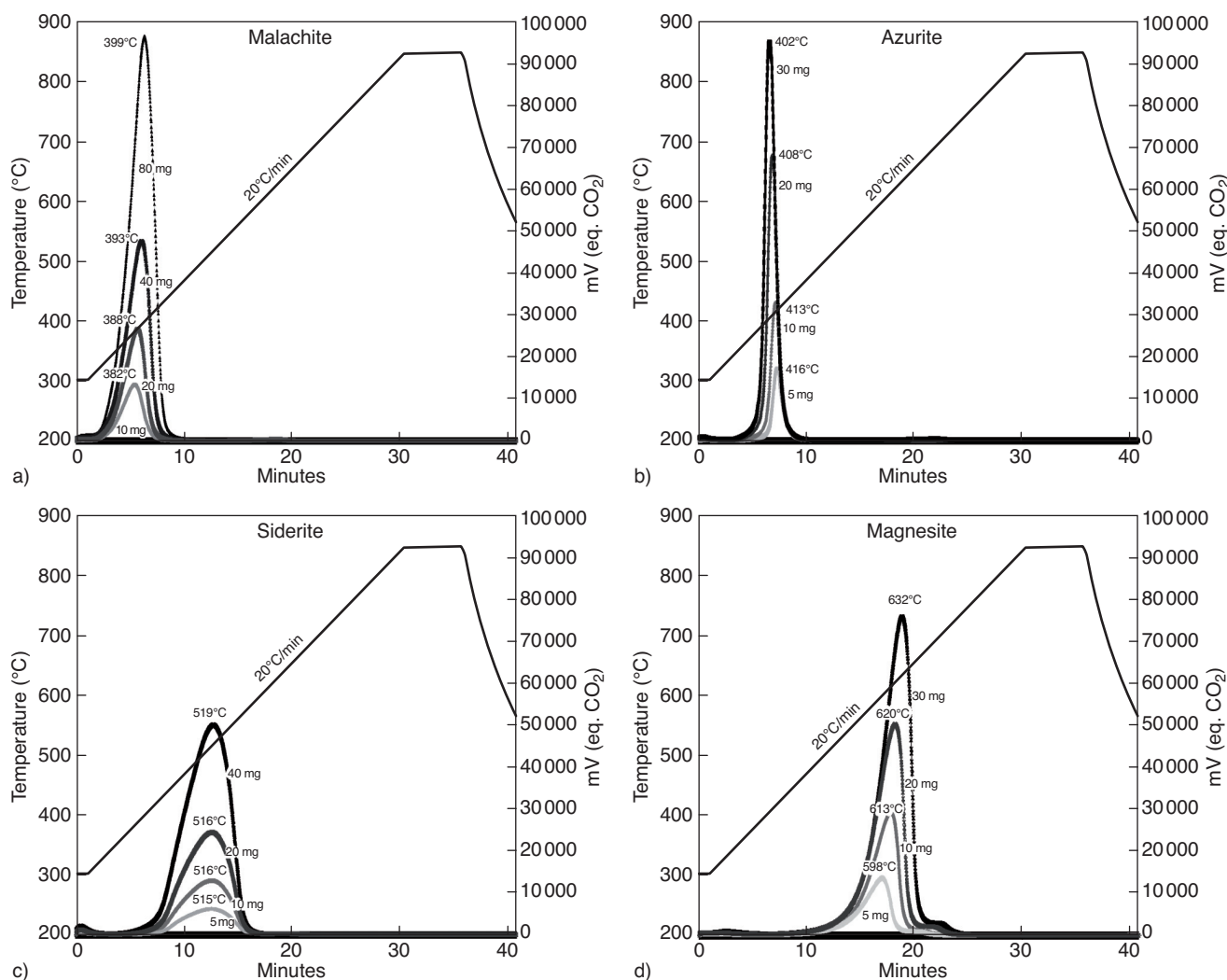


Figure 2

Monitored thermal destabilisation of a) malachite (Morocco); b) azurite (Morocco); c) siderite (Greenland); d) magnesite (Oman).

several peaks. The different types of carbonates are identifiable by the temperature and the shape of the peaks (notably height and area of the peaks). This profile is a unique fingerprint and characterises each type of carbonate within the sample. With this signature, it is possible to discriminate all the types of carbonates present in the sample, such as calcium carbonate (calcite, aragonite), magnesium carbonate (magnesite, hydromagnesite), iron carbonate (siderite), manganese carbonate (rhodochrosite), copper carbonates (azurite, malachite), mixed carbonates (dolomite, ankerite, etc.) and all other types of carbonates rare in nature. It also allows easily distinguishing mixture of carbonates. As mentioned before, complementary to the CO₂ recording, CO measurement allows distinguishing carbon from organic matter (the combustion of organic matter emits CO which is not the case during carbonate destabilisation; Lafargue *et al.*, 1998).

Reference carbonate samples were used to provide reference CO₂ profiles. The reference profiles have characteristic peaks, each peak being associated with the type of carbonate identified. It is thus possible to determine the type of carbonate in any kind of sample by comparison with these reference profiles.

To calibrate the reference profiles, we selected rocks containing only one carbonate and known proportions of this carbonate, preferentially pure minerals (pure calcite, pure aragonite and so on). Figure 1 compares the characteristic destabilisation profiles of different carbonates for the same weight of analysed material (40 mg) and for the same heating ramp (20°C/mn). Globally, at increasing temperature, Cu-carbonates destabilise first, then Fe-carbonates, then Mg and Mn-carbonates and finally Ca-carbonates (Fig. 1-3).

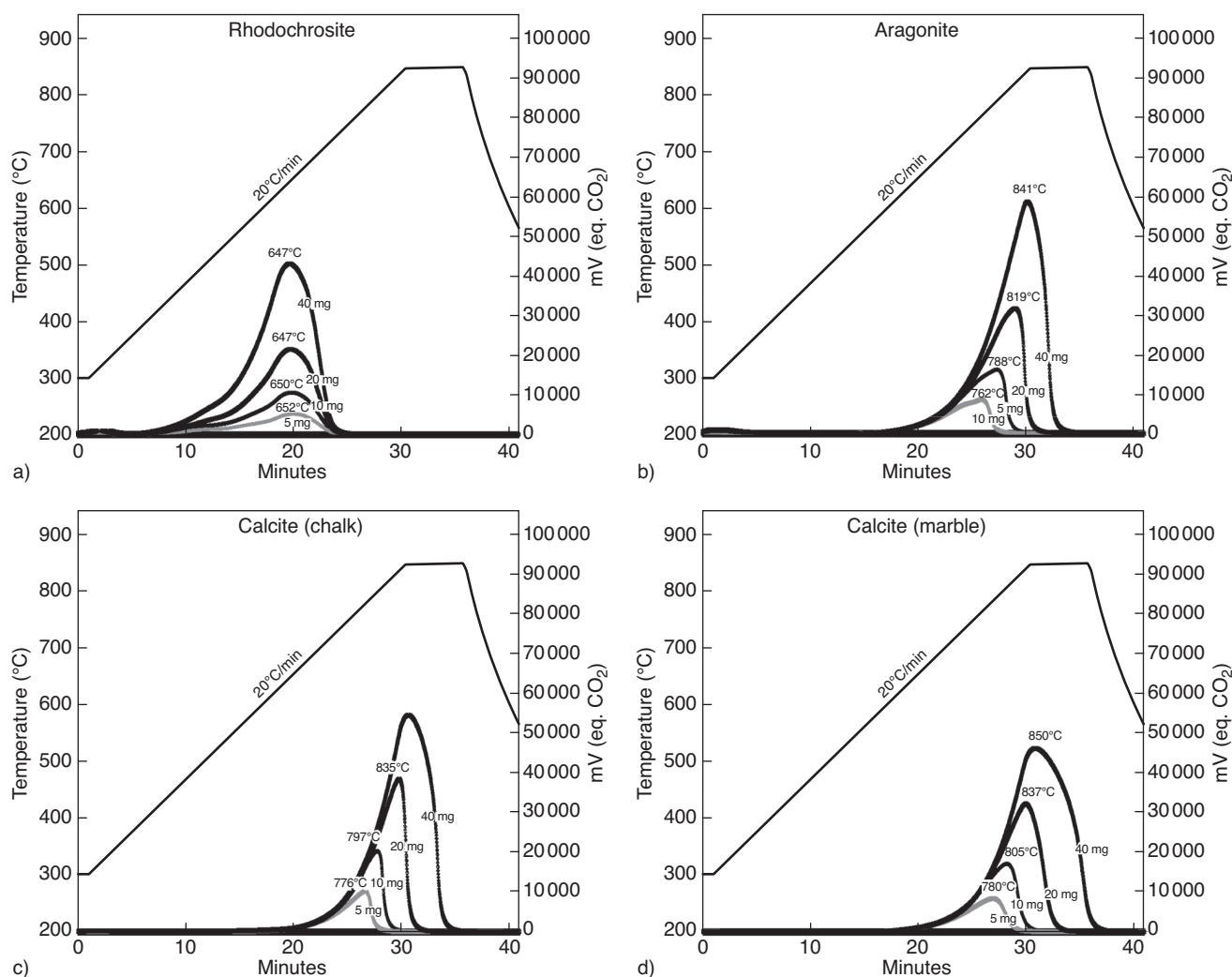


Figure 3

Monitored thermal destabilisation of a) rhodochrosite (Colorado); b) aragonite (Lambi shell from Guadeloupe, France); c) calcite (chalk from the Paris basin, France); d) calcite (marble from Paros, Greece).

2.2 Simple and Complex Carbonates

Simple carbonates such as siderite (FeCO_3), magnesite (MgCO_3), rhodochrosite (MnCO_3), aragonite (CaCO_3) and calcite (CaCO_3) show a single decomposition peak (Fig. 2, 3), whereas complex carbonates (carbonate of several elements) such as dolomite ($\text{MgCa}(\text{CO}_3)_2$) and ankerite ($\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$) show several decomposition peaks (Fig. 4). Simple carbonates linked with hydroxide anions also show a single peak. For instance, malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) and azurite ($\text{Cu}_2(\text{CO}_3)_2(\text{OH})_2$) show just one peak (Fig. 2). Hydrated carbonates such as hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) show several peaks (Fig. 4). For the same weight of sample, the height and width of the peaks vary in function of the composition of each specific mineral.

2.3 Mass Effect

With the adopted procedure and the device that we used (Rock-Eval 6), we observed a mass effect characterised by an influence of the mass of the analysed sample on the peak temperature of the same reference sample, whereas all the samples were thinly crushed according to the same procedure with a laboratory crusher. The amplitude of this effect depends on the different carbonate types and it corresponds to a shift of temperature of the maximal release of CO_2 . This effect is notably observed for small samples and it tends to disappear for all carbonate samples around 40 mg (Fig. 2-5). On the other hand, over 40 mg, we observed a saturation effect of the cell of the Rock-Eval for some carbonates, notably for magnesite (due to sudden high flux of CO_2). It is

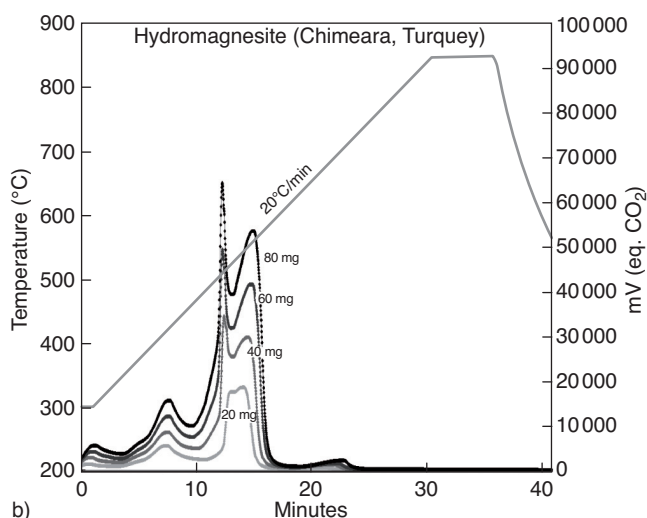
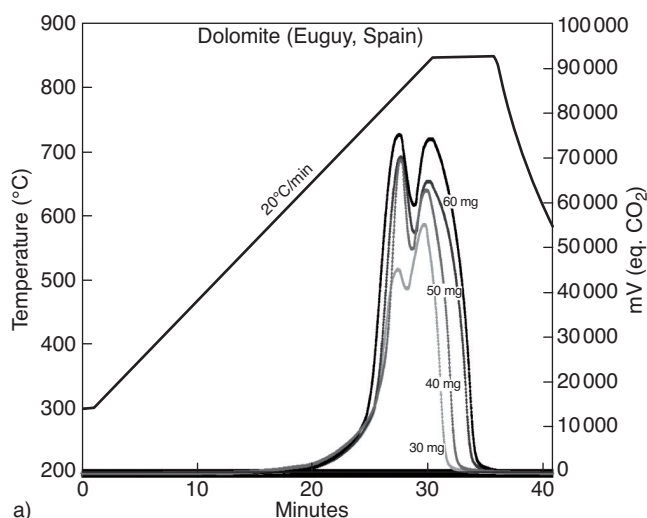


Figure 4

Monitored thermal destabilisation of a) dolomite pure crystal from Euguy (Spain); b) hydromagnesite (Chimaera, Turkey).

thus preferable to proceed with samples of weight close to 40 mg to optimise the reliability of the determination and quantification, but in cases where only small samples are available, it is necessary to take into account this effect (see chart shown in Fig. 5). Also, as we already mentioned above, the analyser we used does not allow one to monitor high-temperature thermal decomposition ($> 850^{\circ}\text{C}$), which is a limiting factor for a good definition of the calcite peaks which are higher than 850°C for samples > 20 mg (Fig. 2, 6).

2.4 Crystallisation Effect

The size of the mineral growths very probably also has an effect in terms of thermal destabilisation of some carbonates.

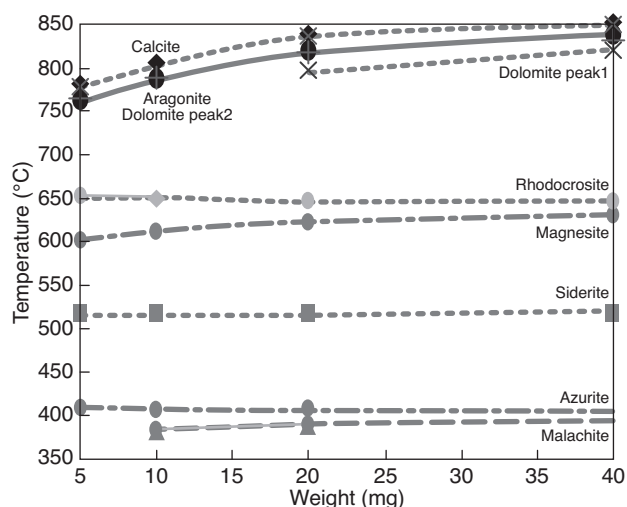


Figure 5

Simplified chart illustrating the mass effect on the determination of the peak of decomposition of the different carbonates using a Rock-Eval 6. For samples heavier than 40 mg this mass effect is negligible.

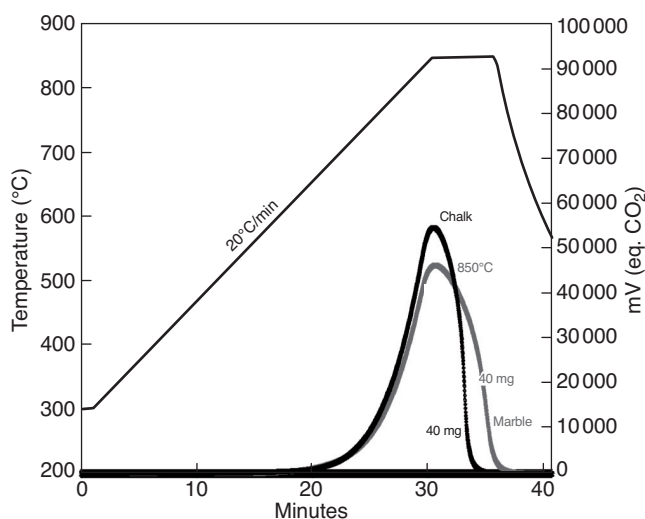


Figure 6

Compared monitored thermal destabilisation of chalk and marble.

This phenomenon is very moderate for most carbonates but it is clear for the case of calcite. Small calcite minerals destabilise more easily than large calcite minerals. For instance, chalk destabilises at a lower temperature than marble. Figure 6 illustrates an example of the difference in shape of the respective destabilisation profiles. The destabilisation profile of chalk is relatively similar to that of aragonite (slightly higher temperature), whereas the destabilisation profile of a metamorphic marble extends to higher temperatures (Fig. 6). In this example, for the case of marble, the strong asymmetry

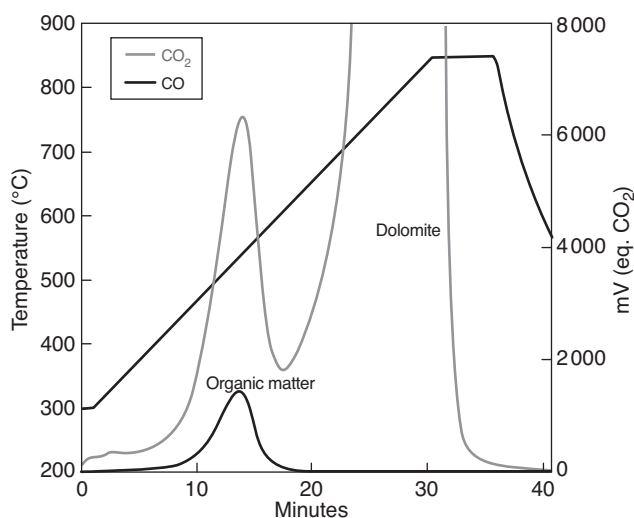


Figure 7

This figure shows an example of the presence of organic matter associated with carbonate (here dolomite). During the Rock-Eval oxidation cycle the combustion of the organic matter produces CO and CO₂, whereas the thermal decomposition of carbonate produces only CO₂.

and the highest value of the peak of temperature is imposed by the heating ramp which is limited to 850°C. As mentioned above, this problem will not remain with the new Rock-Eval 7 with which it will be possible to have a heating ramp up to a temperature of 1 200°C.

2.5 Organic Matter Effect

The occurrence of organic matter associated with carbonates can be easily detected using Rock-Eval 6 (Lafargue *et al.*, 1998). During the oxidation cycle the combustion of organic matter produces CO and CO₂, whereas the decomposition of carbonates (without organic matter) produces only CO₂. Figure 7 shows an example of how we can distinguish the occurrence of organic matter associated with carbonate (CO₂ and CO peaks for organic matter and only a CO₂ peak for carbonate). In the specific case of an interference with CO₂ released by organic matter (*i.e.* for copper carbonates, siderite and magnesite), it is necessary to conduct a classical Rock-Eval run (pyrolysis and oxidation) which allows one to correctly distinguish organic matter and carbonates.

3 QUANTIFICATION OF THE CARBONATE CONTENT

3.1 Principle

The content of the different types of carbonates can be easily quantified from the surface area of each characteristic peak

provided by the thermal destabilisation of each carbonate present in the sample. For this, we compare the surface area of the peak of CO₂ of a reference sample containing a known proportion of carbonate with the peak of CO₂ of the analysed sample. This allows one to directly deduct the content of the different carbonates present in the sample analysed operating according to a constant procedure. The CO₂ content of the analysed sample is given by:

$$\text{CO}_2 \text{ sample} = \text{CO}_2 \text{ ref} [\text{RFi} / \text{RFref}]$$

- CO₂ ref: CO₂ content emitted by a reference sample;
- RFi: response factor (CO₂ equivalent) of the analysed sample;
- RFref: response factor (CO₂ equivalent) of the reference sample.

The response factors are expressed in millivolts (mV) in the device that we used (in a Rock-Eval the recording corresponds to the infrared signal directly proportional to the CO₂ flux).

Using the procedure described previously, knowing the temperature of destabilisation of each characteristic peak of a single carbonate, we can determine the nature of this carbonate and knowing the amount of CO₂ released by each carbonate, we can directly deduct the amount of the different carbonates present in the sample.

Indeed, knowing the CO₂ mass released during destabilisation, $m(\text{CO}_2)$, it is possible to deduce the mass of mineral carbon, $m(\text{C})$, initially present in the sample:

$$m(\text{C}) = [\text{M}(\text{C}) / \text{M}(\text{CO}_2)] m(\text{CO}_2) = 0.2729 m(\text{CO}_2)$$

$\text{M}(\text{C})$ being the atomic mass of carbon and $\text{M}(\text{CO}_2)$ being the molecular mass of CO₂.

The mass concentration in % of mineral carbon is given by:

$$\text{wt}\%(\text{C}) = 100 [m(\text{C}) / m(\text{sample})]$$

with $m(\text{sample})$ the mass of the analysed sample, the mass concentration in % of the different carbonates (*i*) is thus given by:

$$\text{wt}\%(\text{carbonate } i) = \text{wt}\%(\text{C}) [\text{M}(\text{carbonate } i) / \text{M}(\text{C})]$$

$\text{M}(\text{carbonate } i)$ being the molecular mass of carbonate *i*.

3.2 Application Example

Figure 8 shows the results obtained with a synthetic mixture (50% – 50% by weight) of two different pure carbonate standards (20 mg of magnesite, 20 mg of calcite, *e.g.* total weight 40 mg). Following the method described above, we find that the surface area of the two peaks is indeed equivalent and we obtain a result of 50% of magnesite, 50% of calcite and 100% of total carbonate. Similar tests were done with several tens of different known mixtures and we always obtained a good match with an error of less than 1%.

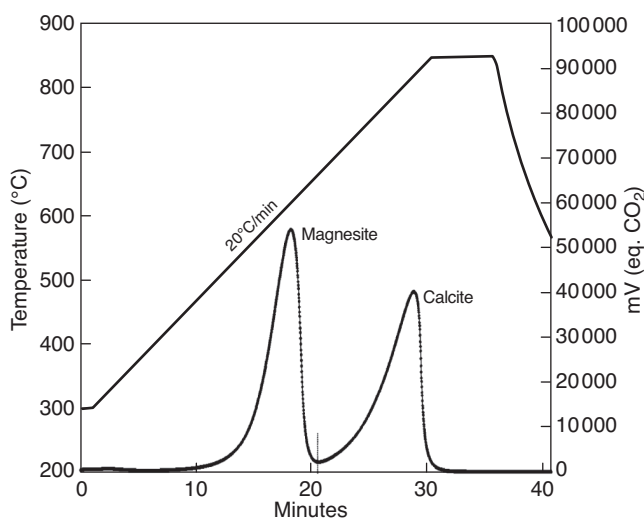


Figure 8

Results obtained with a synthetic mixture (50% – 50% by weight) of two different pure carbonate standards (20 mg of magnesite, 20 mg of calcite: total weight 40 mg). With the method used, we find that the surface area of the two peaks is indeed equivalent (see comments in the text).

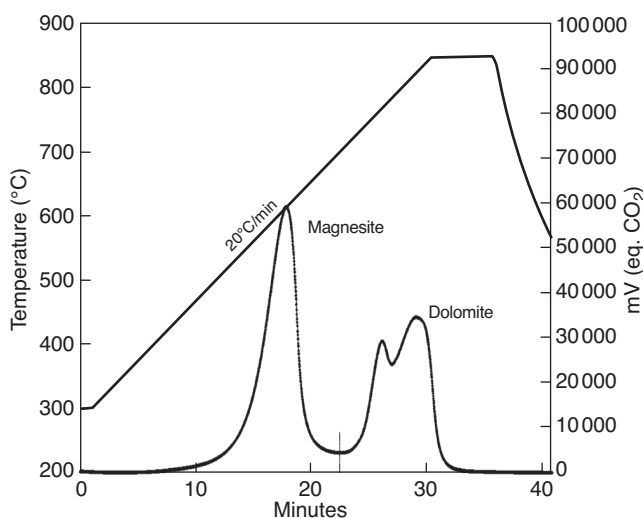


Figure 9

Results obtained on a real rock (carbonate vein of Oman). The method determines the carbonates and quantifies their respective contents (here: 49% of magnesite, 43% of dolomite and 8% of non-carbonate minerals; see comments in the text).

Figure 9 shows an example of application to a natural carbonate rock in a vein filling a fracture within the peridotite nappe of Oman. In this example, we can determine that the carbonates are a mixture of magnesite and dolomite (very characteristic by its double peak). The respective amounts can be determined easily by the proposed method. They are, in this example, 49% of magnesite, 43% of dolomite and 8% of non-carbonate minerals.

CONCLUSION

The method presented in this paper, using a standard Rock-Eval pyrolyser, allows a rapid characterisation and quantification of the whole range of carbonates in any kind of solid sample by monitoring the CO₂ flux released during the progressive thermal destabilisation of the carbonated fraction. Indeed, using the oxidation cycle of the Rock-Eval, the characteristic peaks of destabilisation allow one to identify the different types of carbonates present in the analysed sample. The calibration characteristic profiles presented in this paper for the main natural carbonates as reference data show that copper carbonates are destabilised first, then iron carbonates, then manganese carbonates, then magnesium carbonates, then finally calcium carbonates. Complex carbonates such as dolomite and hydrated carbonates such as hydromagnesite show a signature with several peaks. Moreover, the quantification of each peak allows one to give the respective proportions of these different types of carbonates in the sample even in cases of mixing of different species as

well as a quantification of the non-carbonated fraction. Finally, this simple method should find easy application in a wide range of disciplines, either academic or industrial.

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