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# Classification of amber based on thermal analysis

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## Abstract

The present study considered a possible way of classifying fossil and sub-fossil resins by means of thermal analysis, by using thermogravimetric (TG) and differential thermogravimetric (DTG) profiles. We used samples of resins of different origin and ages, ranging from present-day to Triassic (225 million years ago (Ma)), in order to extend the knowledge of thermal patterns of very ancient resins. Under differential thermogravimetric analysis, all the samples presented a main exothermal event, whose temperature varied among resins of different age. The increasing value of the main exothermal peak varies with the increase of the age of the specimen and a significant linear correlation was found ($r = 0.701$, $P < 0.01$) with a slope of 0.216. Additional information came in relation to paleobotanical origin, lithology and diagenesis of the fossil samples.

Thermal analysis of fossil resins appears therefore as a useful method that may improve the characterization of fossil resins and well correlates with the maturation grade.

*Keywords:* Fossil resins; Amber; Thermogravimetric analysis; Elemental analysis

## 1. Introduction

It is difficult to determine the chronological age of different fossil resins (amber) by means of chemical analysis alone, because the rate of chemical transformations is determined by the rate constant of a particular reaction and the temperature at which the reaction occurs [1]. Therefore, different amber specimens can be of the same geological age, and have differing maturities due to higher temperatures and chemical changes occurred during fossilization. Several methods of analysis have been proposed to classify fossil resins, such as infrared spectroscopy, X-ray diffraction, pyrolysis–gas chromatography–mass spectrometry and nuclear magnetic resonance [1–11].

Thermogravimetric (TG) analysis provides a rapid quantitative method to examine the overall pyrolysis process and to estimate the effective rates of overall decomposition reactions. Thermogravimetry has been used to study and better understand the combustion properties and devolatilisation characteristics of coals [12–14]. Recently, thermogravimetric analysis has been proposed also for the study of amber [15].

The study by Rodgers and Currie [15] presents a thermal analysis of various kinds of recent and fossil resins, with the oldest sample dating Eocene (about 40–45 million years ago (Ma)). Thermal characteristics of older resins, such as Cedar Lake amber (Upper

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Cretaceous, about 70 Ma) were reported also in the pioneer paper by Broughton [3].

Recently, in the Dolomites (northern Italy) we found a new kind of fossil resin, whose peculiar characteristic is the age, belonging to Upper Triassic, about 225 Ma [16]. A further search in the discovery site permitted us to collect additional amounts of this fossil resin that have been used for a more complete chemico-physical characterization of the material (including NMR, unpublished results). This fossil resin occurs as 2–5 mm-size droplets, whose color ranges from light yellow to dark red. Moreover, Triassic amber provided several kinds of microscopic inclusions, still under investigation. Infrared spectrum of Triassic amber from the Dolomites shows the classical appearance of fossil resins, but with unique patterns that allowed an hypothesis on its paleobotanical affinities [16,17].

The availability of this old fossil resin suggested us to carry out thermal studies to extend the knowledge of thermal patterns of very ancient resins, adding also a comparison with various types of ambers from several places of the world. In order to find any relation between thermal analysis data and resin composition, an elemental analysis of all the samples was carried out.

## 2. Materials and methods

The principal characteristics of the specimens analyzed are presented in Table 1. Solubility was determined by holding a small drop of solvent (ethyl ether or ethanol) on the sample for 30 s, and looking for any dissolution of the surface. The age of each resin has been attributed according to stratigraphic data or specific amber studies published in the literature; in some cases, as for copals, the age range may be wide, due to uncertain stratigraphic data of resin deposit. The absolute age was considered according to the International Stratigraphic Chart (GSSP, January 2002, available at: http://micropress.org/stratigraphy/cheu.pdf).

## 3. Thermogravimetric and differential thermogravimetric analysis (DTG)

Thermogravimetric and differential thermogravimetric profiles for each sample were obtained using a prototypal CNR instrument (IGG-CNR, Padua, Italy) “Le Chatelier”. A type S (Pt-10% Rh/Pt) thermocouple placed inside an electric furnace, provided sample and furnace measurements.

When possible, samples were taken from the internal part of the pieces of resins, in order to avoid the influence of degradation processes occurred in the surface, or to limit the influence of a concentration gradient of the different chemical species present in the sample. To analyze Triassic amber, which occurs as small droplets, some specimens (sorted according to yellow or red color) were pooled together and used as a whole.

The samples were pulverized in an agate mortar before the measurement (mass 500 mg, particle size $<75\,\mu m$) and were inserted in a platinum crucible, placed on quartz glass support interfaced by Mettler Toledo AB 104 balance. The heating rate was 10 °C/min, in air, starting from room temperature (20 °C) and reaching a maximum temperature of 700 °C. A computer equipped by home-made software, written in LabView 5.1 language, recorded sequential temperature and weight of sample (TG signal) and derived DTG data from the recorded TG signal. The TG and DTG profiles were edited by graphing software GRAPHER (version 2).

## 4. Determination of total carbon, hydrogen, nitrogen and sulfur

A CE-Instruments EA 1110 automatic elemental analyzer, equipped with AS 200 autosampler and Mettler Toledo AT21 Comparator, was used in this study. The instrument is a simultaneous carbon–hydrogen–nitrogen and sulfur analyzer based on the reliable dynamic flash combustion and GC separation (He carrier gas) followed by thermal conductivity detectors (TCD). A workstation permits complete automation from weight entry to storage of results. It consists of the Eager 200 Software installed on compatible XT/AT microcomputer with a graphics printer. The Eager 200 software offers the possibility to use $K$ factors and linear regression for calculation. Weight entry via the RS-232 link is fully automated. Chromatograms are displayed in real time on the screen and the results can be viewed on video, printed and/or stored on disk. The working conditions were those recommended by the manufacturer.

Table 1
Characteristics of the specimens used for thermal and elemental analysis

| No. | Sample | Age | Surface solubility in ethyl ether | Surface solubility in ethanol | Color | Paleobotanical origin or affinities | References on age and/or paleobotanical origin |
|---|---|---|---|---|---|---|---|
| 1 | Modern resin (Italy) | Present-day | Soluble | Soluble | Light yellow | *P. abies* (Pinaceae) | – |
| 2 | Copal (Madagascar) | Holocene/Recent (10000–100 y) | Slightly soluble | Soluble | Light yellow | *H. verrucosa* (Fabaceae) | [21,36] |
| 3 | Copal (Colombia) | Pliocene/Recent (2.5 Ma–200 y) | Slightly soluble | Soluble | Light yellow | *Hymenaea*(Fabaceae) | [22,23,24,25,30,37,38,39] |
| 4 | Dominican amber, (Dominican Republic) | Early Miocene/Middle Miocene (20–15 Ma); other estimate: Middle Eocene/Early Oligocene (45–30 Ma) | Insoluble | Insoluble | Reddish–blue | *H. protera*, *H. verrucosa* (Fabaceae) | [35,40] |
| 5 | Dominican amber (Dominican Republic) | Early Miocene/Middle Miocene (20–15 Ma); other estimate: Middle Eocene/Early Oligocene (45–30 Ma) | Insoluble | Insoluble | Dark yellow | *H. protera*, *H. verrucosa* (Fabaceae) | [35,40] |
| 6 | Mexican amber (Chiapas, Mexico) | Late Oligocene/Early Miocene (26–22.5 Ma) | Insoluble | Insoluble | Golden yellow | *H. mexicana*, *H. courbaril*, *H. verrucosa* (Fabaceae) | [19,22,35] |
| 7 | Simetite, Sicilian amber (Sicily, Italy) | Oligocene/Upper Miocene/Pliocene (28–11.5–5 Ma) | Insoluble | Insoluble | Dark red | *Agathis* (Araucariaceae), (also Fabaceae) | [19,41,42] |
| 8 | Lessini amber (Monte di Malo, Italy) | Lower Eocene/Middle Eocene (Upper Ypresian/Lower Lutetian) (50–49 Ma) | Insoluble | Insoluble | Dark red-brown | Unknown | [31] |
| 9 | Baltic amber (Poland) | Eocene (40–35 Ma) | Insoluble | Insoluble | Golden yellow | Pinaceae, Araucariaceae, Burseraceae | [19,22,43,44] |
| 10 | Cedar Lake amber (Manitoba, Canada) | Upper Cretaceous (Campanian) (78 Ma) | Insoluble | Insoluble | Golden yellow | Araucariaceae | [19,22,24,45] |
| 11 | New Jersey amber (NJ, USA) | Upper Cretaceous (Raritan Fm., Turonian), (94–90 Ma) | Insoluble | Insoluble | Dark yellow | Cupressaceae, Araucariaceae, Hamamelidaceae | [2,24,46,47] |
| 12 | Amber from Dolomites (Cortina d'Ampezzo, Italy) | Upper Triassic (Carnian) (225 Ma) | Insoluble | Insoluble | Dark red | Conifer (Cheirolepidiaceae) | [16,17] |
| 13 | Amber from Dolomites (Cortina d'Ampezzo, Italy) | Upper Triassic (Carnian) (225 Ma) | Insoluble | Insoluble | Light yellow | Conifer (Cheirolepidiaceae) | [16,17] |

Ma: Million years ago; y: years.

Table 2
Elemental analysis of resin samples

| No. | Sample | N (%) | C (%) | H (%) | S (%) | O and other elements (%) |
|---|---|---|---|---|---|---|
| 1 | *P. abies* resin | 0 | 77.91 | 10.06 | 0 | 12.03 |
| 2 | Madagascar copal | 0.005 | 78.89 | 10.64 | 0.12 | 10.34 |
| 3 | Colombia copal | 0.005 | 79.05 | 10.45 | 0.15 | 10.34 |
| 4 | Blue Dominican amber | 0.071 | 81.99 | 10.93 | 0.20 | 6.81 |
| 5 | Dominican amber | 0.020 | 78.86 | 10.56 | 0.02 | 10.54 |
| 6 | Mexican amber | 0.053 | 83.65 | 11.24 | 0.37 | 4.74 |
| 7 | Simetite | 0.070 | 75.38 | 9.63 | 0.34 | 14.58 |
| 8 | Lessini amber | 0.010 | 79.60 | 10.91 | 0.06 | 9.42 |
| 9 | Baltic amber | 0.011 | 77.42 | 10.14 | 0.42 | 12.01 |
| 10 | New Jersey amber | 0.004 | 78.41 | 10.06 | 0.29 | 11.24 |
| 11 | Cedar Lake amber | 0.013 | 80.23 | 10.55 | 0.24 | 8.97 |
| 12 | Red Triassic amber from Dolomites | 0.050 | 81.27 | 10.35 | 1.74 | 6.59 |
| 13 | Yellow Triassic amber from Dolomites | 0.038 | 80.87 | 10.43 | 1.47 | 7.19 |

Each datum is the mean of at least three determinations.

### *4.1. Procedure*

The powdered sample (about 2 mg) is placed into a tin capsule. The sample is loaded into the AS 200 autosampler which allows the automatic analysis. The calibration standards for carbon–hydrogen–nitrogen and sulfur were prepared from known amounts of sulfanilamide ($C_6H_8N_2O_2S$).

Analytical results for total carbon, hydrogen, nitrogen and sulfur in the amber samples obtained from at least three determinations are given in Table 2.

## 5. Statistical analysis

In order to determine a relationship between the age of the resins and the value of main DTG peak, a linear regression was constructed through the experimental points by using the least squares method. The linear correlation coefficient $r$ of Bravais–Pearson was calculated and tested against zero using a Student's $t$-test with $n-2$ degrees of freedom. A statistically significant relationship between the two variables was accepted at the probability level of $P < 0.05$.

## 6. Results

### *6.1. Thermogravimetric patterns of resins*

As illustrated in Figs. 1–3 (thick lines), all fossil/sub-fossil resins presented a TG combustion profile which began after 200 °C. Conversely, present-day resin from *Picea abies* showed a significant weight loss already after 100 °C. Total combustion occurred before 600 °C for all the tested resins (range about 560–600 °C).

The slope of TG curves among resins did not show univocal pattern. However, the oldest samples (New Jersey Cretaceous amber and Italian Triassic amber) presented a steeper profile. Overall aspect of TG curves was in some cases characterized by multiple components.

### *6.2. Differential thermogravimetric analysis of resins*

Under differential thermogravimetric analysis of combustion patterns of resins (Figs. 1–3, thin lines), all the samples presented a main exothermal event, as consequence of maximal rate of weight loss. Here we defined as “main” peak the first major thermal event detected from the beginning of combustion. The temperature of the peak varied among resins of different age. In particular, the increasing value of the main exothermic peak well correlates to increase of the age of the specimen. A linear correlation between these two parameters (age and main DTG peak) was detected (Fig. 4). The regression line plotted considering all the fossil resins provided a statistically significant correlation ($r = 0.701$, $n = 13$, $P < 0.01$) with a slope of 0.216. From this equation, it results that each 100 million year period caused an increase

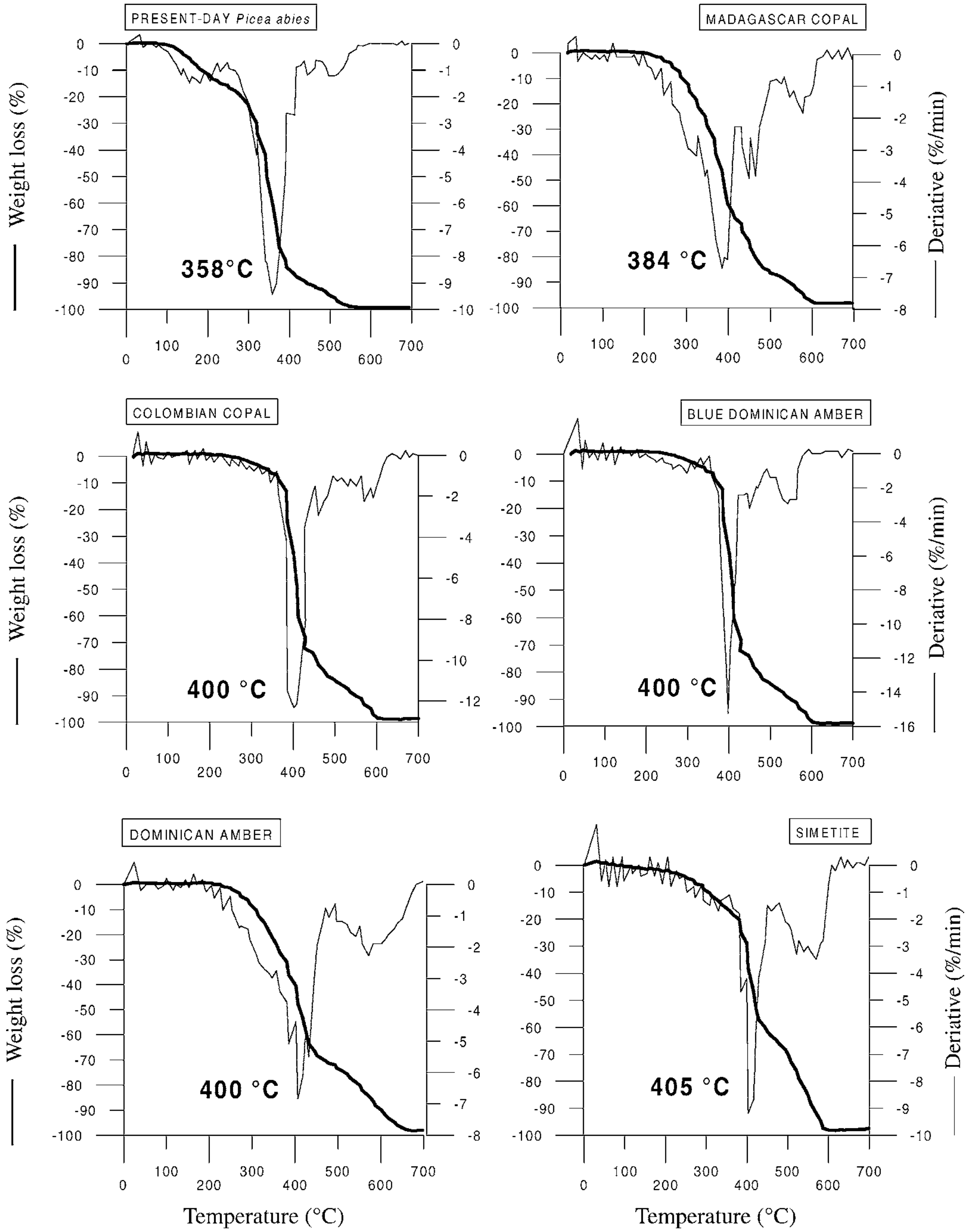

Fig. 1. Thermogravimetric (TG: thick line) and differential thermogravimetric (DTG: thin line) analysis of recent to cenozoic resins of various origin. The value of the main DTG peak is indicated.

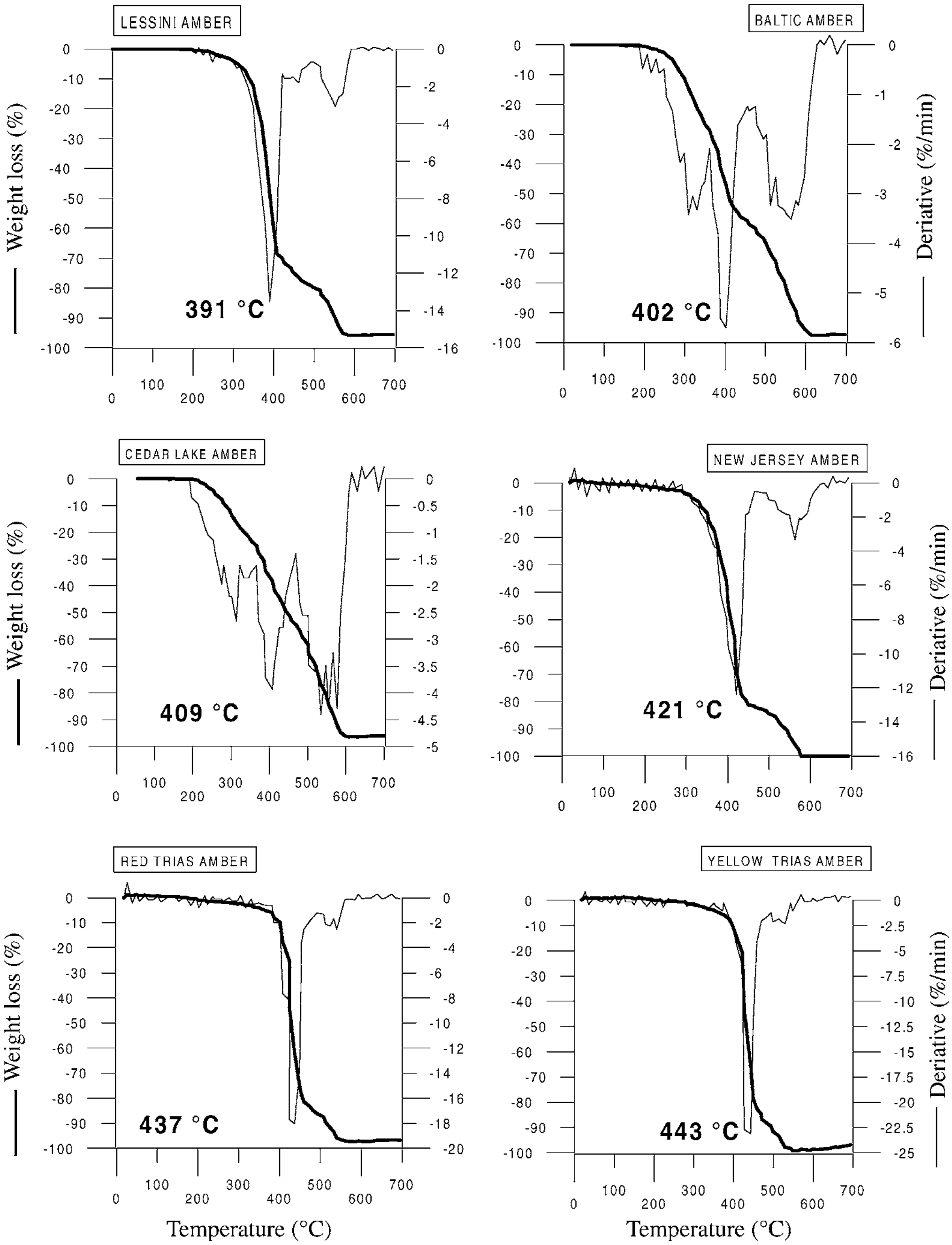

Fig. 2. Thermogravimetric (TG: thick line) and differential thermogravimetric (DTG: thin line) analysis of cenozoic to mesozoic resins of various origin. The value of the main DTG peak is indicated.

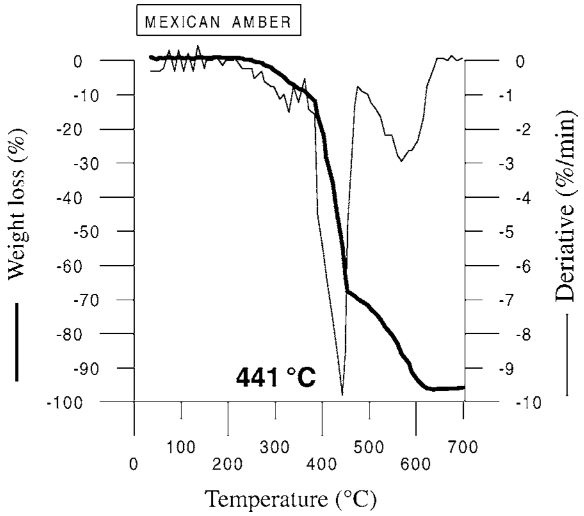

Fig. 3. Thermogravimetric (TG: thick line) and differential thermogravimetric (DTG: thin line) analysis of amber from Mexico.

of about 21 °C in the value of main exothermic event.

Mexican amber and Lessini amber, despite their geological age, presented, respectively, a higher and a lower temperature of the main DTG peak (Figs. 2 and 3), in comparison with the predicted line constructed through the experimental points (Fig. 4).

Additional peaks were found in the DTG profile of all the resins, both before and after the main peak. In one case these additional peaks were even more pronounced than the "main" peak itself (Cedar Lake Cretaceous amber).

As a general pattern emerging from the comparative analysis of the data, the older is the resin, the lower are

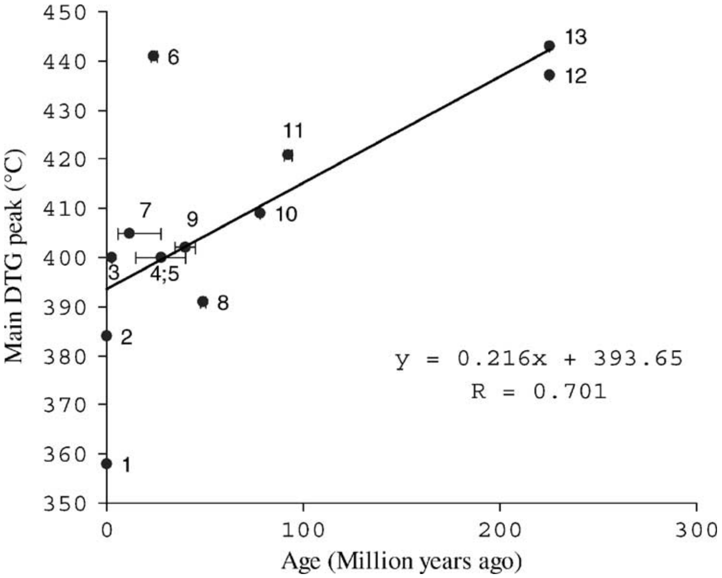

Fig. 4. Correlation between the age of the resin and the main DTG peak. When the amber deposit occurred within a wide range of age, an interval on the *x*-axis has been drawn through the point indicating the more probable age of the resin.

the additional peaks. Italian Triassic amber, being the oldest among the studied resins, presented only one relevant exothermal event (maximum at 437–443 °C), characterized by a very narrow amplitude, and a minimal secondary peak after 500 °C (Fig. 2).

### 6.3. Elemental analysis

As shown in Table 2, the carbon content in modern and fossil resins varied in a range of 75.38–83.65%, and hydrogen was between 9.63 and 11.24%. Nitrogen appeared only in traces (0–0.071%). Sulfur was detected in small amount in various kinds of resins, and the highest content was in Triassic Italian samples (1.47–1.74%). Also Cedar Lake amber, New Jersey amber, Simetite, Mexican and Baltic amber presented a modest sulfur amount (0.24–0.42%), while in the other fossil resins the content was lower.

The quantity of oxygen and trace elements was calculated as difference from the total. This value ranged between 4.74% (Mexican amber) and 14.58% (Simetite).

## 7. Discussion

The present study took in consideration a possible way of classifying fossil and sub-fossil resins by means of thermal analysis. Our results suggest that a progression of DTG exothermal profile well correlates to the age of fossil resins, particularly with the oldest ones.

A paper by Rodgers and Currie [15] has recently shown that when used judiciously, thermal behavior of resins may indicate maturation histories and resin associations.

During resin fossilization, after water and monoterpene hydrocarbon loss, polymerization of non-volatile components accompanied by crosslinking and isomerization, yields resin maturation [4,18–20], along the process called *amberization*, which is, to date, not fully understood.

In our study, the DTG exothermal profile of present-day resin shows early significant weight loss even before 200 °C. Other resins, such as Madagascar and Colombia copals, which are generally considered either recent or sub-fossil resins [21–25], show absent or minimal exothermal early events before 200 °C. In a natural resin, even after several thousands of years, up to 50% of unpolymerized material can still be found. Diffusion of volatile components can take several million years or more and the organic compounds polymerize very slowly [26]. Therefore, the present thermal analysis might suggest that the age of these copals is not very recent, but that a maturation of the resin has occurred.

Some exothermal peaks before the main thermal event were detected by our study also in Baltic amber (Eocene, about 40 Ma) and Cedar Lake Canadian amber (Cretaceous, 78 Ma). This thermogravimetric behavior was already found by Broughton [3] who analyzed some resin samples from North America and Europe. Comparison of the overall profile of DTG showed a close similarity between Baltic amber and Cedar Lake amber, suggesting a similar composition, although their geological ages are different. This fact supports the view, evidenced by infrared spectrometry analysis [2] that Baltic amber has similarities with Canadian amber and other North American ambers that contain succinic acid in close amounts. Probably the trees that produced these resins may be botanically related [24] and close to a Conifer of Araucariaceae family [27] or of the genus *Pseudolarix* [24]. Baltic amber (succinite) is a polylabdanoid copolymer of communic acid and communol [9,28] belonging to the Class Ia fossil resins, as demonstrated by pyrolysis–gas chromatography–mass spectrometry and NMR [1,9,23].

Our DTG curves show similarity in the pattern of Dominican amber (particularly for blue amber) and Colombian copal; these resins are believed to come from close botanical source, that is Leguminosae (Caesalpiniaceae or Fabaceae) of the genus *Hymenaea* [19]. They are composed by copolymers of labdanoid diterpenes (class Ic resins in the classification by Anderson et al. [9]) that do not incorporate succinic acid. Moreover, the value of the main exothermal event (400 °C) is equal. In this case it is difficult to determine whether the value of this peak depends on similar botanical affinities or to similar ages. The exact age of Colombian copal, at present, has not yet been clearly established, although experts suggest a wide range from 50 years to 1.6 million years [24]. Further $^{14}$C radiometric assays carried out by Kosmowska-Ceranowicz et al. [29] indicated that age of this resin did not fall within the range of detection, suggesting an age over 60,000 years [30].

Lessini amber is a newly discovered fossil resin which occurs in small amounts within marl-limestone levels dated Early Eocene (Upper Ypresian/Lower Lutetian, 49–50 Ma) [31] found near the town of Monte di Malo (northern Italy) [32]. This amber is of particular interest also because the stratigraphic determination allowed a very accurate determination of the age. In comparison with other Tertiary fossil resins (i.e. Dominican amber, Simetite, Baltic amber), the major exothermal event occurred earlier (391 °C). This datum is still being evaluated also by comparison with other Tertiary resins of northern Italy, recently acquired by our research group.

Mexican amber, and to a lesser extent, Lessini amber, presented a main DTG peak that does not fit within the regression line constructed with temperature/age data. The cause for this discrepancy may be due to different reasons, linked to paleobotanical different origin, or environmental and diagenetic modification. The structure and composition of fossil resins undergo changes over the course of geologic time [9]. The rate at which these processes proceed are temperature-dependent and are consequence of structure and composition of the original resin, the age and thermal history of the sample [9]; therefore it is correct to describe changes in the structure and composition of ambers as a function of “maturity” depending on both age and thermal history.

Also pyrolysis analysis [10] suggests that ambers from different geographical origin have different principal component mapping. Mexican and Dominican ambers, although closely related, are different. Our data from DTG measurements confirm this hypothesis. Also IR and NMR studies have indicated differences between Dominican and Mexican amber. While Dominican amber is similar as composition to the resin of present-day African species *Hymenaea verrucosa* (Fabaceae), Mexican amber appears to be different [5]. Vegetal inclusions in Dominican amber confirm the paleobotanical origin due to *Hymenaea protera* sp. n., closely related to *H. verrucosa* [33]. Mexican amber has been considered closer to the resin of *Hymenaea courbaril*, Mesoamerican–South American present-day resin-producing tree [19,22,34]. However, a recent study by Poinar and Brown [35], on the basis of botanical comparison, challenges previous views and suggests that also the species which produced Mexican amber is closely related to *H. verrucosa*. The new species has been named *Hymenaea mexicana* sp. nov. [35], similar but distinct from *H. protera*.

Also the resin sample from present-day conifer *P. abies* showed a main DTG peak lower than expected from the regression line. This finding might be just a trivial consequence of immaturity of the resin, whose components are poorly polymerized and still rich in volatile substances. It should be pointed out that diffusion coefficients are rather low, and especially for younger resins, strong concentration gradients of the different chemical species can be present. Perhaps the scattering in age/thermal behavior correlation at small age is in part related to the concentration gradients and to the thickness of the original piece of resin.

Additionally, differences found among ambers, and particularly in the DTG behavior of Mexican and Lessini amber, could be due to diagenetic changes consequent to the sediment composition and deposition history. As reported in Table 3, the resins were found in various embedding sediments with different composition which might have influenced the “maturation” of the amber itself.

One peculiar aspect of our research was the opportunity to analyze very ancient fossil resin dated Upper Triassic. This kind of fossil resin has been referred to Coniferalean origin [16]. The pattern of DTG analysis showed a late (after 300 °C) onset of combustion and a narrow exothermal event with peak at 437–443 °C that renders this resin unique among all the others here studied. Diagenetic resin maturation probably was one of the causes of this peculiar thermal analysis behavior. Other resins, such as Dominican amber, Colombian copal and, to a lesser extent, Simetite, presented a narrow major combustion event that occurred at a temperature much lower than that of Triassic amber.

Rodgers and Currie [15], through the comparison between Tertiary and modern copals and amber from New Zealand, also suggested a progressive changing of the major thermal combustion events with the age. This different thermal behavior is surely, at least in part, due to the differences of the chemical groups and bounds with the age.

Our results confirm these findings and add more information on the value of thermogravimetric analysis in amber research. By using the wide range of age among fossil resins we were able to find a statistically

Table 3
Stratigraphic characterization of sediments embedding the fossil resins

| No. | Sample | Stratigraphic formation | Lithology |
|---|---|---|---|
| 1 | *P. abies* resin | – | – |
| 2 | Madagascar copal | Unknown | Soil |
| 3 | Colombia copal | Unknown | Soil and volcanic ash |
| 4 | Blue Dominican amber | La Toca Fm., Yanigua Fm., Sombrerito Fm. | Sandstone |
| 5 | Dominican amber | La Toca Fm., Yanigua Fm., Sombrerito Fm. | Sandstone |
| 6 | Mexican amber | Balumtun Sandstone, Mazantic Shale, La Quinta Fm. | Lignite and sandy clay |
| 7 | Simetite | Unknown | Sandstone/sand |
| 8 | Lessini amber | “Nummulitic limestone” | Marl limestone |
| 9 | Baltic amber | “Blue earth” | Clay |
| 10 | Cedar Lake amber | Foremost Fm. | Lignite |
| 11 | New Jersey amber | Raritan Fm. | Clay with lignite |
| 12 | Red Triassic amber from Dolomites | Dürrenstein Fm. | Sandstone and palaeosol |
| 13 | Yellow Triassic amber from Dolomites | Dürrenstein Fm. | Sandstone and palaeosol |

For references see Table 1.

significant correlation between age and temperature of the major combustion event, suggesting that it could be assumed as an index of resin maturation.

Resin specimens we had access were also used to study the quantity of the base elements (C, N, H, O and S). No clear relation was observed between age and composition of the resins, although oxygen amount was overall more abundant in recent resins than in older ones. This may also be the consequence of the process of maturation of the resin, oxygen being replaced by crosslinking and polymerization reactions. It should be pointed out that also the elemental composition may depend on the botanical source and diagenetic conditions of amberization.

Mexican amber, which presented anomalous DTG pattern if compared on the basis of age regression line, also had high carbon content, suggesting a peculiar pattern of resin maturation. Consequently, the oxygen content was very low.

The higher sulfur content found in Triassic amber could be the consequence of the diffusion of the element from the sediment embedding the amber, or might result from elevated paleo-environmental sulfur content.

In conclusion, our results suggest that TG and DTG analysis of fossil resins is a useful source of information that may help the identification of age, diagenetic processes and paleobotanical origin of resins. This analysis, also completed by means of IR analysis and DSC measurements [26], could be of great interest in the study of fossil resins. It must be remembered that thermal analysis by itself cannot be used as a crude indicator of chemical composition of resins, but well correlates with the maturation grade of the resins.

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