# Thermal analysis of Cretaceous ambers from southern France


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Ragazzi E., Giaretta A., Perrichot V., Néraudeau D., Schmidt A. R. & Roghi G. 2009. — Thermal analysis of Cretaceous ambers from southern France. *Geodiversitas* 31 (1): 163-175.



**ABSTRACT**

Thermal properties of French Cretaceous ambers were investigated and compared with other ambers from various sites of the world. The amber samples came from 10 different localities in southern France, in the Charentes, Languedoc, and Provence regions, ranging from Late Albian to Santonian in age. Thermogravimetric (TG) and Differential Thermogravimetric (DTG) profiles were obtained at heating rate of 10 K/min in air, starting from room temperature (20°C) and reaching a maximum temperature of 700°C. Elemental Analysis for total Carbon, Hydrogen, Nitrogen and Sulphur was also carried out. The TG combustion profile of the resins started after 200°C and complete combustion took place near 600°C. The DTG behaviour is characterized by a main exothermal peak situated between 394 and 420°C, accompanied by minor peaks and shoulders. The increasing value of the main exothermal peak correlates well to the increase of the age of the specimens, with a significant correlation coefficient ($r$ = 0.7721, $p$ = 0.0089). A significant correlation ($r$ = 0.6728, $p$ = 0.0004) is also found with other samples of different age and origin. By considering the whole pattern of DTG peaks, a possible fingerprinting model of the French ambers is evaluated by multivariate analysis. Cluster Analysis and Principal Component Analysis show the presence of several clusters, according to the geological age and possibly to the palaeobotanical origin. The elemental analysis is consistent with that of other Cretaceous samples from different sites of the world. Carbon and hydrogen are the main constituents (range 73-80% and 9.5-11.5% respectively). Sulphur is detected in small amounts (0.8-2.4%). Nitrogen is absent or appears as traces only (0-0.008%). Oxygen and other elements range from 4.6 to 16.8%. No successful clustering was possible according to the elemental composition. Thermal analysis, completed with multivariate statistics, is a useful source of information also for French ambers, as a help for identification of the age, diagenetic processes and palaeobotanical origin.

**KEY WORDS**
Thermal analysis,
elemental analysis,
amber,
Cretaceous,
France.

**RÉSUMÉ**

*Analyse thermique des ambres crétacés du Sud de la France.*

Les propriétés thermiques des ambres crétacés de France sont évaluées et comparées avec celles d'autres ambres de sites variés. Les échantillons d'ambre proviennent de 10 localités différentes du Sud de la France, dans la région des Charentes, en Languedoc, et en Provence, et ont un âge compris entre l'Albien terminal et le Santonien. Les profils thermo-gravimétriques (TG) et thermo-gravimétriques différentiels (DTG) ont été obtenus à un taux de réchauffement de 10 K/min dans l'air, débutant à température ambiante (20°C) et atteignant une température maximale de 700°C. L'analyse élémentaire du total de carbone, hydrogène, azote et soufre a également été effectuée. Le profil TG des résines débute après 200°C et la combustion complète se situe autour de 600°C. Le comportement DTG est caractérisé par un pic exothermique principal situé entre 394 et 420°C, ainsi que par des pics et variations mineurs. Les valeurs croissantes du principal pic exothermique et de l'âge des échantillons d'ambre montrent un coefficient de corrélation significatif ($r$ = 0,7721, $p$ = 0,0089). Une bonne corrélation ($r$ = 0,6728, $p$ = 0,0004) est aussi observée avec d'autres ambres d'origine et d'âge distincts. Une analyse statistique multivariée considérant l'ensemble des pics DTG permet d'établir un profil caractéristique des ambres français. Une analyse de clusters et une analyse en composantes principales montrent plusieurs regroupements en accord avec l'âge géologique et possiblement l'origine paléobotanique des résines. La composition élémentaire est cohérente avec celle d'autres ambres crétacés. Carbone (73-80 %) et hydrogène (9,5-11,5 %) sont les principaux constituants, alors que le soufre est présent en petite quantité (0,8-2,4 %) et que l'azote est absent ou présent seulement à l'état de traces

(0-0,008 %). L'oxygène et les éléments traces varient entre 4,6 et 16,8 %. La composition élémentaire ne permet pas d'établir de regroupements significatifs des différents ambres analysés. L'analyse thermique, complétée par des analyses statistiques multivariées, s'avère donc informative tant du point de vue de l'âge que de celui des processus diagénétiques et de l'origine paléobotanique, et permet d'affiner la caractérisation des ambres de France.

**MOTS CLÉS**
Analyse thermique,
analyse élémentaire,
ambre,
Crétacé,
France.

## INTRODUCTION

Amber is a fossil organic polymer which originates from tree resins through complex maturation processes collectively named "amberization" (Anderson & Winans 1991; Anderson *et al.* 1992; Anderson & Crelling 1995). This process includes oxidation, oligomerization and cross-linking, which take place in the resin soon after its secretion by the plant. Several different parameters can play relevant roles in amber composition, for example the original environment (as a complex mixing of temperature, light irradiation, climate and possible pathogen intervention, which influence the resin composition), the palaeobotanical origin, the diagenetic history, the geological age, and also possible alterations which occurred after amber mining.

The characterization of amber can be achieved using several methods of analysis, such as Fourier transformed infra-red analysis (FTIR), pyrolysis-gas chromatography-mass spectrometry and nuclear magnetic resonance (Broughton 1974; Lambert & Frye 1982; Beck 1986; Grimalt *et al.* 1988; Anderson & Winans 1991; Anderson *et al.* 1992; Anderson & Crelling 1995; Carlsen *et al.* 1997; Martínez-Richa *et al.* 2000). The chemical analysis of the basic components of the polymer may fail to reveal differences among fossil resins since the specimens, although of the same geological age and similar composition, may display different maturity grades, for example as a consequence of higher temperatures and chemical linkages which occurred during fossilization.

Thermogravimetric analysis has been introduced as a new method to provide additional information on the physico-chemical properties of amber from different geographical sources (Broughton 1974; Rodgers & Currie 1999; Ragazzi *et al.* 2003; Feist *et al.* 2007). It is a rapid quantitative method which aims to examine the overall pyrolysis process and then to estimate the effective rates of overall decomposition reactions. The first studies (Broughton 1974; Rodgers & Currie 1999) have demonstrated the ability of thermal analysis to detect specific characteristics of various kinds of recent and fossil resins, with the oldest samples from the Eocene (about 40-45 Ma) and the Late Cretaceous (about 70 Ma). Further investigations conducted in our laboratory extended the application of the thermal analysis to more ancient fossil resins, till the Upper Triassic (about 225 Ma; Ragazzi *et al.* 2003). Under differential thermogravimetric (DTG) analysis, all samples presented a main exothermal event, whose temperature varied among resins, showing significant linear correlation, on the basis of the geological age (Ragazzi *et al.* 2003).

The availability of recently discovered Albian to Santonian (about 100 to 85 Ma) amber from France (Néraudeau *et al.* 2002, 2003, 2008, 2009 [this volume]; Gomez *et al.* 2003; Perrichot 2005; Perrichot *et al.* 2007a, b), suggested an investigation of the thermal properties of these peculiar fossil resins, and a comparison with the behaviour of other ambers from various sites of the world. In particular, the mid-Cretaceous ambers from Charentes region, whose deposits are the largest in France, were considered. Besides thermogravimetric investigation, an elemental analysis was also carried out on the same samples in order to further define the amber physico-chemical characteristics.

TABLE 1. — Characteristics of the French amber samples investigated. Abbreviations in brackets are those used elsewhere in this paper.

| Sample no. and label | Origin | Colour | Geological age | Main DTG thermal peak (°C) | Other DTG thermal peaks (°C) |
|---|---|---|---|---|---|
| 1 (**Arc**) | Archingeay (Charente-Maritime) | Opaque dark yellow | Late Albian (Dispar zone, 100.6-99.6 Ma) | 408 | 453, 574, 600 |
| 2 (**Cdl**) | Cadeuil (Charente-Maritime) | Opaque dark yellow | Late Albian (Dispar zone, 100.6-99.6 Ma) | 408 | 473, 586 |
| 3 (**Frs**) | Fouras (Charente-Maritime) | Light yellow | Early Cenomanian (Mantelli zone, 99.6-98.6 Ma) | 420 | 347, 557, 578, 600 |
| 4 (**Aix**) | Île d'Aix (Charente-Maritime) | Light yellow | Early Cenomanian (Mantelli zone, 99.6-98.6 Ma) | 420 | 341, 538, 578, 616 |
| 5 (**Buz**) | La Buzinie (Charente) | Opaque dark yellow/orange | Early Cenomanian (Mantelli zone, 99.6-98.6 Ma) | 411 | 328, 427, 584 |
| 6 (**Fou**) | Fourtou (Aude, Eastern Pyrenees) | Dark yellow/orange | Cenomanian (99.6-93.5 Ma) | 415 | 321, 544 |
| 7 (**Sal**) | Salignac (Alpes de Haute-Provence) | Dark yellow/orange | Cenomanian (99.6-93.5 Ma) | 411 | 334, 427, 578 |
| 8 (**Plc**) | Piolenc (Vaucluse) | Light yellow | Santonian (85.8-83.5 Ma) | 397 | 334, 380, 578, 600 |
| 9 (**Bel**) | Belcodène (Bouches-du-Rhône) | Light yellow | Santonian (85.8-83.5 Ma) | 406 | 557 |
| 10 (**Ens**) | Ensuès-la-Redonne (Bouches-du-Rhône) | Dark yellow/orange | Santonian (85.8-83.5 Ma) | 394 | 446, 557 |

## MATERIALS AND METHODS

The amber samples analysed herein come from 10 different localities in Southern France and their main characteristics are given in Table 1. Samples no. 1-5, coming from Charente-Maritime and Charente, originate from different deposits of Late Albian and Early Cenomanian age and are of different varieties of colour and transparency. Their geological age was attributed according to palynological (dinoflagellate cysts), micropaleontological (foraminifers and ostracods), or stratigraphical data as provided in former publications (Néraudeau *et al.* 2002, 2003, 2008, 2009 [this volume]; Gomez *et al.* 2003; Perrichot *et al.* 2004, 2007a; Dejax & Masure 2005; Peyrot *et al.* 2005). The absolute age was considered according to the International Stratigraphic Chart (International Commission on Stratigraphy 2007, available at http://www.stratigraphy.org/upload/ISChart2008.pdf) and Gradstein *et al.* (2004).

### THERMOGRAVIMETRIC (TG) AND DIFFERENTIAL THERMOGRAVIMETRIC ANALYSIS (DTG)

Thermogravimetric (TG) and Differential Thermogravimetric (DTG) profiles were obtained for each sample using a prototypal C.N.R. instrument (IGG-CNR, Padua, Italy) named "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 resin, 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. Samples were pulverized in an agate mortar before the measurement (mass 500 mg, particle size < 75 µm) and were inserted in

TABLE 2. — Elemental analysis of the resin samples. Each value is the mean ± sd of duplicate determinations. Abbreviations refer to samples as indicated in Table 1.

| Sample no. and label | Carbon (%) | Hydrogen (%) | Sulphur (%) | Nitrogen (%) | Oxygen and other elements (%) |
|---|---|---|---|---|---|
| 1 (**Arc**) | 78.65 ± 0.27 | 10.92 ± 0.08 | 0.38 ± 0.08 | 0.005 ± 0.007 | 10.05 ± 0.26 |
| 2 (**Cdl**) | 77.43 ± 0.34 | 10.80 ± 0.02 | 0.33 ± 0.09 | 0 | 11.44 ± 0.41 |
| 3 (**Frs**) | 79.69 ± 0.60 | 10.91 ± 0.01 | 0.46 ± 0.01 | 0 | 8.95 ± 0.60 |
| 4 (**Aix**) | 80.15 ± 0.06 | 10.93 ± 0.07 | 0.59 ± 0.01 | 0 | 8.33 ± 0.13 |
| 5 (**Buz**) | 77.27 ± 0.45 | 10.75 ± 0.01 | 1.12 ± 0.06 | 0 | 10.86 ± 0.50 |
| 6 (**Fou**) | 77.79 ± 0.65 | 10.47 ± 0.10 | 2.40 ± 0.02 | 0 | 9.33 ± 0.73 |
| 7 (**Sal**) | 73.32 ± 1.76 | 9.55 ± 0.32 | 0.37 ± 0.01 | 0.008 ± 0.012 | 16.76 ± 2.08 |
| 8 (**Plc**) | 83.14 ± 4.88 | 11.47 ± 0.75 | 0.81 ± 0.08 | 0 | 4.59 ± 5.71 |
| 9 (**Bel**) | 78.23 ± 0.30 | 10.48 ± 0.04 | 0.98 ± 0.01 | 0.002 ± 0.003 | 10.31 ± 0.25 |
| 10 (**Ens**) | 78.21 ± 0.70 | 10.50 ± 0.06 | 1.58 ± 0.01 | 0.004 ± 0.005 | 9.71 ± 0.74 |
| *Mean values ± sd* | *78.39 ± 2.71* | *10.68 ± 0.52* | *0.90 ± 0.65* | *0.002 ± 0.005* | *10.03 ± 3.27* |

a platinum crucible, placed on quartz glass support interfaced by Mettler Toledo AB 104 balance. The heating rate was 10 K/min in air, starting from room temperature (20°C) and reaching a maximum temperature of 700°C. The ash residue of the samples was 3.45% ± 1.66 (mean ± sd), and the range was 0.74% (sample no. 3) to 5.4% (sample no. 6). A computer equipped by custom-made software, written in Lab View 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 using the Graphing Software GRAPHER version 2.

### Elemental analysis

A CE-Instruments EA 1110 Automatic Elemental Analyser equipped with AS 200 autosampler and Mettler Toledo AT21 Comparator was used in this study. The instrument is a simultaneous carbon-hydrogen-nitrogen and sulphur analyser based on the reliable dynamic flash combustion and GC separation (with helium as 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 232CC link is fully automated.

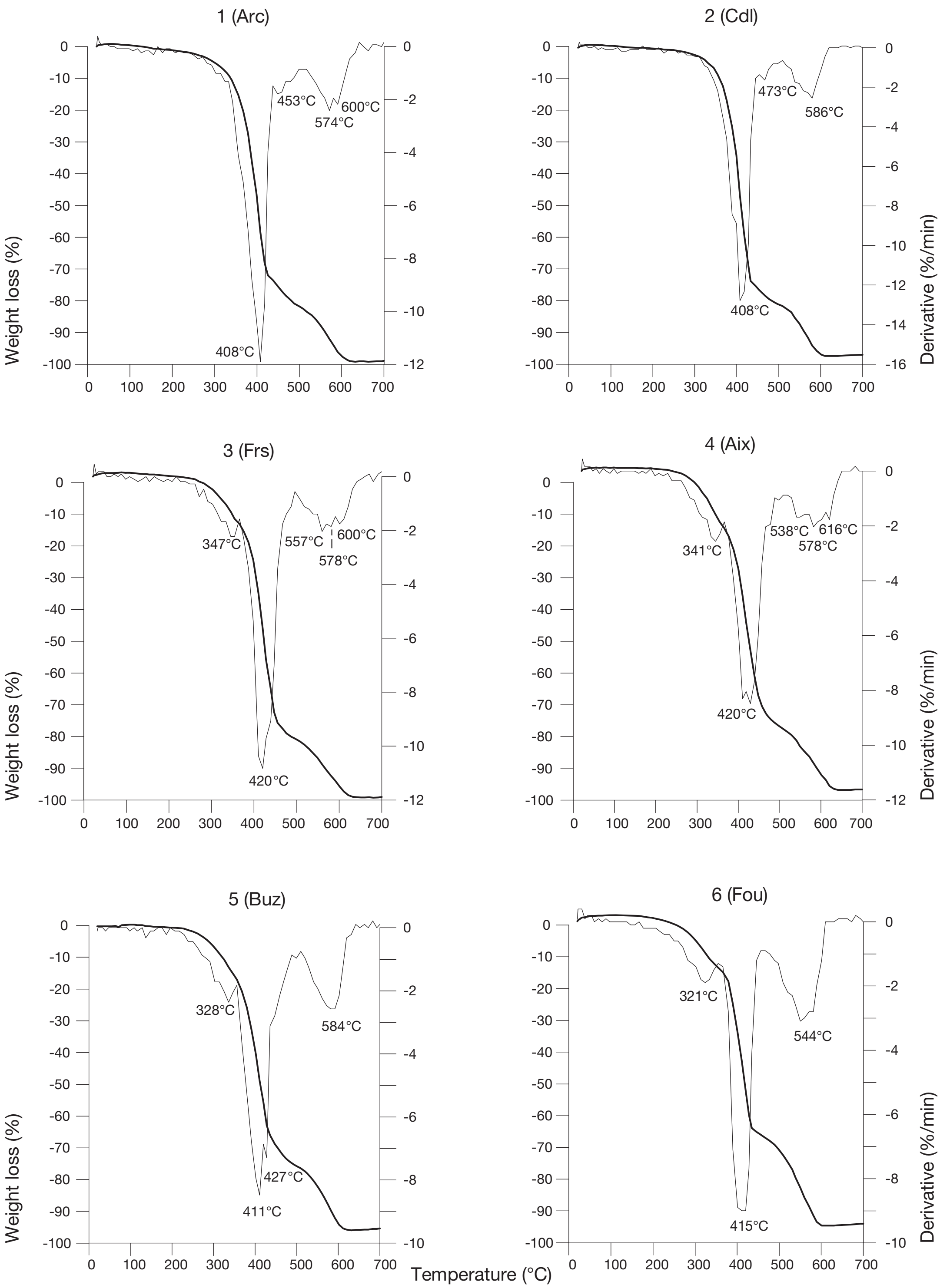
The powdered sample (about 2 mg) was placed into a tin capsule. The sample was loaded into the AS 200 autosampler which allows the automatic analysis. The calibration standards for carbon-hydrogen-nitrogen and sulphur were prepared from known amounts of sulfanilamide ($C_6H_8N_2O_2S$).

Analytical results for total carbon, hydrogen, nitrogen and sulphur in the amber samples obtained from at least two determinations are shown in Table 2.

### Data processing and statistical analysis

To examine whether a link between the main DTG thermal peak and the geological age was present, a scatter-plot was constructed and the Pearson's correlation coefficient ($r$) was calculated. The level of significance of the correlation coefficient was determined using ANOVA; a value of $p < 0.05$ was considered as significant.

A linear regression line was calculated with the method of least-squares; the main DTG thermal peak was considered as the explanatory variable ($x$) and the geological age as the dependent variable ($y$). To allow a comparison with the characteristics of other amber specimens with different age and geographical origin, a regression was calculated using the thermogravimetric data previously determined in our laboratory (Ragazzi *et al.* 2003). While correlation calculations are symmetrical with respect to $x$ and $y$, and after swapping the variables the same correlation coefficient is obtained, on


1 (Arc)
408°C
453°C
574°C
600°C
2 (Cdl)
408°C
473°C
586°C
3 (Frs)
347°C
420°C
557°C
578°C
600°C
4 (Aix)
341°C
420°C
538°C
578°C
616°C
5 (Buz)
328°C
411°C
427°C
584°C
6 (Fou)
321°C
415°C
544°C
Weight loss (%)
Derivative (%/min)
Temperature (°C)

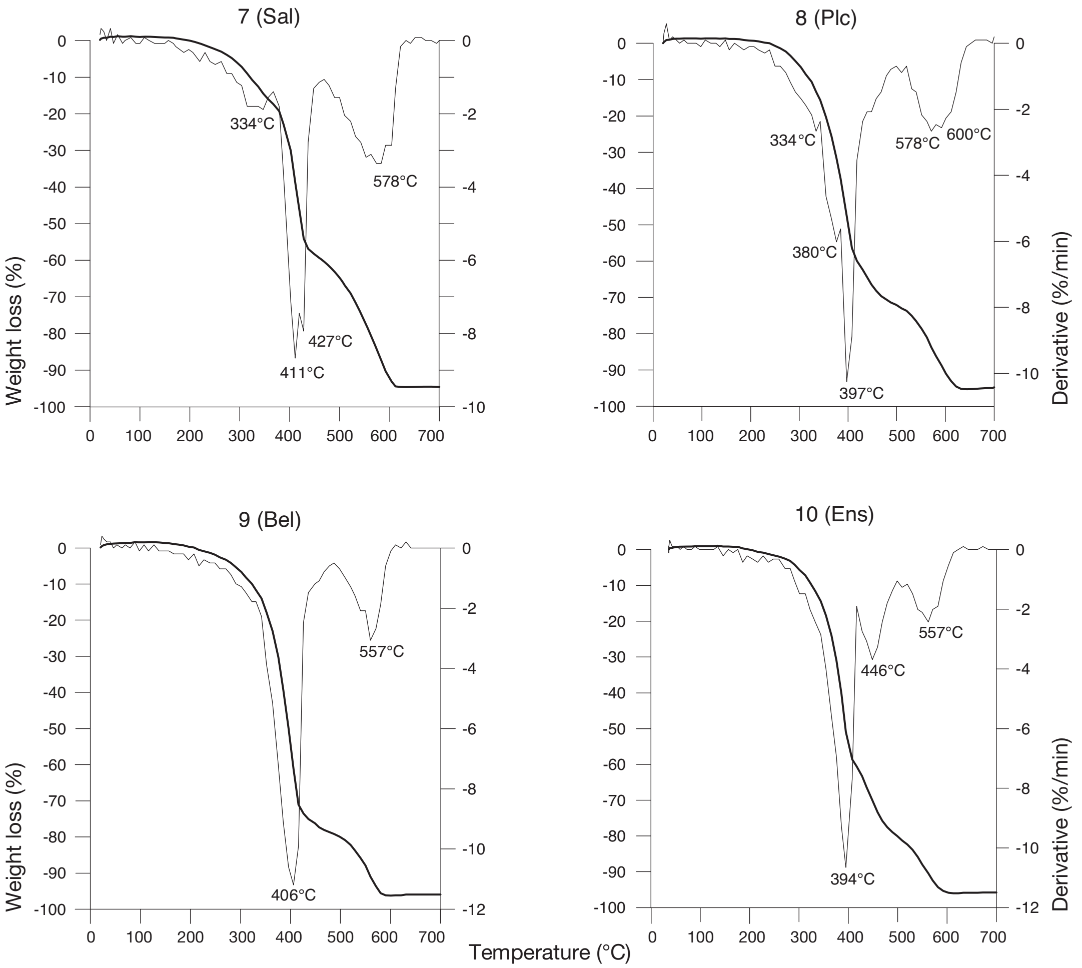



FIG. 1. — Thermogravimetric (TG, thick lines) and Differential Thermogravimetric (DTG, thin lines) analysis of French Cretaceous ambers. Abbreviations refer to samples as indicated in Table 1.

the contrary the regression calculations are not symmetrical and the swapping with respect to *x* and *y* leads to different regression lines. Therefore, both regressions were calculated and the theoretical regression lines presented in the scatter-plot, together with the average result obtained from the two fitting procedures.

### MULTIVARIATE ANALYSIS

#### *Cluster analysis (CA)*

In order to find useful criteria to classify the samples according to the whole DTG pattern, a procedure of hierarchical clustering without any prior knowledge of grouping (unsupervised clustering) was used. The DTG peak values obtained for each sample at various temperatures were inserted in a spreadsheet matrix and analyzed using the software *Kyplot* (version 2.0 beta 13, Yoshioka 2002) to obtain the hierarchical agglomerative clustering of the data. Ward's method of clustering was the linkage rule; the distance measure was determined using non-standardized Euclidean distance.

#### *Principal Component Analysis (PCA)*

DTG peak data were analyzed with PCA in order to detect the presence of clusters within experimental

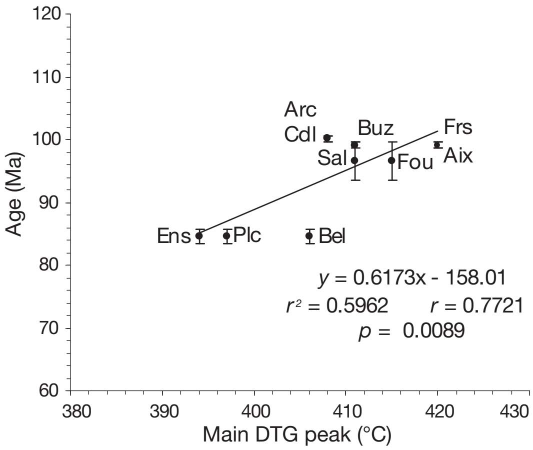



FIG. 2. — Correlation between the main peak of Differential Thermogravimetric (DTG) thermal event and the geological age of samples investigated. The regression is statistically significant ($p = 0.0089$). Vertical lines indicate the range of age of samples. Abbreviations refer to samples as indicated in Table 1.

data. This mathematical procedure transforms a number of possibly correlated variables into a smaller number of uncorrelated variables; these so-called principal components are linear combinations of the original variables; once obtained, the principal components are graphically plotted in order to observe any groupings in the data set. PCA was determined with AMADA software (Xia & Xie 2001) on the matrix of DTG peak data, employing covariance matrix and standardized principal component scores. The first three components were used for the classification of data. A 3D-scatter plot was obtained by means of KyPlot.

### ABBREVIATIONS

See Table 1 for abbreviations of names of the amber localities.

## RESULTS

### THERMOGRAVIMETRIC (TG) PATTERNS OF THE FOSSIL RESINS

Thermogravimetric patterns of the French ambers are presented in Figure 1 as thick lines. All the considered samples were characterized by a TG combustion profile which started after 200°C, corresponding to the temperature at which a significant weight loss occurred. In all cases the TG curve presented a principal biphasic profile and in some cases minor components were detected, which is more evident with samples Frs, Aix and Ens. The complete combustion of the resins took place near 600°C.

### DIFFERENTIAL THERMOGRAVIMETRIC (DTG) ANALYSIS OF THE FOSSIL RESINS

Figure 1 (thin lines) also shows the DTG analysis patterns of combustion of the fossil resins investigated. All samples were characterized by a main exothermal event, evidenced by the principal peak detected from the beginning of combustion, and corresponding to the maximal rate of weight loss. The temperature of the main peak, reported also in Table 1, varied from 394°C for sample Ens, to 420°C for samples Frs and Aix. As shown by the scatter-plot and linear regression of Figure 2, the increasing value of the main exothermal peak correlated well to the increase of the age of the specimen, with a significant correlation coefficient $r$ of 0.7721 ($p = 0.0089$).

Figure 3 compares the data obtained from the French amber specimens with those previously determined with samples of different age and origin (Ragazzi *et al.* 2003). Figure 3A presents the overall data ($n = 23$) with the regression line constructed to link the two parameters (age and main DTG peak), together with the calculated 95% confidence limits. The correlation coefficient $r$ was 0.6728 ($p = 0.0004$), suggesting a significant association between the two parameters.

Being a theoretical construct on the experimental data, and not a search of prediction of age through the determination of the main DTG peak, the inverse plot was also determined by swapping the $x$ and $y$ axes. A new regression was calculated and the theoretical values obtained this way were used to draw a new line. The average regression line (mean between the two previous lines) was also determined and indicated in the plot of Figure 3B. The three lines suggest a possible range for the estimation of the link between the two variables of interest.

The main DTG peaks of ambers from France appeared to fit within the median range of the regression line and were quite well localized, according to their age characteristic (see ellipse superimposed on Figure 3A).

As shown by the DTG profile (Fig. 1), besides the main exothermal event, additional peaks were found both before and after the main peak. The presence of these minor peaks is also reported in Table 1. One or two additional peaks following the main thermal event were generally observed for all samples. The occurrence of early peaks, before the main exothermal event, was detected with samples Frs, Aix, Buz, Fou and Sal.

The whole pattern of peaks registered in DTG profile was considered as a basis for possible fingerprinting model of the French fossil resins. The amplitude of all the DTG peaks was measured and the values inserted in a matrix of data, which was furthermore used for Cluster Analysis and Principal Component Analysis. The results of CA shown in Figure 4 as a dendrogram suggest the presence of several clusters, the most differentiated being those including samples Arc and Cdl, Frs and Aix, and Buz and Sal, respectively. Another cluster, although with less differentiated elements, was that comprising the samples Plc, and then Bel, Ens and Fou.

The three-dimensional plot of the principal components calculated with PCA (Fig. 5) confirmed the results obtained with CA, demonstrating four main groupings of the fossil resins.

## Elemental analysis

Table 2 presents the relative abundance of the different elements analyzed in the 10 samples of French amber. The carbon content varied in a range of 73 to 80%, and hydrogen was between 9.5 and 11.5%. Nitrogen was absent or appeared only in traces (0 to 0.008%). Sulphur was generally detected in small amounts, with highest levels of the element in samples Buz, Fou and Plc, Bel, Ens (with a range of 0.8 to 2.4%).

The amount of oxygen and trace elements was calculated as difference from the total. This value ranged between 4.6% in sample Plc to 16.8% in sample Sal.

A multivariate approach was also tentatively used with the data obtained with elemental analysis of the French amber samples. The dendrogram obtained with hierarchical CA (Fig. 6) does not show clear clustering of the samples, with the greater difference observed for samples Sal and Plc. The other specimens were less clearly differentiated, as indicated by the low distance among clusters. The three-dimensional plot of the principal components

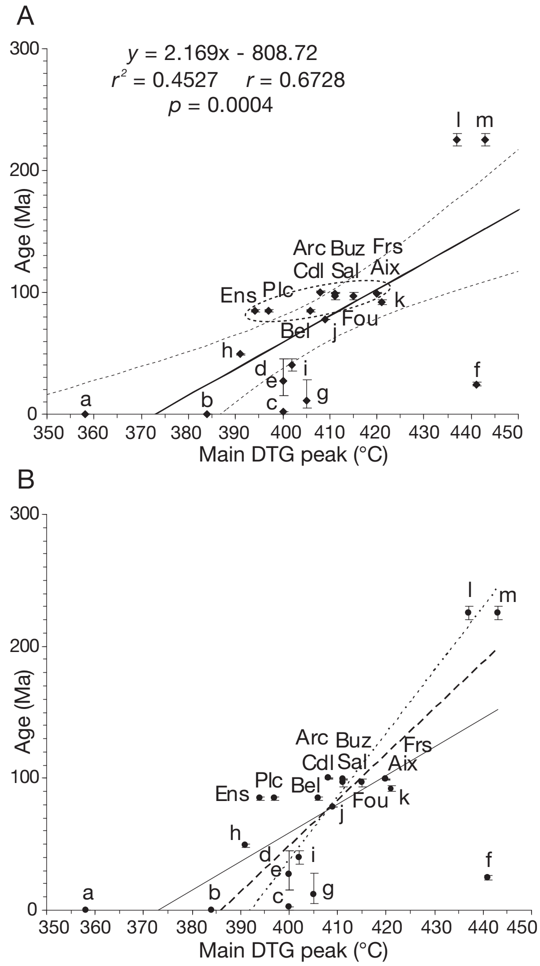



FIG. 3. — **A**, Correlation between the main peak of Differential Thermogravimetric (DTG) thermal event and the geological age of the samples investigated, together with data obtained from amber of different origin and age (data are from Ragazzi *et al*. 2003). The dashed lines indicate 95% confidence limits of the regression. The ellipse includes all samples from France, labelled as indicated in Table 1; **B**, lines indicate the plot obtained with different methods: regression of main DTG peak between age (full line), regression of age between main DTG peak (small-dashed line), average plot from both the previous regressions (large-dashed line). Letters in small case refer to the following samples used as a comparison: **a**, *Picea abies* resin; **b**, Madagascar copal; **c**, Colombia copal; **d**, blue Dominican amber; **e**, yellow Dominican amber; **f**, Mexican amber; **g**, Simetite; **h**, Lessini amber; **i**, Baltic amber; **j**, Cedar Lake amber; **k**, New Jersey amber; **l**, red Italian Triassic amber; **m**, Yellow Italian Triassic amber.

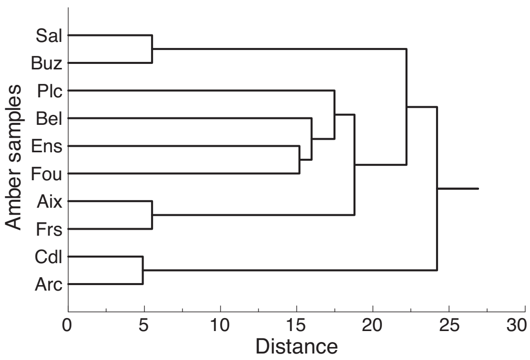



FIG. 4. — Dendrogram obtained with cluster analysis conducted using all the peaks detected from Differential Thermogravimetric (DTG) analysis. Cluster analysis was performed with Ward's method and non-standardized Euclidean distance. Abbreviations refer to samples as indicated in Table 1.

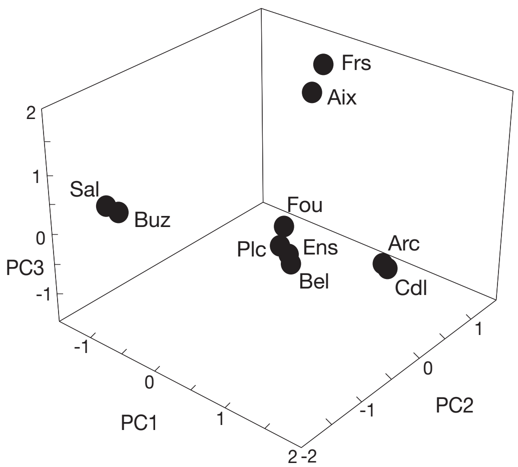



FIG. 5. — Principal Component Analysis (PCA) carried out using all the Differential Thermogravimetric (DTG) peaks detected with the 10 amber samples from France. PCA was obtained with covariance standardized matrix. Abbreviations refer to samples as indicated in Table 1.

calculated with PCA (Fig. 7) confirmed the results obtained with CA, demonstrating poor differentiation among the specimens.

## DISCUSSION

The present data show the typical pattern of thermal analysis of French Cretaceous ambers collected in different localities in southern France. The DTG profiles show typically one main exothermal peak in the range of 394-420°C, which appeared to be consistent with the thermal behaviour of other coeval fossil resins previously investigated (Ragazzi *et al.* 2003).

Our previous experience (Ragazzi *et al.* 2003) suggested that thermal analysis can provide a valuable way for classifying fossil resins, at least under the aspect of age, since a progression of DTG exothermal peak well correlates to the geological age of the specimen.

The amberization process is quite complex since it comprises many different events occurring in resin fossilization after the initial water and monoterpene hydrocarbon loss: polymerisation of non-volatile components accompanied by cross-linking and isomerization reactions, account for resin maturation and several variables may influence the entire process (Langenheim 1969, 2003; Pike 1993; Anderson & Crelling 1995). The presence of a correlation between the age of amber and its thermal behaviour provides further information on the history of the fossil resin, especially when the chemical composition is similar and the diagenetic variables are predominant. Being Late Albian or Early Cenomanian, the amber samples from the Charentes investigated here (samples no. 1-5, see Table 1) are confined within a relatively narrow range of age. Therefore it could be assumed that a similar profile of thermal analysis would have been obtained. This was overall confirmed, but some differences both in main DTG peak and secondary peaks suggest that samples may have undergone a different maturation history. Thermal analysis revealed that samples from Archingeay and Cadeuil (Arc and Cdl) are similar to each other, as are samples from Fouras and Île d'Aix (Frs and Aix), but the DTG profiles of both groups present peculiarities which allow a distinction. The lower main DTG peak suggests that samples from Archingeay and Cadeuil might be relatively younger than samples from Fouras and Île d'Aix, which is in contrast to the stratigraphical data. However, samples from Fouras and Île d'Aix showed an early peak near 340°C, which is completely absent in samples from Archingeay and Cadeuil. This early peak may be linked to the presence of more volatile components, as in younger resins, a fact which is apparently in contrast with finding a following higher main exothermal peak. A possible explanation of these discrepancies may involve the presence of fossil resins originated from different plants, containing components with different characteristics of thermal degradation. According to Perrichot (2005), ambers from Charentes would originate from the conifer family Araucariaceae as the main botanical source. However, since FTIR analysis on various specimens also produced different spectra, the possibility of more than one source is likely, and the plant remains associated in the different amber sites (Gomez *et al.* 2004; Néraudeau *et al.* 2005) also suggest a Cheirolepidiaceae, Podocarpaceae or Taxodiaceae as possible resin producers.

The older the resin is, the lower are the additional peaks. This is a general pattern emerging from the comparative analysis of previously published data (Ragazzi *et al*. 2003). This fact has been particularly evident with Italian Triassic amber, the oldest among the studied resins, which presented only one relevant exothermal event (with the maximum peak at 437-443°C), and a narrow secondary peak after 500°C. The French ambers from Charentes, and particularly samples Arc and Cdl, presented secondary peak(s) in the range 450-600°C, lower than those of the other samples (Fig. 1). This fact suggests that all other studied samples are younger than samples Arc and Cdl, as supported by stratigraphical data (Table 1). This may indicate that these ambers were not redeposited from older sediments and that the amber formation and sedimentation were (at least almost) contemporaneous.

The data obtained from all French localities fit well within the overall information provided by thermal analysis conducted on samples from all over the world and different age. The correlation age vs main thermal peak was confirmed, also when the two variables are swapped, suggesting that the rate of weight loss displayed by the fossil resin can be satisfactorily used as a marker of the age of the resin. The correlation showed outliers, and this may depend from the fact that, as discussed earlier, age is not the only determinant of the thermal behaviour of the resin.

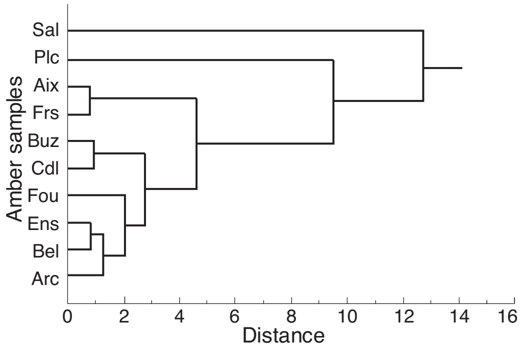



Fig. 6. — Dendrogram obtained with cluster analysis conducted using elemental analysis. Cluster analysis was performed with Ward's method and non-standardized Euclidean distance. Abbreviations refer to samples as indicated in Table 1.

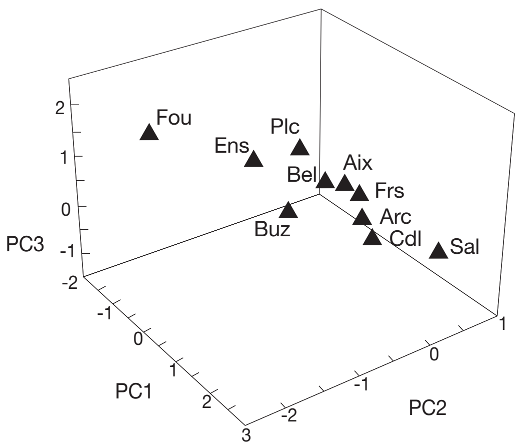



Fig. 7. — Principal Component Analysis (PCA) conducted on elemental analysis of the 10 amber samples from France. PCA was obtained with covariance standardized matrix. Abbreviations refer to samples as indicated in Table 1.

Another result emerged from the multivariate techniques of data analysis. The use of CA in the present investigation permitted to confirm mathematically what has been indicated above after a general inspection of thermal analysis spectra. A quite similar DTG pattern was observed between samples from Archingeay and Cadeuil (Arc and Cdl), as well as between samples from Fouras and Île d'Aix (Frs and Aix), or between samples from La Buzinie and Salignac (Buz and Sal), and among the group of samples from Piolenc, Belcodène, Ensuès-la-Redonne and Fourtou (Plc, Bel, Ens and Fou). Also PCA led to the same result confirming the possibility to obtain a fingerprint of the fossil resins by using a multivariate approach.

As a further consideration, samples Plc, Bel and Ens, coming from Vaucluse and Bouches-du-Rhône and appearing located within a cluster, suggest a similar palaeobotanical origin and/or taphonomic conditions. These samples are Santonian in age, and according to Gomez *et al.* (2003) the region was characterized by a rich flora with large abundance in angiosperms in ancient times, and a different palaeobotanical origin could be the reason for a different thermal profile of the resin, in comparison to the other samples.

As shown also by the mean values of Table 2, the fossil resins presented an overall composition which is consistent with that of other samples from other sites of the world and different age (Ragazzi *et al.* 2003). Carbon revealed to be the main constituent, with a range between 73 and 80% of the total, without any relation with the age of the samples. It is noteworthy that the sulphur content was higher in samples from Piolenc, Belcodène and Ensuès-la-Redonne (Plc, Bel, and Ens) and from La Buzinie and Fourtou (Buz and Fou), in partial agreement with the clustering found on the basis of DTG behaviour. A higher sulphur content has been found also in Triassic amber from Dolomites (Ragazzi *et al.* 2003), and this fact may depend on the diffusion of the element present in the embedding sediment to the resin. An attempt to find a clustering of the samples on the basis of the elemental composition did not achieve appreciable results, using both CA and PCA. Most probably the result depends on the fact that the elemental composition was not different enough among the studied samples of French amber.

In conclusion, thermal analysis is confirmed to be a useful source of information also for fossil resins from France, that may help to identify age, diagenetic processes and palaeobotanical origin of the amber. The use of multivariate data analysis, based on the data provided by DTG spectra, makes it possible to build a reliable fingerprint for each fossil resin.

**Acknowledgements**

We thank all colleagues and persons who helped us in finding some of the amber deposits studied here: Alain Couillard, Christian Devalque, Luc Ebbo, Ginette Lambert, Jean Le Loeuff, André Nel, Gaël de Ploëg, Daniel Roggero. We thank Kerstin Schmidt for the help in the preparation of the manuscript. This work is a contribution to the project AMBRACE no. BLAN07-1-184190 from the Agence nationale de la Recherche (ANR). Support was also provided by the Alexander von Humboldt Foundation (to V.P.), by the German Research Foundation (to A.R.S.), by C.N.R. Institute of Geosciences and Earth Resources, Padova, Italy (to G.R.) and by the M.I.U.R. Italy, grant no. MM04233815/003-De Zanche (to G.R.).

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*Submitted on 4 October 2007;*
*accepted on 23 September 2008.*