

First report of amber from the Early Eocene Belluno Flysch (Southern Alps, Northern Italy)

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ABSTRACT - Amber of Early Eocene age is described for the first time from the Belluno Flysch succession from samples collected in the vicinity of the city of Belluno. The physicochemical properties of the amber have been analyzed with regard to obtaining paleoenvironmental and paleobotanical data in order to facilitate a comparison with other Eocene amber findings in the Venetian Prealps.

RIASSUNTO - [Prima segnalazione di ambra nel Flysch di Belluno (Eocene Inferiore, Prealpi Venete, Italia settentrionale)] - Viene segnalato il primo ritrovamento di ambra all'interno del Flysch di Belluno (Eocene Inferiore). L'ambra è stata ritrovata nell'immediata periferia di Belluno ed è stata sottoposta ad indagini chimico-fisiche per compararla, dal punto di vista paleoambientale e paleobotanico, con le altre ambre eoceniche note nelle Prealpi Venete.

In particolare l'ambra è stata sottoposta ad analisi spettroscopica all'infrarosso (FTIR), analisi termogravimetrica (TG) e analisi termogravimetrica differenziale (DTG). L'ambra, rinvenuta entro sedimenti flyschoidi databili al Cuisiano (parte superiore della zona P7-P9), possiede tutte le caratteristiche che la accomunano alle resine fossili, ma le analisi chimico-fisiche, in particolare l'analisi spettroscopica e quella termica, suggeriscono alcune interessanti ipotesi che andranno ulteriormente studiate. Con certezza l'ambra bellunese non è simile all'ambra baltica (succinite), ed è possibile avanzare l'ipotesi che sia stata originata da una conifera antica, forse del genere *Agathis*, ma non si può escludere anche una leguminosa analoga al genere *Hymenaea*. È probabile che l'ambra abbia subito fenomeni di maturazione conseguenti a rideposizione in un sedimento secondario, e non si può escludere che l'ambra sia originata da un giacimento primario più antico, addirittura compatibile con un'età cretacea.

INTRODUCTION

The Belluno Flysch is a thick (> 1000 m) turbiditic succession interposed between the Scaglia Rossa basinal deposits (Late Cretaceous-Early Eocene) and the Chattian Molasse, alongside the Jurassic palaeogeographic unit known as the Belluno Basin, in the eastern Southern Alps. The Flysch mainly outcrops in the Vallone Bellunese (from the Alpego to the Feltre area) and, to a minor extent, in the Venetian foreland, from Vittorio Veneto to the Piave River.

The Belluno Flysch is composed of alternating layers of clay marls, calcarenites and sandstones, displaying a centimetric to decimetric plane-parallel stratification and sedimentary structures typical of turbiditic successions. The pelitic fraction is generally predominant, while in the arenaceous-ruditic fraction the carbonatic component prevails over the silicoclastic one. Frequent hemipelagites record periods of low sedimentation rate. Several directional structures indicate that the palaeocurrents mainly originated in the north-western sector of the basin (Gnaccolini, 1968; Stefani & Grandesso, 1991).

The Belluno Flysch is dated as Early Eocene in the Bellunese and Alpego areas (Di Napoli Alliata et al., 1970; Grandesso, 1976; Stefani et al., 2007), while in the west (Feltre area) it reaches the Middle Eocene (Grandesso, 1976; Stefani et al., 2007). The diachrony of the top deposits (progressively younger towards west), reflects the westward movement of the basinal depositional centres, as the result of the migration of the Dinaric thrusts (Doglioni & Bosellini, 1987).

AMBER IN THE SOUTHERN ALPS: CURRENT KNOWLEDGE

The first news of the presence of amber in the Southern Alps were found in a private letter dated from 1827. Mr Catullo wrote about the discovery of a "fossil forest" near Roana, in the Asiago Plateau (Vicenza province), which is characterised by inclusions of fossil resins (Catullo, 1827). Unfortunately this discovery was not confirmed by subsequent documents.

A few years later, Stoppani (1886) reported the presence of amber in the Chattian layers of the Monte Brione Formation, near Riva del Garda (Trento province).

Triassic amber was found in the Dolomites by Koken (1913) and his discovery was subsequently mentioned by Zardini (1973) and by Wendt & Fürsich (1980).

In recent years, amber findings in the Southern Alps increased considerably. In 1992, millimetre-sized granules of the oldest Italian amber were found in argillites and sandstones of the late Permian formation Arenarie della Val Gardena, located near the towns of Redagno and Pietralba, in the province of Bolzano (Maffi & Maffi, 1992).

Around ten years ago, thousands of millimetre-sized amber drops were found in an arenaceous layer of the Carnian Dürrenstein Formation near Cortina d'Ampezzo (Belluno province) and in Val Badia in the province of Bolzano (Gianolla et al., 1998). Of particular interest is the presence of several microscopic inclusions: pollen, bacteria, algae and protozoa, perfectly preserved for

over 220 million years (Roghi et al., 2005; Schmidt et al., 2006).

Some small granules of the same age as the amber from the Dolomites have recently been discovered in the Julian Alps (Preto et al., 2005; Roghi et al., 2006).

The first two Cretaceous Italian ambers were reported by Roghi et al. (2004). One is a 3 cm fragment found in the Albian (early Cretaceous) grey marls of the Flysch of Ra

Stua, which outcrops in the Croda Rossa Group (Dolomites). The other finding is represented by two samples found in the Coniacian-Santonian (Late Cretaceous) plant and fish fossil deposits of Vernasso (Julian Prealps, Udine). Both ambers can be ascribed to precise plant remains: *Araucaria macrophylla* (Araucariaceae) and *Cunninghamites elegans* (Cupressaceae s.l.), respectively.

Amber was also recently found in the Cenozoic of the Southern Alps: the Monte di Malo amber (Vicenza province), discovered in Early Eocene marly limestones (Boscardin & Violati Tescari, 1996; Trevisani et al., 2005) and the amber of Early Eocene fish and plant laminated limestones, which form the well known fossil deposit of Pesciara di Bolca (Verona province; Trevisani et al., 2005). Millimetre-sized fragments of amber were also found in Salcedo, in the Oligocene deposits of the Chiavon torrent (Vicenza) and Sedico, in the province of Belluno (Ragazzi & Roghi, 2003).

PHYSICOCHEMICAL PROPERTIES OF THE BELLUNO AMBER

Mr Giorgio Olivier kindly provided a number of amber samples which were discovered in gray-greenish calcareous siltites on the left bank of the Ardo torrent at Borgo Pra, in the north-west outskirts of the city of Belluno (Fig. 1). The samples were collected in debris (N 46°08'50" - E 12°12'41") constituted of Belluno Flysch. In this area, the Belluno Flysch is entirely Cuisian in age (top part of P7-P9 zone; Di Napoli Alliata et al., 1970; Stefani et al., 2007).

The samples belong to a single piece approximately 3.5 cm in size (Fig. 2); it is transparent, very fragile, with typical conchoidal fracture and with a chromatic variation from golden yellow to red. The relative density is approximately 1.10-1.12 with a hardness of around 2.5-3 on the Mohs scale. The amber is not soluble in ethyl alcohol nor in acetone when subject to a 30 second surface application (according to Currie, 1997), but it is slightly attacked by ethyl ether, which suggests a high maturation degree of the resin.

METHODS

Solid-state Fourier-Transform Infrared analysis was performed on freshly powdered samples of amber included in potassium bromide pellets. A Perkin Elmer 1600 Series FTIR Spectrophotometer with a wavelength range of 2-15 μm (5000-670 cm^{-1}) was used.

TG and DTG patterns were obtained at the Italian National Council of Research Institute of Geosciences and Earth Resources (IGG-CNR, Padova, Italy, Dr Aurelio Giarretta) by using a prototypal instrument, which consists of a thermocouple placed in an electric furnace. Samples (500 mg) were pulverised in an agate mortar, inserted in a platinum crucible, and finally placed on a quartz glass support interfaced with a Mettler Toledo AB 104 balance. The heating rate was 10°C/min from room temperature to 700°C. Analytical data were recorded using LabView 5.1 software, and thermal profiles were edited using Grapher 2 software.

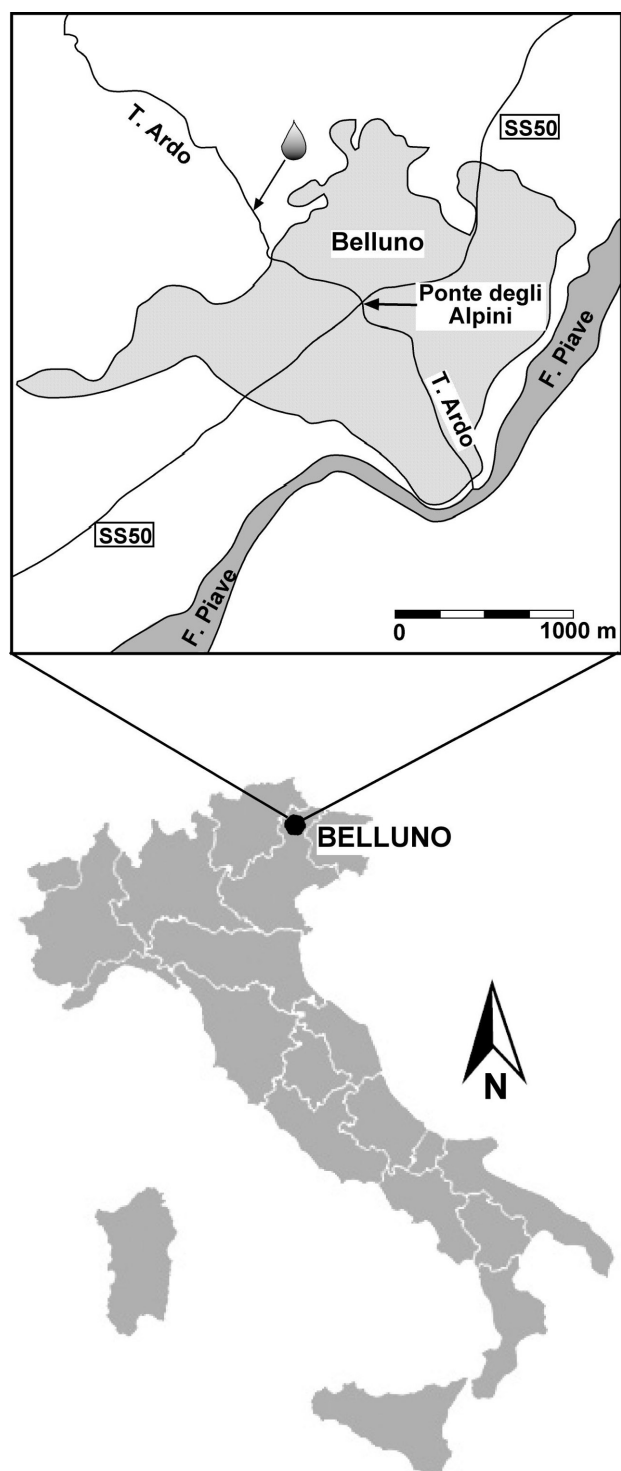


Fig. 1 - Location of the Belluno amber finding.

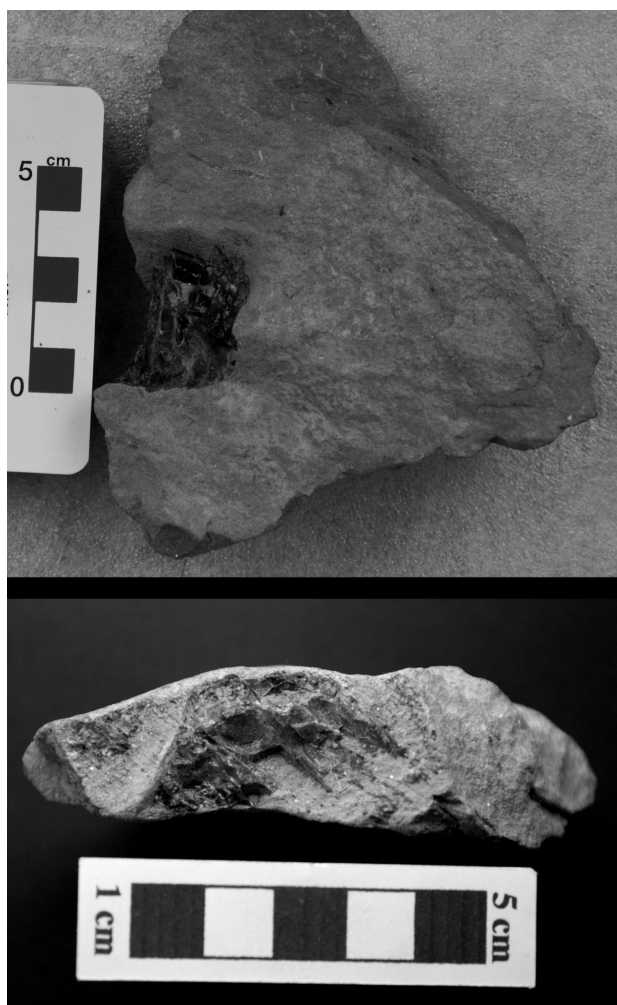


Fig. 2 - Piece of the Belluno amber investigated; the picture shows the two parts of the same sample inserted in the matrix.

RESULTS

FTIR analysis

The FTIR spectrum of the amber is presented in Fig. 3 and is typical of a fossil resin. The main features are reported in Tab. 1. A first strong absorption band occurs at $2.92\ \mu\text{m}$ ($3425\ \text{cm}^{-1}$), due to the stretching of hydrogen-oxygen bonds (Langenheim & Beck, 1968; Broughton, 1974), such as in phenolic and carboxylic hydroxyl functional groups. Parts of these hydroxyl groups responsible for the band can pre-exist in the resin, but they can also depend on water vapour absorption during the analytical procedure (Beck et al., 1966; Langenheim & Beck, 1968).

The strong absorption close to $3.5\ \mu\text{m}$ ($2860\ \text{cm}^{-1}$), here divided into two bands, is caused by the stretching of aliphatic carbon-hydrogen bonds (Langenheim & Beck, 1968) and is considered to be a typical characteristic of resins (Broughton, 1974). Bending motions of the same structures produce absorption peaks near $6.8\ \mu\text{m}$ ($1470\ \text{cm}^{-1}$) and $7.3\ \mu\text{m}$ ($1370\ \text{cm}^{-1}$) (Langenheim & Beck, 1968). The presence of a peak of intermediate intensity at $7.2\text{--}7.3\ \mu\text{m}$ is due to CH_3 functional groups (Broughton, 1974).

Another absorption band typical of fossil resins, called “carbonyl band” (Langenheim & Beck, 1968) is

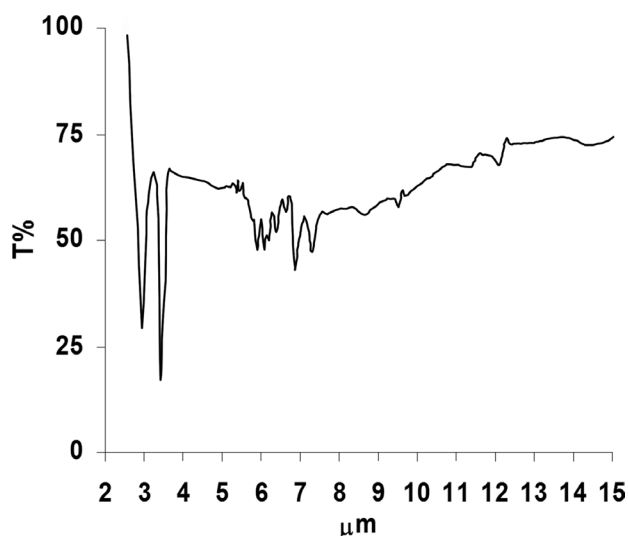


Fig. 3 - FTIR analysis of the Belluno amber.

detected near $5.9\ \mu\text{m}$ ($1695\ \text{cm}^{-1}$), caused by stretching movements of carbon-oxygen double bonds. Different to what is commonly found, the intensity of this band is not high, thus suggesting a process of chemical rearrangement at this site. An additional weak band at $6.42\ \mu\text{m}$ ($1558\ \text{cm}^{-1}$) may be assigned to carboxylate functional groups (Coates, 2000).

The above described absorption bands are found in all fossil resins, and are therefore of no peculiar diagnostic interest. The upper part of the infrared spectrum, higher than $8\ \mu\text{m}$, is difficult to interpret in terms of specific chemical structure (Langenheim & Beck, 1968), because the vibrations are influenced by the carbon skeleton of the whole molecule; nonetheless it is more useful than the lower region since it varies among different resins. The overall aspect of the spectrum region between 8 and $10\ \mu\text{m}$ ($1250\text{--}1000\ \text{cm}^{-1}$) is quite poor in the Belluno amber. In fossil resins, this region generally presents absorption bands caused by carbon-oxygen single bonds (Langenheim & Beck, 1968; Vavra & Vycudilik, 1976), as well as by aromatic ethers and phenols (Broughton, 1974), and can be considered to be a *fingerprint* of a specific fossil resin (Langenheim & Beck, 1968). In this part of the spectrum, Baltic amber (also known as *succinite*, due to the presence of succinic acid, although mainly in a combined form; Tonidandel et al., 2009), shows the typical “Baltic shoulder” (Beck et al., 1964; Langenheim & Beck, 1965; Vavra & Vycudilik, 1976; Beck, 1986; Kosmowska-Ceranowicz, 1999). It consists of a single carbon-oxygen deformation band near $8.6\text{--}8.7\ \mu\text{m}$ (about $1160\text{--}1150\ \text{cm}^{-1}$), preceded by a more or less flat shoulder between 8 and $8.6\ \mu\text{m}$ ($1250\text{--}1160\ \text{cm}^{-1}$). This is attributed to the absorption of ester groups of polyester-like structures (Vavra & Vycudilik, 1976; Matuszewska & Karwowski, 1999). No Baltic shoulder is present in the Belluno amber spectrum.

Absorption near $11.3\ \mu\text{m}$ ($885\ \text{cm}^{-1}$) is caused by out-of-plane bending movements of two hydrogen atoms in a terminal methylene group (Langenheim & Beck, 1965, 1968), which may occur in the resin acid molecules (such as copalic and agathic acid). This characteristic is

Functional group	Band, wavelenght, μm	Band, wavenumber, cm^{-1}	Intensity	Assignment
-O-H	2.92	3425	strong	O-H stretching
-CH ₂ -CH ₃	3.42-3.58	2924-2793	strong	Stretching of C-H bonds
	6.83	1464	medium	Scissoring and bending of C-H bonds
	7.33	1364	medium	Bending of C-H bonds
	11.36	880	weak	C-H out- of-plane-bending of H atoms
-C=O	5.90	1695	medium	Stretching of C=O double bonds
	6.42	1558	weak	Carbonyl group (possibly carboxylate)
-C-O-	8.62	1160	weak	Absorption of C-O single bonds
	9.50	1053	weak	Absorption of C-O single bonds
C=C	6.10	1640	weak/medium	C=C stretching
	6.67	1500	weak	Aromatic ring, C=C stretching
-C-H aromatic	12.10	826	weak	Out-of-plane bending of aromatic C-H

Tab. 1 - Main FTIR spectrum features of the Belluno amber.

typical of recent resins, such as the Madagascar copal, which is produced by species of the genus *Hymenaea* (Leguminosae/Fabaceae family). Mexican and Dominican ambers (Oligocene-Miocene in age), which also have botanical affinity with the genus *Hymenaea* (Poinar, 1991; Poinar & Brown, 2002), present the absorption band near 11.3 μm (Langenheim, 1969), although of weak intensity, and it testifies to resin maturation. The spectrum of the Belluno amber shows a very weak peak at 11.36 μm , which is most likely the result of a high degree of resin maturation.

It is not possible to compare with a high degree of accuracy the fingerprint region of this amber with those of other fossil resins, since, as already mentioned, the pattern is very poor, except for two very weak peaks at 8.62 and 9.50 μm . However, tentatively, a similarity can be found with the spectrum of resins produced by *Agathis* (see

spectra in Langenheim & Beck 1968, p. 108, Kosmowska-Ceranowicz, 1999, p. 94, and Beck, 1999, p. 43).

An additional peak is found at 12.10 μm (826 cm^{-1}), but any assignment to particular functional groups in the region 12-14 μm is only tentative (Broughton, 1974). Sometimes this peak is believed to be due to condensed aromatics or substitution in the benzene rings; similarly, the weak band at 6.67 μm (1500 cm^{-1}) may depend on the stretching of C=C bonds in aromatic rings (Coates, 2000).

It is difficult to attribute any palaeobotanical affinity to a fossil resin based only on infrared spectra and lacking an accurate association to identified fossil vegetal remains. During the process of *amberisation* (resin maturation), the chemical composition undergoes several changes (Anderson et al., 1992), which are in turn influenced by several factors, such as age and thermal history. Resins with similar palaeobotanical origins may present, as indicated by infrared spectra, different compositions, as a consequence of several taphonomic variables.

Thermogravimetric (TG) and Differential Thermogravimetric (DTG) analysis

Thermal, namely thermogravimetric (TG), and differential thermogravimetric (DTG) analyses, have recently been applied to the study of fossil resins (Rodgers & Currie, 1999; Ragazzi et al., 2003, 2009; Schmidt et al., 2010). The DTG main peak has been demonstrated to be proportional to the fossil resin's age and degree of maturation (Ragazzi et al., 2003, 2009). Thermal analysis provides a rapid and quantitative method to examine the overall pyrolysis process, linked to the chemical structure and the degree of resin polymerization during the amberisation stages.

The Belluno amber shows a TG combustion profile which starts after 250°C, while total combustion occurred before 600°C (Fig. 4). DTG shows a main thermal event, as a consequence of a maximal rate of weight loss, at 419°C, and another lower peak at 579°C. When comparing the Belluno amber thermal behaviour with that of other resins (Ragazzi et al., 2003; Trevisani et al., 2005) through a linear regression, the DTG main peak is higher than the one obtained from the predicted line (Fig. 5), indicating

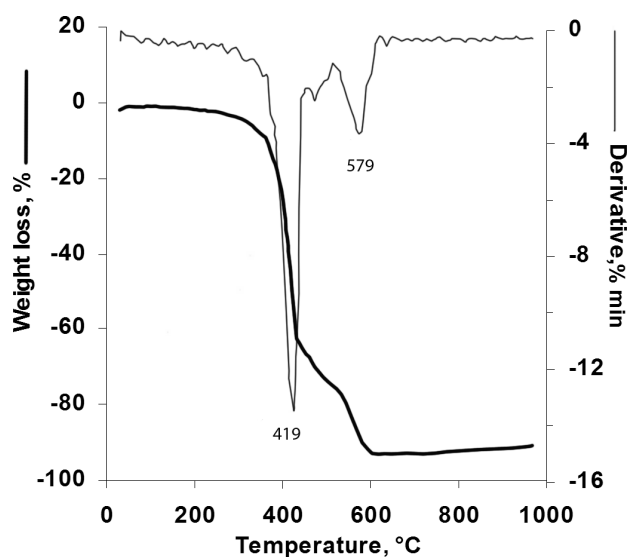


Fig. 4 - Amber thermal analysis. The thin line represents the DTG curve with the main thermal event indicated by the peak at 419°C; an additional peak is at 579°C. The thick line indicates the TG curve.

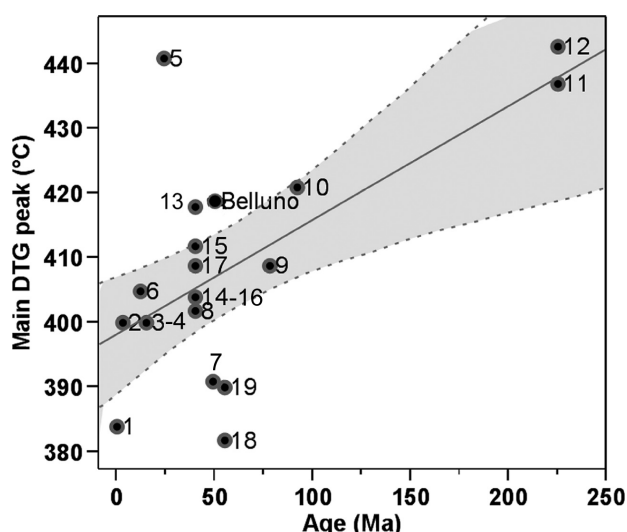


Fig. 5 - Correlation between the age of the fossil resin and the main DTG peak. The correlation coefficient of the regression line was $r = 0.638$, $p < 0.003$. The shaded area indicates the 95% confidence intervals of the fitted line. Numbers correspond to data from ambers of different age and origin previously analysed in our laboratory (from Ragazzi et al., 2003; Trevisani et al., 2005): 1 = Madagascar copal; 2 = Colombia copal; 3 = Blue Dominican amber; 4 = Dominican amber; 5 = Mexican amber; 6 = Simetite; 7 = Lessini amber; 8 = Baltic amber; 9 = Cedar Lake amber; 10 = New Jersey amber; 11 = Red Trias amber; 12 = Yellow Trias amber; 13 = Baltic amber; 14 = Swedish amber; 15 = Swedish amber; 16 = Baltic amber; 17 = Baltic amber; 18 = Bolca amber; 19 = Monte di Malo amber; Belluno = Belluno amber.

an estimated age older than the one suggested by the stratigraphic features of the sediment.

The main thermal peak of the Baltic amber, which belongs to the Upper Eocene (40-35 Ma), is about 402°C (Ragazzi et al., 2003) and two Italian Eocene ambers, found at Bolca and Monte di Malo (both Middle Cuisian, about 55 Ma) show a main combustion peak at 382° and 390°C, respectively (Trevisani et al., 2005). Mexican amber, although younger (Late Oligocene/Early Miocene, 26-22.5 Ma) presents a higher DTG peak of 441°C (Ragazzi et al., 2003). This discrepancy can be due to various causes, which can be linked to different palaeobotanical origins, or to environmental and diagenetic modifications.

The DTG peak of 419°C detected in the Belluno amber could reflect a peculiar resin composition, linked to a particular plant, but this hypothesis seems unlikely, since the FTIR spectrum (Fig. 3) is quite inconclusive in the fingerprint region and is instead more indicative of a degradation history of the original resin, either during the burial of the resin in the sediment, or following secondary deposition changes. The Belluno amber was discovered in flysch, a sediment that was deposited in a deep marine facies in the foreland basin during an early stage of orogenesis. The hypothesis of a sustained reworking of the fossil resin remains the most likely explanation for the peculiar physicochemical characteristics of the Belluno amber. Therefore, the FTIR and thermal characteristics can be interpreted in terms of strong maturation processes during the resin's diagenetic history, rather than its original composition. Alternatively, another explanation of the

thermal behaviour, can be that the resin is truly older, accordingly to the DTG peak, and it derived from an older primary sediment (possibly Cretaceous) that was transported into a secondary deposit, to which the Belluno Flysch belongs.

CONCLUSIONS

The Belluno Flysch has been dated as Cuisian (higher part of P7-P9 zone; Di Napoli Alliata et al., 1970; Stefani et al., 2007). The amber presents the typical features of a fossil resin, but the physicochemical investigation, namely FTIR and thermal analysis, provided limited evidence about the possible palaeobotanical affinity. However, its FTIR spectrum is significantly different to that of Baltic amber (succinite), indicating the absence of succinic acid. It can be hypothesised that the Belluno amber was generated by a Conifer, possibly a relative of *Agathis*, or by a Leguminous plant, since some features of its FTIR spectrum can be found in *Hymenaea*. The latter hypothesis may be plausible, if we consider the extensive fossil assemblage of the substantially isochronous site of Bolca (Trevisani et al., 2005), which is quite rich in Angiosperm palaeoflora. Regarding the former hypothesis, since fossil (both pollen and macrofossil) record indicates that Araucariaceae family (and therefore *Agathis* genus) was restricted to Southern hemisphere by the Eocene (Stockey, 1994; Wolfe et al., 2009), the similarity with *Agathis* FTIR spectrum would suggest that the fossil resin had originated from an older (also Cretaceous) sediment. However, the spectrum of this amber does not strictly indicate a specific palaeobotanical entity, and it is more likely that the peculiar FTIR spectroscopy and thermal analysis results, reflect a high degree of "maturation" of the fossil resin. Alternatively, the DTG main peak would suggest that this amber may derive from an older primary deposit that was reworked into the younger Eocene flysch, as also indicated by FTIR spectrum similarity with that of *Agathis*. At present, none of the possibilities regarding the nature of this amber may be excluded. Findings of amber associated to plant remains or palynomorphs are needed to clarify the true history of the fossil resin from this locality and its botanical origin.

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