13C Solid State Nuclear Magnetic Resonance and μ-Raman Spectroscopic Characterization of Sicilian Amber

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Abstract

13C cross-polarization magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) and μ-Raman spectroscopy were applied to characterize Sicilian amber samples. The main goal of this work was to supply a complete study of simetite, highlighting discriminating criteria useful to distinguish Sicilian amber from fossil resins from other regions and laying the foundations for building a spectroscopic database of Sicilian amber. With this aim, a private collection of unrefined simetite samples and fossil resins from the Baltic region and Dominican Republic was analyzed. Overall, the obtained spectra permitted simetite to be distinguished from the other resins. In addition, principal component analysis (PCA) was applied to the spectroscopic data, allowing the clustering of simetite samples with respect to the Baltic and Dominican samples and to group the simetite samples in two sets, depending on their maturity. Finally, the analysis of loadings allowed for a better understanding of the spectral features that mainly influenced the discriminating characteristics of the investigated ambers.

Introduction

Among organic gems having a gemological value, fossil resins are fashionable ones widely used since ancient times for manufacturing jewels and decorative objects. Fossil resins are transformed plant exudates consisting of a mixture of volatile and non-volatile terpenoid compounds. Due to a process known as fossilization,[1] polymerization of terpenoid compounds leads to the fossilization of the resin, whose maturity allows to distinguish copal (young resin) from amber (fossil resin). Amber is translucent, exhibiting a color ranging from yellow to red and from brown to green. It is insoluble in water and usually contains interesting inclusions represented by plant debris such as seeds, leaves, and bark fragments, as well as insects, animal remains, mineral crystals, and bubbles of air and water. Several deposits of amber have been discovered throughout the world, relating to exudates from different ancient and recent plants.

The best known and diffused fossil resins in the actual gemological trade come from the Baltic region of Northern Europe and from the Dominican Republic. Sicily is a source of a rare and fashionable amber, mainly found along the

hydrographic basin of Simeto River, from which it takes its name simetite.[2] Samples of simetite have also been found in the center of Sicily (near the town of Enna), even if the main source is represented by the Ionian coast, especially near the city of Catania. Sicilian amber is considered by gemological studies to be one of the most valuable for its physical–chemical properties and rarity. Historical sources testify that it has been used since ancient times for local jewelry. In the last two centuries, the demand of Sicilian amber exceeded the supply so that

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imported amber, instead of simetite, was used to satisfy the market demand.[3] Due to the lack of authentic simetite samples in the mineralogical collections, limited studies about simetite are available in the scientific literature.

Sicilian amber is characterized by various shades of red, but it also occurs in a black variety. Very poor information has been reported in literature about its origin, even if rare inclusions of vegetal fragments consisting of leguminosae leaves and angiosperm wood have been found in some ambers, suggesting a possible angiosperm origin. However, this attribution should be proved by additional paleobotanical analyses. It has been reported that Sicilian amber was formed in the mid-Miocene, therefore being about 11–17 Ma old[4] and being relatively younger than Baltic (35–50 Ma) and Dominican (25–45 Ma) amber.[5]

Considering the wide use of amber over the centuries and the interest of different disciplines in fossil resin characterization, several papers have been focused on the knowledge of the chemical structure of fossil resins. The non-crystalline nature of amber and its poor solubility prevent the use of many analytical techniques. Furthermore, in several cases, the value and the rarity of these gems requests the use of micro- and/or noninvasive or, at least, nondestructive analytical methods. Among them, ^{13}C solid state NMR and μ-Raman spectroscopy have been reported as useful tools in characterizing fossil resins, allowing to obtain the chemical fingerprint of different fossil resins and supplying useful information on maturation degree.[3,6–8]

In general, the chemical features of amber depend on both the biological origin and the geological environment in which the oxidative processes of maturation have took place. The use of ^{13}C solid state nuclear magnetic resonance (NMR) spectroscopy in characterizing amber has been demonstrated to be a powerful method for obtaining information on biological origin and geological environment.[9–13] In detail, ^{13}C solid state NMR has allowed the grouping of European amber in two sets, one grouping amber from North Europe and one grouping amber from South Europe.[3] In a pioneering paper by Lambert and Frye,[7] the ^{13}C cross-polarization magic angle spinning (CPMAS) NMR spectrum of Baltic amber with the assignment of carbon functionalities was reported. Dominican amber has also been investigated and compared with Baltic and Mexican ambers.[8] A wide variety of North American ambers dating back to the Cretaceous period and samples from Greenland, France, Switzerland, Lebanon, Jordan, Israel, Australia, and Papua New Guinea have been investigated by Lambert et al.[12] These studies have demonstrated that NMR spectral features allow the distinction of five groups of ambers based on their paleobotanical origins, specifically: Group A, worldwide provenance and related to Araucariaceae (gen. Agathis); Group B, worldwide provenance and related to Dipterocarpaceae; Group C, Baltic ambers or succinites having coniferous plants as a source; Group D, from Latin America, Africa, and the Caribbean having leguminous sources (from the Fabaceae); and Group E, fossil polystyrene.[11] In addition, experimental studies have demonstrated that NMR spectra also allow the detection of possible heating treatments used in the gemological field.[13] Recently, one-dimensional and two-dimensional ^{1}H NMR spectroscopy together with principal component analysis (PCA) has provided the same five amber groupings obtained from ^{13}C solid state NMR spectroscopy.[14]

^{13}C solid state NMR, Raman, and Fourier transform infrared (FT-IR) spectroscopic techniques have been applied to study the geographical origin of fossil resins[15,16] and determine their maturity,[5,17,18] to investigate plant and animal remain inclusions[19] as well as to define the authenticity of invaluable archeological resin artifacts,[20–22] and to distinguish ambers from imitations.[5]

The above-mentioned literature data indicate that a great interest has been devoted to fossil resins. Nevertheless, really poor literature data are available on simetite, especially due to the rarity of this amber variety. Therefore, in the present study a spectroscopic characterization of simetite samples from a private collection was carried out by using ^{13}C solid state NMR and μ-Raman spectroscopy. Results obtained on simetite samples were compared with reference data collected on fossil resins from the Baltic region and the Dominican Republic, allowing us to determine the peculiar features of Sicilian amber that are useful when distinguishing it from others. Finally, in order to highlight the discriminating features among the studied resins, the PCA was applied to μ-Raman and solid state NMR spectroscopic data.

Experimental

Materials

Fifteen unrefined simetite samples (labeled as NG) from a private collection were analyzed. In detail, the studied samples washed up by the sea along the southeastern Sicilian coastline (in the area between the outlets of Simeto and Salso rivers) and were collected by the gemologist Ugo Longobardo for jewelry manufacturing purposes. The ambers exhibit colors ranging from deep red to light black and weight about 3 carats (ct).

In order to compare the spectroscopic fingerprint of simetite with that of other ambers, reference samples from the Baltic region of Northern Europe (Poland and Russia) (8NL, 12NL, 13NL, 14NL) and the Dominican Republic (mining sites in Santo Domingo) (9NL, 10NL, 11NL) were also analyzed. Detailed information on the analyzed samples is reported in Table 1 and pictures of representative samples are shown in Figure 1.

Methods

Fifteen simetite samples, four Baltic and three Dominican ambers, have been analyzed by ^{13}C CPMAS NMR. Samples

were packed in 4 mm zirconia rotors with the available volume reduced to 12 µl. ^{13}C CPMAS NMR spectra were carried out on a Bruker Avance III spectrometer operating at the proton frequency of 400.13 MHz. The spin rate was

Sample	Provenance	Color	Weight (carats)
1NG	Sicily (Simeto)	Deep red	3
2NG	Sicily (Simeto)	Deep red	2
3NG	Sicily (Simeto)	Deep red	2
4NG	Sicily (Simeto)	Light black	3.5
5NG	Sicily (Simeto)	Orange-red	2
6NG	Sicily (Simeto)	Deep red	4.5
7NG	Sicily (Simeto)	Orange-red	2.5
8NG	Sicily (Simeto)	Light black	2.5
9NG	Sicily (Simeto)	Orange-red	2.5
10NG	Sicily (Simeto)	Light black	4.5
11NG	Sicily (Simeto)	Light black	4.5
12NG	Sicily (Simeto)	Light black	3
13NG	Sicily (Simeto)	Orange-red	4.5
14NG	Sicily (Simeto)	Light black	3
15NG	Sicily (Simeto)	Deep red	3
8NL	Baltic region	Orange	3.8
12NL	Baltic region	Orange	10.5
13NL	Baltic region	Orange	9.8
14NL	Baltic region	Orange	8.45
9NL	Dominican Republic	Light brown	12.39
10NL	Dominican Republic	Light brown	10.78
11NL	Dominican Republic	Orange	5.4

12 KHz. The contact time for the cross-polarization was 1.5 ms, the recycle delay was 3 s, and the ^{1}H π/2 pulse width was 3.5 µs. The cross-polarization was achieved applying the variable spin-lock sequence RAMP–CPMAS,[23] the RAMP was applied on the ^{1}H channel, and during the contact time, the amplitude of the RAMP was increased from 50% to 100% of the maximum value. Spectra acquired with a time domain of 1024 data points were zero filled and Fourier transformed with a size of 2048 data points applying an exponential multiplication with a line broadening of 8 Hz.

µ-Raman spectra were acquired on 12 samples of simetite, two samples of Dominican ambers and two Baltic ones with a Raman Jasco NRS-3100 apparatus, equipped with a microscope with 10 ×, 20 ×, and 100 ×objectives and two laser excitation sources at 532 and 785 nm, the excitation line at 785 nm was used for the measurements. Laser power was controlled by means of a series of density filters to avoid heating effects, depth resolution was set to few micrometers by means of a confocal hole. The system was calibrated using the 520.7 cm^{-1} Raman band of silicon before each experimental session.

Principal Component Analysis

Principal component analysis transforms the multidimensional space of experimental variables into a space with reduced dimensions. These dimensions are a linear combination of mutually orthogonal variables (principal components (PCs)) that retain the information about the variability present in data.

Principal component analysis was applied to NMR and µ-Raman spectral data. In detail, PCA was performed on three groups of spectra corresponding to the three different sets of analyzed amber (Sicilian, Baltic, and Dominican amber).
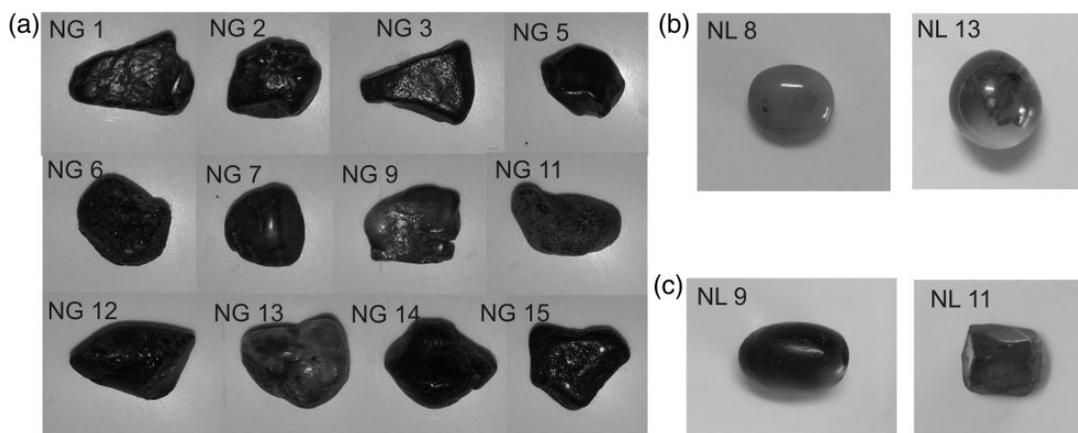
Figure 1. Pictures of some representative samples: (a) Sicilian, (b) Baltic, and (c) Dominican ambers.

The statistical processing of NMR data was performed using Microsoft Office Excel 2003 and Excel macros for PCA written by Tom Thurston.[24] Before the application of PCA the absolute intensities of 3746 points in NMR spectra were normalized to obtain the same total integral value (10 000) for all the samples. PCA was applied to mean-centered 3746 variables.
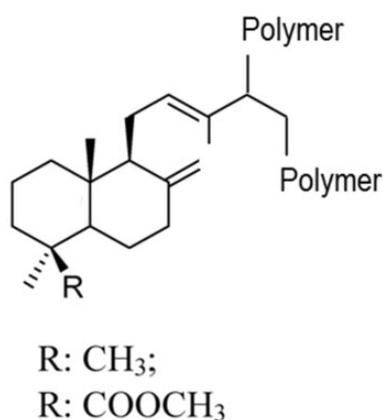
μ-Raman spectra were treated with statistical approach by using an integrated software system freely available, open and extensible, able to process, analyze, and classify Raman spectra.[25] In detail, the system utilizes only the most significant components that account for at least 95% of the variance in the spectra being analyzed. Consequently, each spectrum can be represented in terms of the PC variables called scores.

Results and Discussion

^{13}C Solid State Nuclear Magnetic Resonance Spectroscopy

Ambers whose macromolecular structure is based on polymers or copolymers of labdanoid diterpenes are classified as Class I[26] (Figure 2). Fossilization of amber involves a series of polymerization reactions that change its composition and determine the conversion of unsaturated to saturated bonds. These features can be investigated by using ^{13}C solid state NMR spectroscopy.

In ^{13}C NMR spectra, three regions of amber can be detected: single-bonded carbons (δ 10–90), double-bonded carbons (δ 105–155), and carbonyl and carboxyl carbons (δ 170–200).[7,8] The relative intensity of peaks of di- and tri-substituted alkene carbons (δ 128 and 140) and peaks of exomethylene carbons (δ 110 and 150) can be used for evaluating the maturity of fossil resins. The relative intensity of signals of exomethylenes decreases with increasing resin maturation.[8,12]
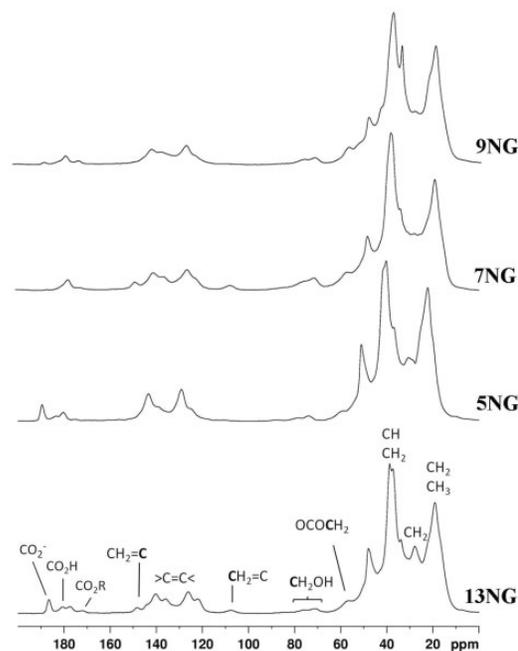
^{13}C CPMAS NMR spectra of simetite samples highlight the typical features of amber[3] (Figure 3). The most intense peaks are observed in the saturated carbon region with the three major peaks at δ 20, 34, and 40, however the intensity of peaks at δ 20 and 34 is rather variable. Between δ 50 and 80 signals of carbon atoms with oxygen substitution are observed. In particular, methylene carbons next to hydroxyl (HOCH_2) resonate at about δ 70, whereas carbons next to carboxyl ((C=O)OCH_2) resonate at about δ 60. Two peaks of di- and tri-substituted alkenes are observed at δ 128 and 140. In some simetite samples, two weak resonances belonging to exomethyelenes are observed at δ 110 and 150, whereas in other samples these two peaks are missing. Peaks with a variable intensity observed between δ 170 and 190 are ascribed to ester (CO_2R), acid (CO_2H), and possibly ionized acid (CO_2^-).[7] In many samples the intensity of the peak at δ 177 ascribed to carboxyl acid group was found to be relevant. Recently this peak has been described as distinctive of Recôncavo amber.[27]

Spectra collected on Baltic and Dominican reference samples show some spectral differences with respect to simetite samples (Figure 4).

In the spectra of Baltic amber, the intensity of the peak at δ 20 is weaker than in simetite, at δ 15 a shoulder due to methyl carbons is observed, and the peak at δ 38 is missing. In addition, the intensity of peaks of exomethylenes is higher than in simetite. The fingerprinting of the carbonyl carbon region is different from that observed in the case of

Figure 3. ^{13}C CPMAS NMR spectra of some representative simetite samples. The assignment of carbon functionalities is also reported.

Figure 2. Structure of precursor of Class I amber.

simetite. In this region three weak peaks are observed, with a characteristic resonance at $\delta \sim 170$ ascribed to succinic acid (Figure 4b).
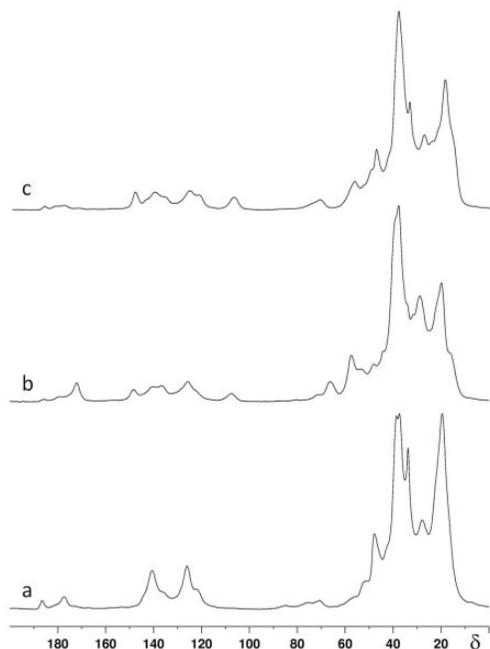
Figure 4. ^{13}C CPMAS NMR spectra of (a) simetite, (b) Baltic, and (c) Dominican amber.

In the spectra of Dominican ambers (Figure 4c), the peak at δ 20 is weaker than in simetite, and a shoulder at δ 15, absent in simetite spectra, is observed; moreover, a shoulder at $\sim \delta$ 35 is detected. Finally, the intensity of peaks of exomethylenes is higher than in simetite, while in the functional group region a broad and really weak peak related to the carbonyl resonance at about δ 170, is observed (Figure 4c).

μ-*Raman Spectroscopy*

Referring to the Raman analysis of amber, the most important spectroscopic region is that between 1800 and 1100 cm^{-1}, where the CC stretching modes due to CH$_2$ and CH$_3$ groups are observable. In detail, the main Raman vibrational modes typical of fossil resins are centered at ~ 1654 cm^{-1} (related to the ν(C=C) stretching vibration of the olefinic group C–CH$_2$) and ~ 1450 cm^{-1} (related to δ(CH$_2$), δ(CH$_3$) twisting modes). The relative intensity of these two bands is able to provide information on maturation, aging, and oxidation degree of resins.[6,17,21] In particular, the greater the band at 1450 cm^{-1}, with respect to that at 1654 cm^{-1}, the more mature the resin. In fact, in fossil resins, the degradation of ν(C=C) determines a lower intensity of the band at 1654 cm^{-1}, while in copal the presence of more unbroken C=C bonds produces a higher intensity of it. As a consequence, immature resins exhibit an intensity ratio $I_{1650\ cm^{-1}} / I_{1450\ cm^{-1}} > 1$, while a ratio < 1 indicates mature fossil resins. The second

**Table 2.** Wavenumbers (cm^{-1}) of bands in the μ-Raman spectra of all investigated samples (simetite, Baltic, and Dominican ambers) and their assignments. The intensity ratio ($I_{1650\ cm^{-1}} / I_{1450\ cm^{-1}}$) is also reported.

Simetite												Baltic amber		Dominican amber		
1NG	2NG	3NG	5NG	6NG	7NG	9NG	11NG	12NG	13NG	14NG	15NG	8NL	13NL	9NL	11NL	Assignment
														691	694	ν(CC) isolated
704	716	717	711	714	715	714	713	715	714	710	713			745	729	ν(CC) isolated
754	753	757	747	747	751	747	747	755	744	745	746	737	734	781	755	ν(CC) isolated
881	886	888	887	882	883	893	879	887	889	884	885	882	884	882	891	ν(COC)
938	939	938	938	939	941	939	940	939	939	936	940	–	954	953		ρ(CH$_2$), ρ(CH$_3$)
972	976	976	975	979	978	974		975	976	975	978	977	975	969	975	ρ(CH$_2$), ρ(CH$_3$)
1201	1202	1201	1198	1203	1202	1204	1200	1203	1200	1203	1202	1203	1200	1200	1202	δ(CH$_2$), δ(CH$_3$)
	1275	1276			1274	1275		1269		1276	1274	1257	1272	1275	1270	δ(CH$_2$), δ(CH$_3$)
1292	1297	1295	1296	1292	1296		1293	1290		1294		1291				δ(CH$_2$), δ(CH$_3$)
1354	1356	1355	1351	1351	1353	1363		1354	1354	1353	1351	1331	1355			δ(C–H)
1377	1380	1379	1376	1373	1379	1374	1368	1382	1380	1376	1376	1360	1378	1362	1361	δ(C–H)
1445	1442	1443	1439	1442	1443	1440	1443	1443	1445	1445	1440	1448	1448	1449	1450	δ(CH$_2$), δ(CH$_3$)
1463	1467	1462	1463	1469	1469	1466	1467	1465	1466	1464	1464	1475		1456	1478	δ(CH$_2$), δ(CH$_3$)
												1611	1618	1608	1634	ν(C=C)
1655	1654	1652	1651	1652	1656	1655	1652	1654	1655	1651	1654	1649	1639	1653	1652	
0.85	0.85	1.02	0.44	0.49	0.54	0.33	0.42	0.33	0.55	0.41	0.52	0.53	0.78	0.77	0.89	($I_{1650\ cm^{-1}} / I_{1450\ cm^{-1}}$)

interesting range spans between 1100 and 600 cm^{-1}, where the ring breathing modes of the terpenoid components of amber can be observed and discrimination among different type of resins can be achieved. Additionally, in the region between 800 and 600 cm^{-1}, further information on maturation degree of fossil resins can be obtained.[5] In detail,

strong bands at about 710 and 740 cm^{-1} related to $\nu(C=C)$ vibrations are typical of immature resins and tend to disappear with the maturation process due to the degradation of olefinic bonds.

In Table 2, the main bands detected in Raman spectra collected on simetite samples with the relative Raman
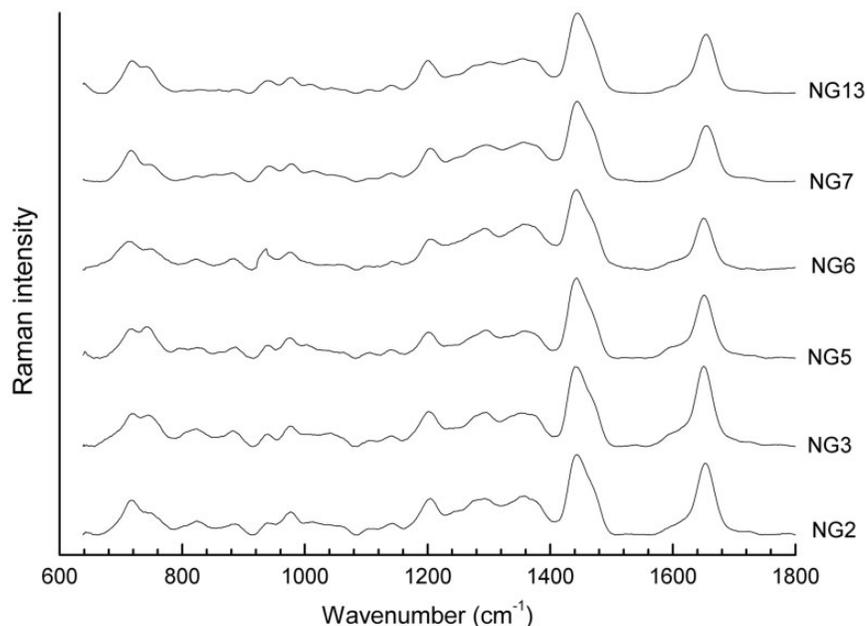
Figure 5. μ-Raman spectra of some representative simetite samples in the range 600–1800 cm^{-1}.
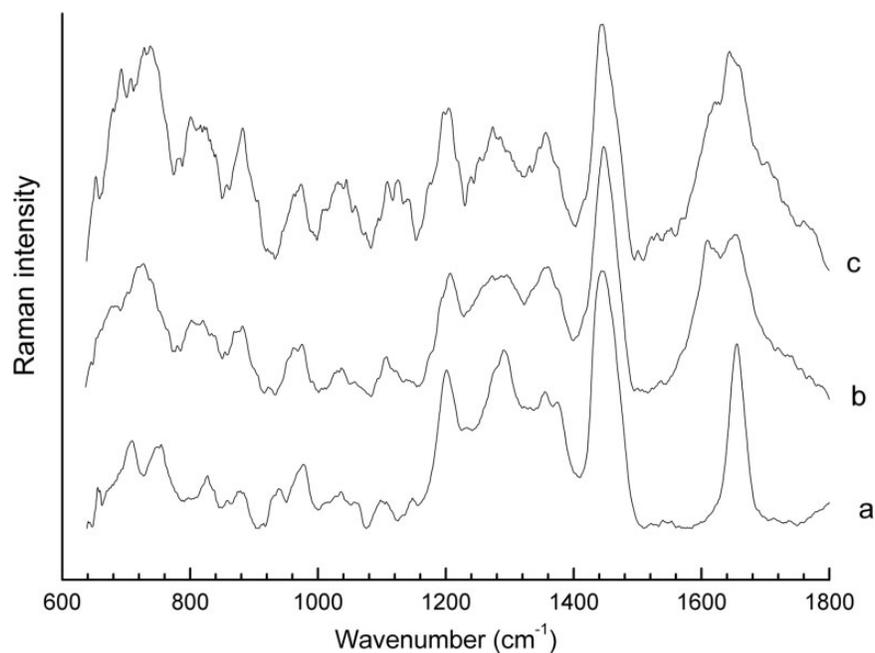


Figure 6. μ-Raman spectra of (a) simetite, (b) Baltic, and (c) Dominican ambers in the range 600–1800 cm^{-1}.

modes assignments and the intensity ratio (I_{1650} cm^{-1}/I_{1450} cm^{-1}) are reported, while in Figure 5 spectra collected on representative samples are shown.

In the spectral region 1800–1400 cm^{-1}, simetite samples are characterized by two strong bands at about 1445 and 1650 cm^{-1}. The intensity of the band at $\sim$1450 cm^{-1} is higher than that of the band centered at $\sim$1650 cm^{-1}. In order to obtain the intensity ratio of these two bands, peak fittings with background correction were performed and the areas of the two peaks were used to calculate this ratio. The obtained results showed a significant variability with values in the range of $\sim$0.3–0.8 (except in the case of the sample 3NG whose intensity ratio was found to be 1.02). It is worth noting

that the band centered at about 1450 cm^{-1} is asymmetric in shape, due to the contribution at $\sim$1464 cm^{-1}. According to the literature,[5] this feature is also an indicator of the maturation degree of the resin; in detail, the greater the contribution of the shoulder, the younger the resin. Therefore, a weakness of the shoulder at 1464 cm^{-1} is indicative of maturity. In all studied simetite samples, the contribution of the shoulder is about 30–40% of both the height and the area of the peak.

In the region between 1400 and 1100 cm^{-1} the majority of the samples exhibits three characteristic bands centered at about 1200, 1270, and 1370 cm^{-1}, ascribable to the $\delta(CH_2)$, $\delta(CH_3)$ twisting modes, and to the $\delta(C–H)$ in plane symmetric modes. In all samples, the band at
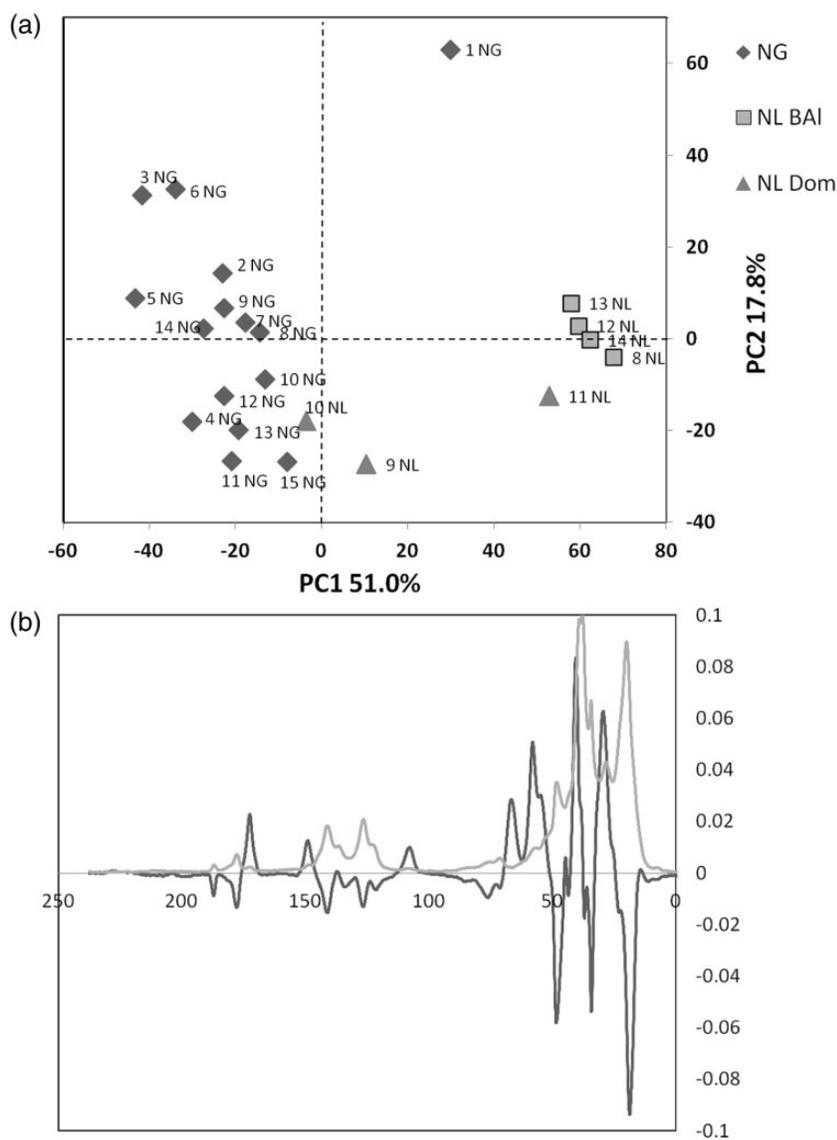
Figure 7. Principal component analysis of ^{13}C CPMAS NMR spectroscopic data: (a) scores of the principal component variables PC1 and PC2, (b) plot of the loadings.

about 1370 cm^{-1} is a doublet with two peaks centered at 1375 and 1353 cm^{-1}, respectively.

The spectral features in the range 1000–900 cm^{-1} can be assigned to the rocking vibrations of $\rho(CH_2)$ and $\rho(CH_3)$. In detail, the collected spectra exhibit two peaks centered at about 975 and 939 cm^{-1}. Moreover, the presence of a band centered at about 885 cm^{-1} can be ascribed to the ring deformation bands of aromatic compounds and $\nu(COC)$ stretching vibrations of cyclic ethers.

In the region 765–680 cm^{-1}, related to $\nu(CC)$ ring breathing modes of terpenoid components of amber and correlated to the maturity of the resin (i.e., the intensity of these bands tends to decrease during the maturation process), the presence of a doublet centered at around 750 and 715 cm^{-1} can be considered a characteristic feature of simetite.

Eventually, in order to highlight the discriminating spectroscopic features between Sicilian ambers and the others, µ-Raman spectra were acquired on four reference samples, two from the Baltic region and two from the Dominican Republic.

Spectra of Baltic and Dominican amber samples show the typical Raman bands of fossil resins (Table 2), highlighting some differences with respect to simetite samples (Figure 6). Specifically, in the Raman spectra of Baltic amber (Figure 6b) characteristic bands are a doublet around 1650 cm^{-1} (peaks centered at $\sim$1610 and $\sim$1650 cm^{-1}) and a single band at about 730 cm^{-1}. Otherwise, in the case of Dominican amber (Figure 6c), distinctive features are represented by a peak centered at 1652 cm^{-1} with a shoulder at 1634 cm^{-1} and by a triplet at 694, 729, and 755 cm^{-1}.[5] Finally, in both cases, the band centered at $\sim$1450 cm^{-1} is quite symmetric, with a variable contribution of a shoulder at 1464 cm^{-1} at least for 10% of the total intensity of the peak. The intensity ratio (I_{1650} cm^{-1}/I_{1450} cm^{-1}) calculated for both Baltic and Dominican ambers gives values in the range of 0.5–0.9 (see Table 2).

Principal Component Analysis

Nuclear magnetic resonance and µ-Raman spectra evidenced significant differences between simetite and other ambers. It is possible to enhance the discriminant power
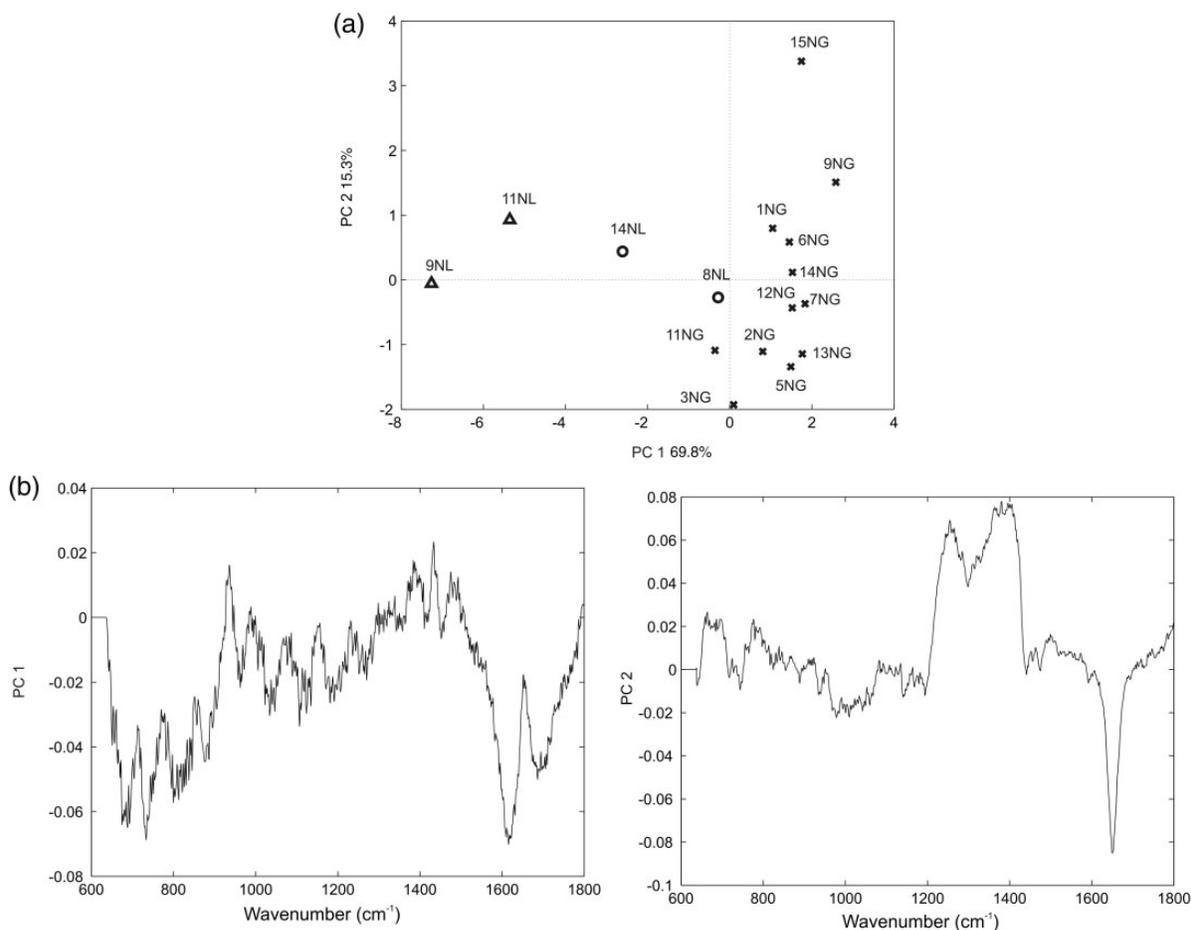
Figure 8. Principal component analysis of Raman spectroscopic data: (a) scores of the principal component variables PC1 and PC2, (b) plot of the loadings. Symbols: cross, Simetite; empty circle, Baltic amber; empty triangle, Dominican amber.

of these two analytical techniques by applying PCA on spectral data.

Principal component analysis has been widely used to treat NMR data obtained from food matrices and biological fluids.[24,28,29] Moreover, PCA has been recently applied to NMR data obtained from exudates derived from conifers and angiosperms to distinguish them on the basis of molecular structure.[30]

Figure 7 shows the scores of the PCs (Figure 7a) and the plot of the loadings (Figure 7b) obtained applying the PCA to ^{13}C CPMAS NMR spectral data. The first two PCs account for 68.8% of the variability within the data, PC1 providing for 51% and PC2 for 17.8% (Figure 7a). Principal component PC1 allows the discrimination of the three sets of amber. The Baltic amber and simetite form two well separated groups, while the group of Dominican amber is more dispersed. An outlier corresponding to sample 1NG is observed in the simetite samples. Note that the ^{13}C CPMAS spectrum of sample 1NG is very similar to the characteristic spectrum of Baltic amber. In the simetite group, PC2 allows the discrimination of ambers based on the maturation degree; in fact, samples lying below the horizontal dotted line, namely 4NG, 10NG, 11NG, 12NG, 13NG, and 15NG, are younger than those lying above this line, namely 2NG, 3NG, 5NG, 6NG, 7NG, 8NG, 9NG, and 14NG. It is worth noticing that the spectra of the former group show weak resonances of exomethylenes whereas in the spectra of the latter group these resonances are missing. The plot of loadings of PC1 is reported in Figure 7b. The larger the loading of a particular peak onto PC1, the larger the discrimination power of the corresponding variable. Therefore, it is evident that peaks of all spectral regions contribute to PC1.

Similar results were obtained by applying PCA to μ-Raman spectral data. Five PCs accounting for 96% of the total variability were determined. By considering the scores of the first two PCs (Figure 8a), namely PC1 providing for 69.8% and PC2 for 15.3%, a good discrimination, mainly influenced by PC1 (Figure 8b), can be observed among the three sets of analyzed samples. Indeed, in this case, PC2 does not give any further information on the maturation degree. The observed outlier corresponds to sample 15NG and is different from that observed in the case of PCA applied to NMR data.

Conclusions

In this paper, a ^{13}C CPMAS NMR and Raman spectroscopic investigation of Sicilian amber was carried out. Both spectroscopic methods allowed the characterization of fossil resins and discrimination of ambers from different geological areas. Specifically, the investigation highlighted the characteristic spectroscopic features of simetite with respect to Baltic and Dominican ambers. The complementary use of both techniques allowed us to obtain information on the maturation degree of the resins, according to the relative age assigned to them by literature data. In fact, even if the intensity ratio determined by using μ-Raman data covers a similar range of values for simetite, Baltic, and Dominican ambers, it is noteworthy that the I_{1650}/I_{1450} value and the rate of maturation is not just a function of time but is also related to the burial environment.[6] Therefore, more realistic information has been gained from the use of additional spectroscopic features, such as the intensity of the shoulder of the Raman band at $\sim 1450\,cm^{-1}$, as well as the relative intensity of alkene and exomethylene peaks in NMR spectra.

The application of the PCA to NMR and Raman spectroscopic data allowed us to establish a general method for distinguishing Sicilian amber from the others. Basically, the discrimination among the three investigated sets of fossil resins was clearly evidenced by the PCA carried out on the whole spectroscopic set of data. In fact, the plot of the loadings indicated that all peaks contributed towards differentiating the provenance of samples. Furthermore, PCA on NMR data also showed a clear grouping of younger simetite samples with respect to the older ones, possibly indicating the existence of two types of Sicilian amber.

To summarize, the obtained results allowed us to obtain a complete spectroscopic characterization of a representative set of simetite samples, supplying useful discriminating parameters for the identification of Sicilian amber and valuable data for mineralogists, gemologists, and conservation scientists.

Conflict of Interest

The authors report there are no conflicts of interest.

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