



The molecular composition of Sicilian amber[☆]



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ABSTRACT

In this study for the first time the bulk chemical composition of Sicilian amber (simetite) was determined using pyrolysis–gas chromatography–mass spectrometry with thermally assisted hydrolysis and methylation (Py(THM)–GC–MS). The results evidenced that the polymer fraction of Sicilian amber is based on a polyabdanoid structure with an *enantio* configuration, mainly including ozic acid and biformene. In addition, numerous monocyclic and bicyclic terpene degradation products could be detected. At higher retention times several characteristic compounds were found. Very low amounts of succinic acid could be revealed. The chemical data allowed to classify simetite as a Class 1c resinite and to suggest a botanical origin from *Fabaceae*.

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1. Introduction

Sicilian amber is a rare and precious amber of uncertain geological age since it is found in secondary and higher deposits, but it probably dates back to the upper Pliocene/Miocene [1]. Its mineralogical name *simetite* derives from the Simeto river and has been proposed by Helm and Conwentz who performed the first investigations on Sicilian amber, *i.e.*, determination of the physical properties and gross chemical composition [2] and study of botanical inclusions [3].

Simetite was already known in the Aeneolithic and early Bronze Age and was exploited in Sicily and other parts of the Mediterranean area [4], although since the middle and late Bronze Age Baltic amber gradually became predominant [5,6]. The oldest archaeological evidence of amber artefacts in Sicily is a pendant found in the Calafarina Cave (Pachino, Sicily, Italy) dating back to the mid-4th millennium cal. BC. No chemical analyses have been performed but there is evidence that the amber pendant was locally made [4]. Other amber finds of the mid-3rd millennium cal. BC have been found in the cemetery of Laterza (Apulia, Italy). In this case Fourier transform infrared (FTIR) spectroscopy data allowed to classify these archaeological amber objects as probable simetite [7,8].

Concerning the location of fossil resins in Sicily, according to 16th and 17th century written sources deposits of simetite could be found along the valleys of the Simeto and Salso rivers [9], whereas geological investigations carried out in the 19th century assessed the presence of fossil resin deposits not only along the Simeto river but also in the Hyblean region (Ragusa) [4]. Actually, no simetite deposits are known and, therefore, archaeometric studies cannot make use of natural amber finds, but have necessarily to recur to fragments that had been collected in the past, such as those conserved in Museums or private collections. As a consequence, uncertainty about the geographical and geological origin as well as degradation phenomena may affect the research results.

Several analytical techniques have been applied to the characterisation of amber for both gemmological and archaeological purposes [10]. Archaeometric studies of Sicilian amber are, however, few. An exhaustive FTIR spectroscopic study by Beck and Hartnett [8] of supposed simetite samples coming from Museum collections of all over the world evidenced that a relatively large number of these amber finds (16% of the investigated samples) is in fact composed of Baltic amber (succinite). Indeed, from the beginning of the 18th century, since Sicilian amber had become rare and the supply could not satisfy the increasing demand, succinite was often sold as simetite. Other purported simetite samples are composed of African copal or Dominican amber. In the same FTIR study [8] the main spectral features of simetite could be established. More recent studies have confirmed these data and showed that diffuse-reflectance infrared Fourier transform (DRIFT) spectroscopy can be efficiently used for the discrimination of various types of amber with the advantage that it may be applied directly to the surface

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(non-invasive mode) or to very low amounts of sample powder (0.2–0.1 mg), which is particularly important for archaeological amber finds [6]. Indeed, thanks to the possibility of obtaining information on intact samples in a non-destructive way FTIR spectroscopy has often been used for investigation of (archaeological) amber [11–13].

The same advantage can be offered by FT-Raman spectroscopy, although this technique has been less extensively applied since it has not proved as informative as infrared spectroscopy for the identification of ambers or copals. Edwards and Farwell [14] published a set of FT-Raman data obtained on various fossil resins and it was suggested that the intensity ratio of the bands at 1646 and 1450 cm^{-1} , corresponding to $I\nu(\text{C}=\text{C})/I\nu(\text{CH}_2)$, might be used to assess the maturity of resinates [15]. Simitite has been investigated as well by this technique [16].

Carbon-13 solid state nuclear magnetic resonance (NMR) spectroscopy has also been applied for characterisation purposes [17, 18], requiring, however, a minimum sample amount of ca. 50 mg. It was found that simetites form a reasonably homogeneous group with carbon-13 spectra that lack the exomethylene resonance and showing an acid (CO_2H) resonance which is stronger than that of the ester (CO_2R) [19]. More recently, proton magnetic resonance spectroscopy has been used for distinguishing copal and amber classes including several simetite samples of different provenience [20]. This technique, however, although offering higher availability, better sensitivity, greater resolution, finer functional group distinctions and applicability beyond powders as compared with the C^{13} technique, requires liquid state samples and can thus only be performed on the extractable fraction of ambers. On the basis of this study and previous data (see bibliography in [20]) a NMR classification of ambers was made collocating Sicilian amber in Group A. This class should correspond to Class 1b, i.e., resinates based on regular configuration, including communic acid, communol, and biformentenes, and absence of succinic acid (see below).

Thermal analysis has also been applied, although less frequently, to the study of amber and copal [21], including simetite [22]. Sicilian amber, alike Dominican amber and Colombian copal, was found to present a narrow major combustion event that occurred at a temperature much lower than that of Triassic amber.

Finally, gas chromatography (GC), possibly combined with mass spectrometry (MS) and/or pyrolysis (Py), has widely been used for the molecular study of ambers and resinates [23–38]. Information on a possible botanical origin can in some cases be obtained [39–43] and, when pyrolysis is applied, structural investigations of the polymer fraction can be efficiently performed [30,44].

These data allow for a chemical classification of ambers on the basis of the chemical nature of the macromolecular structure. The most common class of ambers (Class I) is composed of polymerised labdanoid diterpenes and is sub-classified on the basis of the stereochemical nature of the latter and on the presence or absence of succinic acid [23,24,26]. Two types of labdanoid diterpenes are found in Class I ambers: the so-called regular and *enantio* series. Regular polylabdanoid ambers containing succinic acid are classified as Class Ia (e.g., Baltic amber or succinite). Class Ib ambers, which are the most common, are also based on regular polylabdanoids, but these do not incorporate succinic acid. Class Ic ambers contain polymers of the *enantio* series and also lack succinic acid. As had already been hypothesised by Anderson and LePage in 1995 [45], recently, a new sub-category of Class I resinates, designated as Class Id, has been described. These resinates, which have been found in distinct deposits in Canada, are based on polymers of labdanoid diterpenes having the *enantio* configuration, incorporating significant amounts of succinic acid [46].

However, although GC–MS of solvent extracts or Py–GC–MS of bulk samples are extensively applied for the chemical characterisation of ambers, only few gas chromatographic or mass spectrometric studies have been carried out on simetite. The most exhaustive research has been

performed by Beck and co-workers [47]. In that study a sample of simetite from the Musée National de l'Histoire Naturelle of Paris was extracted with ether (solubility of 2.1%wt.), derivatised with diazomethane, and then subjected to GC–MS analyses. Mass spectral data of over 100 compounds have been reported and constituted a very useful dataset for comparison of our data. Other gas chromatographic studies of simetite have been addressed to demonstrate the potential of the use of composed mass spectra [48] or Py–GC fingerprints [49] to assess the geographical origin of archaeological amber finds.

Examination of these studies evidenced that there is a need for a comprehensive and systematic study of simetite in order to enable a correct identification of numerous geological amber finds which are stored in Museums and private collections and, in particular, to determine the nature of archaeological finds. So far, classification of genuine simetite is mainly based on the acquisition of FTIR spectra. However, although this technique may present various advantages such as the possibility of performing non-invasive measurements, also on site thanks to portable instrumentation, the spectral data may not always provide sufficient information for the discrimination of non-Baltic ambers and do not allow for a chemical classification. In fact, given the difficult interpretation of the amber spectroscopic data, the combined use of two or more analytical techniques is a valuable tool to address complex amber-related problems.

Py–GC–MS allows to obtain a complete chemical characterisation requiring very low sample amounts (<100 μg) and is thus particularly suitable for provenance studies, also of archaeological objects [37,50, 51]. However, systematic reference databases are still lacking and the aim of this study is to provide information on the chemical composition of simetite which can be used as reference data.

To this purpose four simetite samples of the Earth Sciences Museum of the University of Bari Aldo Moro were investigated with Py–GC–MS with on-line thermally assisted hydrolysis methylation (THM) using tetramethylammonium hydroxide (TMAH). The use of THM for the characterisation of resinates has been introduced by Anderson and Winans. Although some dehydration of alcohols and other side reactions of hydroxyl- and carboxyl containing resin acid methyl esters may occur, Py–GC–MS analyses without *in situ* methylation have been found to provide generally less adequate data for structural and compositional analyses [23]. As a consequence THM is nowadays frequently adopted, although in some more recent papers on-line silylation with hexamethyldisilazane (HMDS) has been preferred [37,44,46].

In a preliminary phase of this study attenuated total reflectance (ATR) FTIR spectroscopy was carried out in order to confirm the classification of the geological samples as genuine simetite.

2. Experimental

2.1. Materials

Four dark red, apparently black, rough ambers from the Earth Sciences Museum of the University of Bari Aldo Moro (samples EMB1, EMB2, EMB3 and EMB4) were studied (Fig. 1). In Fig. 1B sample EMB1 is shown in transmitted light in order to illustrate the ruby red colour of simetite – highly appreciated in jewellery – which might be obtained after removal of the external dark layer and careful polishing. The samples are labelled as simetite but their provenience is unknown.

Tetramethylammonium hydroxide (TMAH) was purchased from Sigma-Aldrich (Milan, Italy) and a solution of 2.5% in methanol (Sigma-Aldrich, Italy) was prepared.

2.2. ATR–FTIR spectroscopy

ATR–FTIR spectroscopy analyses were performed on small fragments (ca. 0.2 mg) with a Cary 600 instrument (Agilent Technologies)

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