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Fruit and seed biomineralization and its effect on preservation

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Abstract Mineralised fruits and seeds are frequently found in archaeological sediments but their chemical nature has not been often examined. The nature and the origin of these archaeobotanical remains have to be investigated to understand their taphonomic history. Fruits or seeds can be mineralised not only by replacement mineralisation but also by biomineralisation during the plant life. The mineral components of three fossil fruits sampled on the Pleistocene site of Dmanisi were analysed and compared with their modern analogues. Analyses were carried out by means of an environmental scanning electron microscope, equipped with an energy dispersive X-ray device and by means of a Fourier transform infrared spectrometer. Biogenic carbonates and/or biogenic silica were identified in the fossil and modern fruits of some taxa. Comparison between fossil and modern specimens has shown that molecular reorganisation occurred in carbonate and in biogenic silica during

fossilisation, through diagenetic processes. The resulting stable mineral structures confer an exceptional preservation to fruits in sediments. Taking into account these taphonomic specificities (transformation and differential preservation), the chronological and palaeoenvironmental aspects of the mineralised fruits are discussed.

Keywords Fruit remains · Biomineralisation · Taphonomy · X-ray EDS · Scanning electronic environmental microscopy · Fourier transform infrared spectroscopy

Introduction

Plant macroremains recovered from archaeological sites are most commonly charred (e.g. fruits, seeds and wood charcoals), which preserves them from decomposition by micro-organisms in various kinds of deposits. However, mineralised botanical remains (Green 1979) often appear in global charred assemblages and do not seem to be linked with the archaeological context, which makes them difficult to be used by archaeobotanists (van Zeist and Buitenhuis 1983; van Zeist and de Roller 1995). Their occurrence in various contexts and stages of preservation raises questions about their origin and taphonomy (McCobb et al. 2001, 2003). Mineralised archaeobotanical remains can be classified into two groups depending of the nature of mineralisation. The first group, recovered in geological and archaeological deposits (respectively, Wilby and Briggs 1997; McCobb et al. 2001, 2003), has been impregnated with mineral solution. The organic structures have been replaced or replicated and the plant tissues hardened, especially by phosphatisation (Green 1979). The second group corresponds to fossils that have been preserved because some living plants have the capacity to produce

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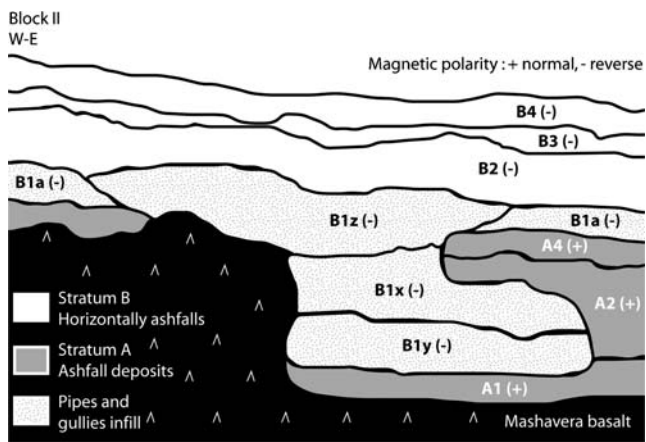


Fig. 1 Stratigraphic interpretations made in *Block II*. Section (*W-E*) is 10 m long, with ca. 1.8× vertical exaggeration (modified from Lordkipanidze et al. 2007)

mineral matter, i.e., biomineralisation processes in organisms before deposition and burial. Carbonates are most commonly involved in such mineralisation, along with silica (Wang et al. 1997; Jahren et al. 1998, 2001; Pustovoytov et al. 2004; Pustovoytov and Riehl 2006). As mineralised fruits or seeds are commonly collected in archaeological sites or natural deposits, their specific preservation status has to be taken into account and studied. Their detailed analysis is essential for understanding their exact composition and fossilisation to investigate one of the taphonomic features: preservation.

Materials and methods

Materials

The fruits analysed in this study comprise fossil fruits and their closest modern analogues. The fossil assemblage comes from the Dmanisi site located in the Lesser Caucasus (Georgia). At the present time, this site is considered as one of the oldest palaeoanthropological sites in Eurasia, with an age close to 1.7 million years. It corresponds to one of the first human dispersal waves out of Africa (Dzaparidze et al. 1989; Gabunia et al. 2000a; Vekua et al. 2002; Lordkipanidze et al. 2007). The sequence at Dmanisi has been divided into two main stratigraphic units: stratum A and stratum B. Piping and gullying of stratum A deposits occurred at the initiation of stratum B deposition (Ferring et al. 2008). Rapid burial by low energy slope processes led to the excellent stratification and preservation of bones in pipe–gully facies, which contain all of the hominin remains. A diagenetic laminar carbonate horizon occurs across the site and helps to preserve faunal and hominin remains which underlie this horizon. The carpological assemblage was collected mainly by sieving, although some remains

were recovered during excavation. As with other archaeological remains from the site, almost all fruits come from the several stratum B deposits (Fig. 1). All these mineralised remains were identified by means of ESEM and were classified into eight different groups (Messenger et al., 2008). Among these groups, three taxa (Fig. 2) were selected for this study because fragments were available for chemical analysis: fruits of *Celtis* cf. *tournefortii*, a small tree of the Ulmaceae family and fruits of *Lycopsis* cf. *orientalis* and *Buglossoides* type *arvensis/sibthorpiana*, herbaceous plants of the Boraginaceae family.

To identify the fossil remains from the Dmanisi site, a modern fruit reference collection was augmented with specimens from the Herbarium of the ‘Museum national d’Histoire naturelle’ in Paris and fruits collected during fieldwork in Caucasus. For this study, modern analogues of the three fossil morphotypes (Fig. 2) in the collection were selected from available material of: *Celtis* sp. L., *L. orientalis* L., *B. arvensis* L. (mix of *B. arvensis* subsp. *sibthorpiana* and *B. arvensis* subsp. *tenuiflora*). Fossil and modern fruits were cleaned with distilled water and only the mineralised coats were used for analysis.

Methods

Environmental scanning electronic microscopy and energy dispersive X-ray analysis

Fruit observation and composition measurements were made by means of a Philips XL 30 environmental scanning electron microscope (ESEM). Unlike standard electron microscopes, this equipment allows objects to be examined in the ESEM chamber without the need for gold or carbon coating (Deniaux 2002). The samples were first mounted

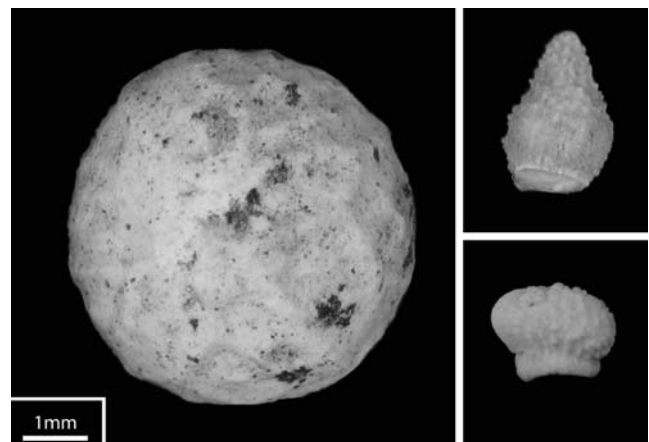


Fig. 2 The three studied fruit morphotypes: *Celtis* cf. *tournefortii* (left), *Buglossoides* type *arvensis/sibthorpiana* (top right) and *Lycopsis* cf. *orientalis* (bottom right)

on stubs using carbon double-sided adhesive tape and then introduced into the chamber.

We conducted energy dispersive X-ray (EDX) measurements to identify the elemental composition of the fruit coat from the three taxa groups described above. In EDX, the X-ray detector measures the number of emitted X-rays as a function of their energy. Since elements have a characteristic energy, the EDX spectrum can be used to identify them and to give semi-quantitative results. The energy dispersive X-ray detector of the Philips XL 30 ESEM was used for these analyses.

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) quantitative analyses were performed using the KBr pellet standard method (Pichard and Fröhlich 1986; Fröhlich 1989; Fröhlich and Gendron-Badou 2002). Samples were first mechanically ground down to a size smaller than the shortest wavelength used (2.5 μm), before mixing with KBr (0.25% standard dilution). A pellet (300 mg, 13 mm in diameter) is obtained by compressing the mixture under vacuum. The pellets are dried at 110°C in order to remove absorbed water and then analysed with a Brüker Vector 22 FTIR spectrometer (32 scans—2 cm^{-1} resolution) in the 4,000–370 cm^{-1} range (Fröhlich and Gendron-Badou 2002; Gendron-Badou et al. 2003). Quantitative analyses were performed with reference

to the mineralogical infrared standard data bank (Centre de Spectroscopie Infrarouge–MNHN).

The FTIR measurement yields indications about fruit coat composition. In this study, this method permits characterisation of the carbonate and silica components involved in fruit mineralisation and to compute the percentage of each present.

Results

Celtis-type (Ulmaceae)

EDX analysis

EDX spectra (Fig. 3) of the fossil *Celtis* fruit show the prevalence of carbon, oxygen and calcium elements. Silica is also recorded. This suggests that carbonate (CaCO_3), and most probably silica is involved in *Celtis* coat structure, but part of these components may be due to sediment residues.

FTIR analysis

a. Fossil *Celtis*-type

The IR spectrum of fossil *Celtis* fruit (Fig. 4) shows only two minerals, calcite (79%) and aragonite (15%). Organic matter and quartz are present as traces. Quartz is probably due to contamination.

Fig. 3 Surface of fossil *Celtis* fruits and corresponding EDX spectra

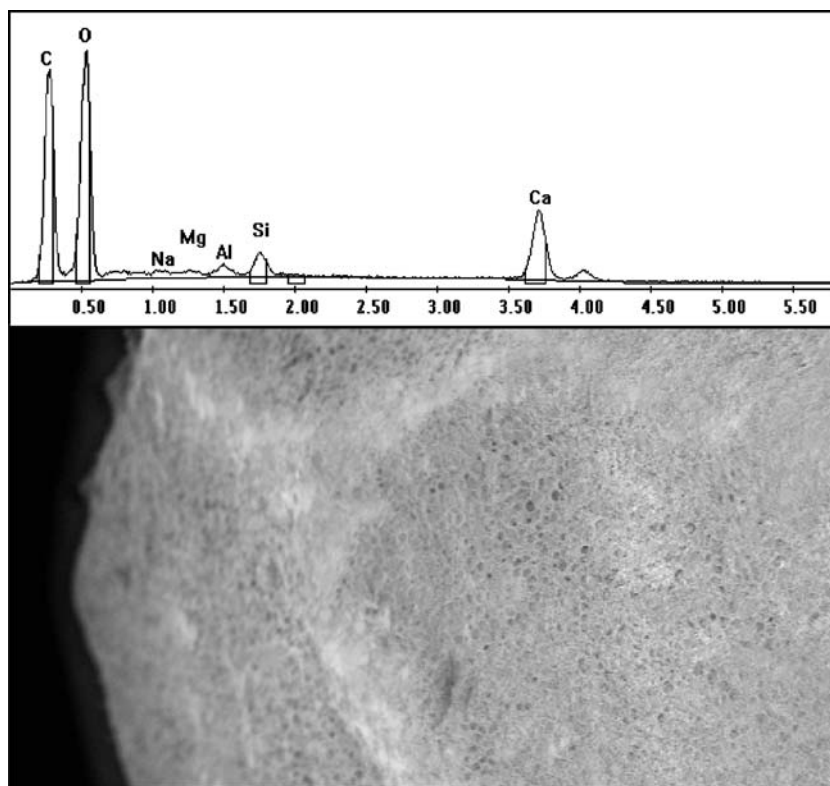
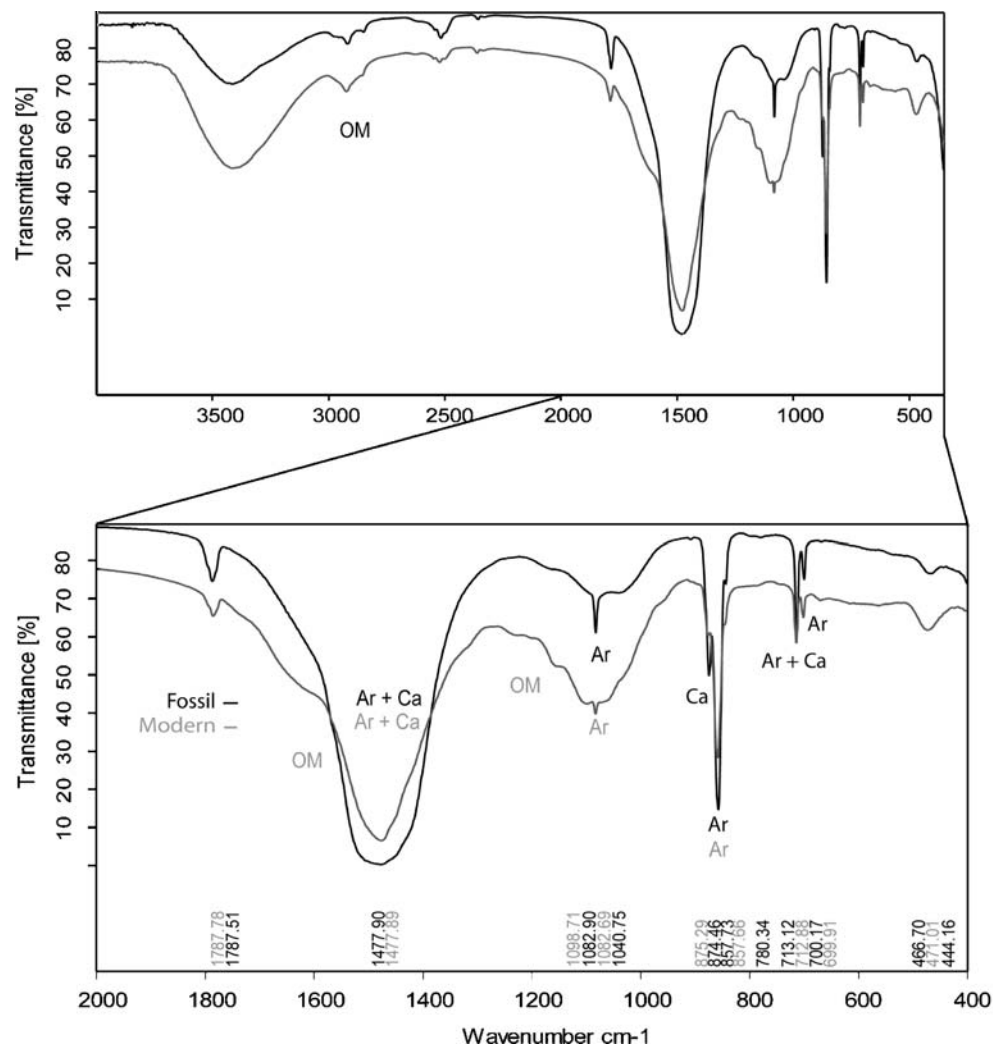


Fig. 4 IR spectra of fossil *Celtis* fruit (0.75 mg analysed) and modern *Celtis* fruit (0.75 mg analysed). *Ar* aragonite, *Ca* calcite, *OM* organic matter, *Q* quartz



b. Modern *Celtis*-type

The infrared spectrum of modern *Celtis* fruit (Fig. 4) shows organic matter associated with carbonate minerals: aragonite (44%) and minor calcite (4%). Quartz traces are probably due to contamination.

Fossil and modern *Celtis* fruits are biomineralised mainly by carbonates. As expected, organic matter is more abundant in the coat of the modern type than in the fossil one. In the modern specimen, aragonite is the major component and calcite in the fossil type.

Lycopsis-type (Boraginaceae)

EDX analysis

a. Fossil *Lycopsis*-type

Measurement spots on the fossil coat section have been indicated in the ESEM image. The A measurement was done on the external epidermis and B, C and D on internal structures.

No major difference has been observed between the four analyses on fossil *Lycopsis*. Oxygen and silica are the most represented elements in the spectra (Fig. 5). Carbon and calcium are also present but in lower proportions.

b. Modern *Lycopsis*-type

Measurement spots on the modern *Lycopsis* coat section have been indicated in the ESEM image. The A measurement was done on the external epidermis and B and C on internal structures.

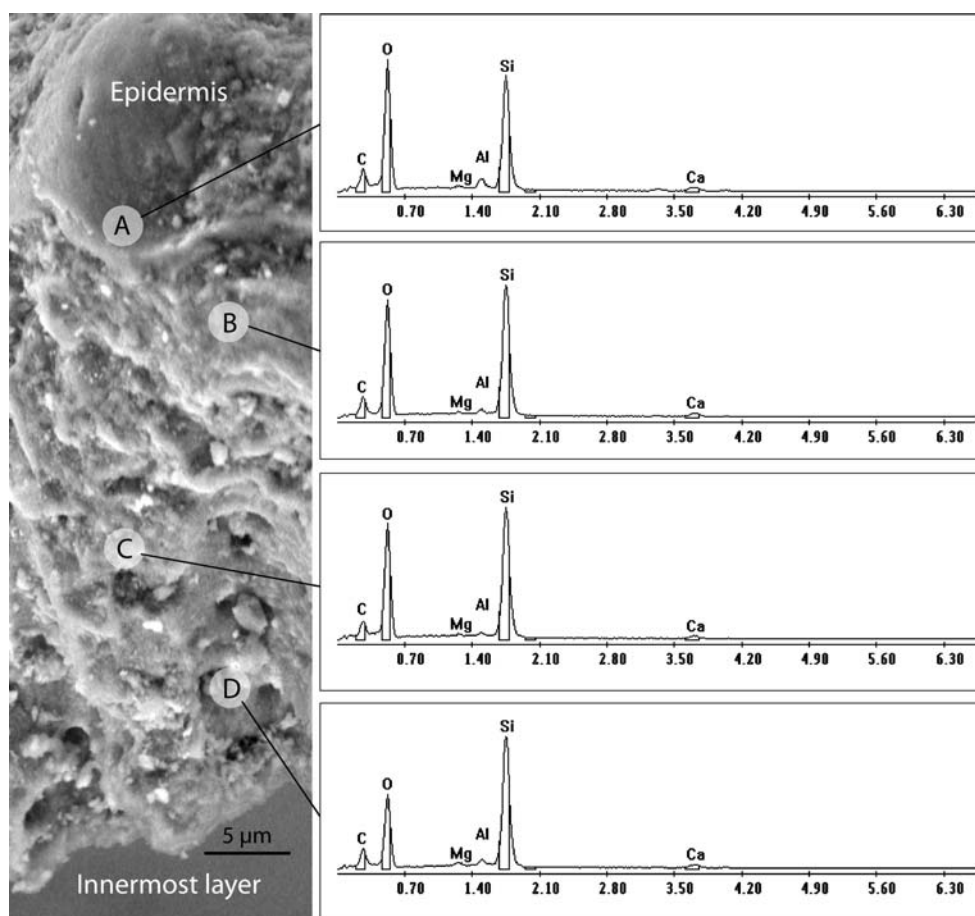
The three EDX spectra (Fig. 6) of the modern *Lycopsis* fruit section show the prevalence of carbon and oxygen. In the epidermis, the amount of silica is significant. This A measurement suggests that silica has impregnated the surficial layer of the living fruits of this taxon, but not the internal tissues.

FTIR analysis

a. Fossil *Lycopsis*-type

The infrared spectrum (Fig. 7) shows that fossil *Lycopsis* fruit contains predominantly biogenic, amorphous silica

Fig. 5 Fossil *Lycopsis* fruit coat section with corresponding EDX measurements



(opal: 79%) with a low calcite content (4.5%) and organic matter traces.

b. Modern *Lycopsis*-type

The infrared spectrum of modern *Lycopsis* (Fig. 7) is dominated by organic matter, along with amorphous silica, as indicated by the weak absorption bands at 800 cm^{-1} (diagnostic of Si-O-Si bond), $1,100\text{ cm}^{-1}$ (Si-O bond) and 960 cm^{-1} (Si-OH), which are typical for amorphous biogenic silica.

The coat composition of the *Lycopsis* specimens indicates that both modern and fossil fruits are biomineralised. The calcite content (4.5%) of the fossil specimen is very low. Amorphous silica is the main mineral component in both modern and fossil specimen, but their infrared spectra exhibit two important differences:

- the 800 cm^{-1} band, which corresponds to an inter-tetrahedral (Si-O-Si) bending vibration mode (Lecomte, 1949), is stronger in the fossil *Lycopsis* than in the modern.
- the 960 cm^{-1} band, which corresponds to a Si-OH vibration mode (Moenke, 1974), is rather intense in the modern fruit, but is lacking in the fossil. This difference in the molecular structure of modern and

fossil biogenic silica was attributed to diagenesis (OH loss) by Fröhlich (1989) and is also observed in siliceous animals (sponge spicules) and algae (diatoms; Gendron-Badou et al. 2003).

Buglossoides-type (Boraginaceae)

Buglossoides sp. L. belongs to the same family (Boraginaceae) as *Lycopsis* sp. L. No EDX analysis was performed for this taxon and specimens were directly studied in FTIR.

FTIR analysis

a. Fossil *Buglossoides*-type

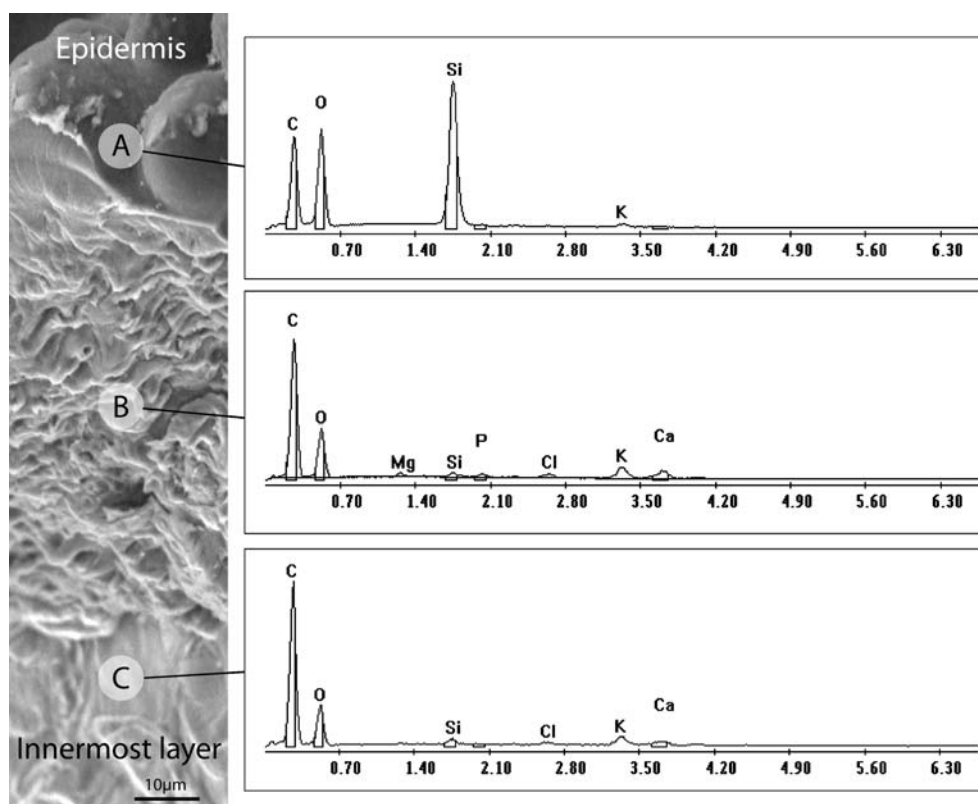
The infrared spectrum of fossil *Buglossoides* (Fig. 8) shows two main minerals: calcite (47%) and biogenic amorphous silica (20%).

b. Modern *Buglossoides*-type

In the infrared spectrum of modern *Buglossoides* (Fig. 8), biogenic hydroxylated (960 cm^{-1}) silica (26%) and calcite (38%) are the main components.

The *Buglossoides* coat composition shows that this taxon is biomineralised with mixed calcite and biogenic silica.

Fig. 6 Modern *Lycopsis* fruit coat section and corresponding EDX measurements



The lack of the 960 cm^{-1} band (Si-OH bond) in the fossil specimen is presumed to be due to diagenesis. The weak absorption bands at 566 and 605 cm^{-1} in the fossil specimen are typical of phosphate minerals (apatite structure).

Discussion

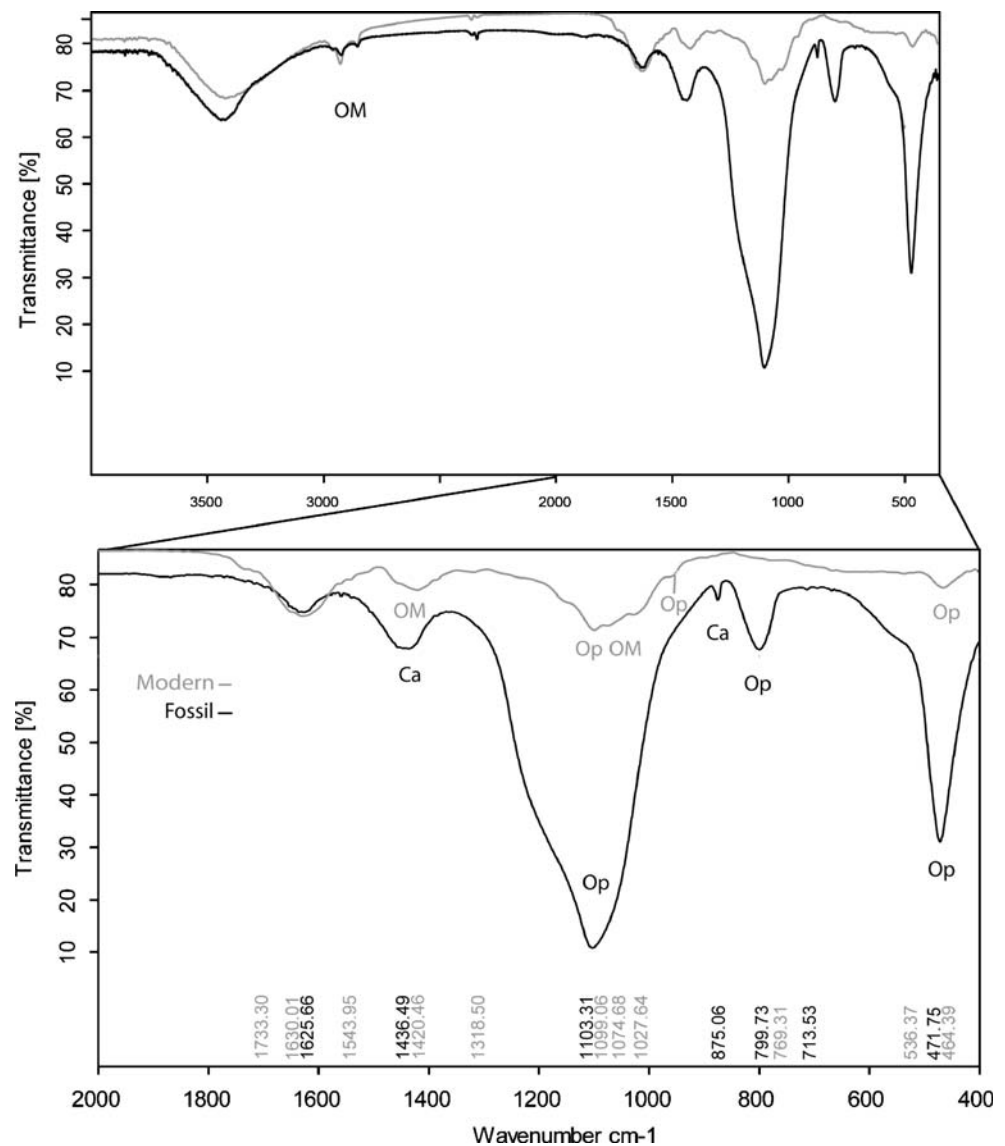
Fruit compositions

Celtis and *Buglossoides* fruits are known to be mineralised, specifically by biogenic carbonates (Yanovsky et al. 1932; Retallack 1990; Cowan et al. 1997; Wang et al. 1997; Jähren et al. 1998, 2001 for *Celtis*; Seibert 1978; Pustovoytov et al. 2004; Pustovoytov and Riehl 2006 for *Buglossoides*). Our analyses confirm the prevalence of carbonates in the fruit walls of both fossil and modern specimens. The *Celtis* modern fruits we studied are mostly composed of aragonite, as is expected for modern material (Cowan et al. 1997; Wang et al. 1997; Jähren et al. 1998). Fruit endocarps of *Celtis* are formed of a silica framework associated with aragonite deposits, even though silica opal structures may be lacking. In *Celtis* fruits, carbonate structure changes significantly between the modern and fossil specimens. The aragonite is replaced by calcite which is prevalent (79%) in the fossil specimen, suggesting that the metastable

aragonite from the endocarp walls is progressively recrystallised in calcite.

As for *Celtis* endocarps, carbonates and opal are involved in the mineralisation of the coat of *Buglossoides* fruits, but for this taxon, there is no significant modification of the carbonate content between modern and fossil specimens. Analyses indicate the prevalence of calcite in both fossil and modern fruits. Significant quantities of biogenic silica are also present in both samples. The three-dimensional organisation of silica in modern *Buglossoides* is characterised by the presence of Si-O-Si bonds (800 cm^{-1}) with silanol groups (Si-O-H) that are not present in the fossil sample. Such a molecular framework is characteristic of hydroxylated amorphous silica and is not linked with proteins. Our analyses indicate that calcite is present in *Lycopsis* fruits, but with a large amount of biogenic silica in both fossil and modern samples. This silica opal is associated with organic matter (probably proteins) in the coat of the modern fruits, while in fossils a three-dimensional reorganisation is observed, with the presence of a Si-O-Si framework. The difference in silica opal organisation between modern *Lycopsis* (Si-O-Protein) and *Buglossoides* (Si-O-H) is probably due to the origin of the material. The *Lycopsis* fruits were collected by one of the authors during fieldwork in Transcaucasia a few years ago, mixing young and mature fruits. The *Buglossoides* fruits are from old collections (more

Fig. 7 IR spectra of fossil *Lycopsis* fruit (0.75 mg analysed) and modern *Lycopsis* fruit (0.36 mg analysed). *Op* opal, *Ca* calcite, *OM* organic matter



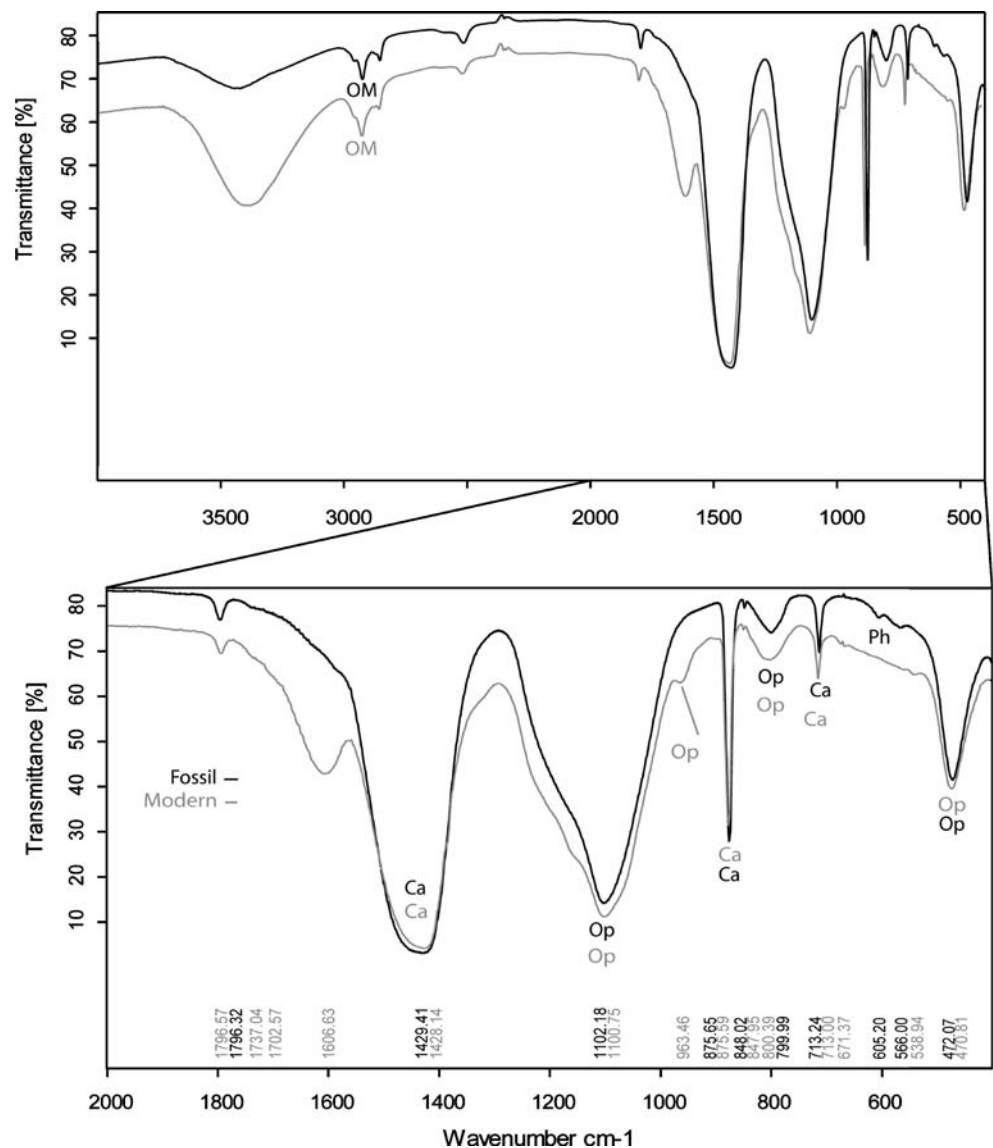
than one century) in the Herbarium and correspond to mature, very dry fruits.

Post-depositional transformations

A loss of organic matter is a feature observed on the three taxa. During fossilisation, the organic matter is destroyed and the inorganic part is restructured. For *Celtis* fruits, aragonite recorded in the modern samples is replaced by calcite (more stable carbonate) in the fossil sample. The replacement of aragonite by calcite is well known as a diagenetic process (Kunzler and Goodell 1970; Carlson 1983; Peric et al. 1996; Berndt and Seyfried 1999; Zhaodong et al., 2008) because aragonite is less stable than calcite in the conditions that prevailed at Earth's surface. However this might require a long period of time because

previous studies of Holocene material have shown that aragonite predominates in some archaeological fruits of *Celtis* (Wang et al. 1997). The difference observed between these fossil carpo-remains and those we studied is probably due to the age of the Dmanisi fossils (1.7 Ma), which are older and have presumably undergone more significant diagenesis. For *Buglossoides* and *Lycopsis* fruits, organic matter disappears and the silica opal is stabilised. The bonds between Si-O and organic molecules and between Si and OH disappear and a new three-dimensional Si-O-Si framework is generated during fossilisation (Gendron-Badou et al. 2003). This confers to the fossil, a condensed mineralogical structure that becomes more stable and thicker. This silica reorganisation leads to a better resistance to dissolution (Fröhlich 1989). Such transformation has been previously observed in very old diatoms from Miocene

Fig. 8 IR spectra of fossil *Buglossoides* fruit (0.75 mg analysed) and modern *Buglossoides* fruit (0.75 mg analysed). *Op* opal, *Ca* calcite, *OM* organic matter, *Ph* phosphate



deposits (Gendron-Badou et al. 2003). For the first time, we observed the effects of diagenesis on biogenic opal in fossil fruits remains.

The fossil remains of *Buglossoides* are shown to contain some phosphate minerals with a typical apatite structure. This can be interpreted as infiltration by a calcium phosphate solution, followed by precipitation within the fruits, representing a phosphatisation process (Green 1979; McCobb et al. 2001, 2003). The *Buglossoides* fruit analysis suggests a double mineralisation: biomineralisation and weak phosphatisation. The phosphatisation process depends upon the structural features of the tissues (McCobb et al. 2001, 2003). Phosphatisation can occur in soft tissues (Briggs and Wilby 1996), but can also affect robust propagules such as *Prunus* or *Rubus* endocarps (McCobb et al. 2001). Our analysis confirms that biomineralisation of *Buglossoides* fruits does not prevent secondary mineralisation by calcium phosphate.

Preservation features and archaeological implications

All of the fruit morphotypes studied in this work have been primarily mineralised through biomineralisation by the living plant. Such fruits naturally have a higher probability of being represented in carpological assemblages. They do not have to be charred to survive, but can also be well represented in assemblages from burned structures. As suggested by our results, the diagenetic history of these remains reinforces their preservation potential because mineral structures are particularly stable (calcite and condensed silica opal) in fossil specimens. Comprising mainly mineral components, they can be preserved in various kinds of deposits, although calcium carbonate is unstable under low-pH conditions and would not be predicted to survive in acidic deposits. The present study illustrates how this kind of carpo-remains can be preferentially preserved in some

geological or archaeological deposits because of their natural mineralised components.

As mentioned previously, fossil mineralised botanical remains exhibit a fresh appearance which makes their contemporaneity with other archaeological finds questionable (Green 1979). For the Dmanisi site, the botanical remains are from a very well-known stratigraphical context. They are mostly recovered in the upper part of the stratigraphy corresponding to the archaeological layers. In this part of the sequence, remains are sometimes embedded in the laminated calcrite (cf 'Materials' section). Moreover, several fruits come from the lower part of the stratigraphy (pipes) located under the carbonate horizon. These stratigraphical locations restrict post-depositional disturbance because this laminated carbonate zone appears to not have been penetrated before very recent times (Gabunia et al. 2000a). The comparison between the modern and the fossil samples that we performed can be considered as a good indication of the influence of the ageing process on the mineral structure. The results suggest a very advanced state of diagenesis for the fossil carbonates (not observed in Holocene samples) and for fossil silica opal (previously observed in Miocene material). The timing of such alteration processes are in agreement with the age of the Dmanisi assemblage.

Because of the highlighted taphonomical bias, these fruit remain assemblages cannot give an accurate picture of the whole flora that lived on the site. However, they can be used profitably for complementing environmental interpretations because they can be recovered in sedimentary contexts where other botanical remains have disappeared (e.g., where there has been no fire and organic matter is rare). Carpo-remains which were mineralised by phosphatisation processes show variable degrees of preservation (Green 1979; McCobb et al. 2001; Matterné 2001). In contrast, biomineralisation by the living plant permits much better preservation of the coat ornamentation, as has also been observed for algae and animals (Gendron-Badou et al. 2003). For a site of that age, and taking into account the taphonomical bias, the palaeobotanical assemblage of Dmanisi is a good indicator of the plants which occupied the site during the period when stratum B was deposited (Messenger et al. 2008). The recognised taxa indicate local open vegetation with rather dry climatic conditions. A pioneer and xeric meadow vegetation probably grew in the Dmanisi area during the drought event recorded by other proxies in the upper part of the stratigraphy (Gabunia et al. 2000b; Messenger 2006).

Conclusion

EDX and FTIR analyses carried out on modern and fossil fruits revealed three different styles of mineralisation in the

taxa examined. They are all biomineralised with amorphous silica or/and carbonates, but not in the same proportions. Silica is over-represented in *Lycopsis* and *Buglossoides* fruits. *Celtis* and *Buglossoides* fruit walls are mostly composed of carbonates, but *Lycopsis* contains very few. Carbonates are present in two different forms, aragonite and calcite in the specimens of *Celtis* fruits and calcite only in *Buglossoides*. These biological mineralisations confer on the fruits a preservational advantage, although other, post-depositional, processes have certainly occurred during fossilisation. Although fresh and fossil carpo-remains are not at the same stage of post-depositional evolution, this does not limit their preservation potential because certain mineral structures are relatively stable in fossil specimens. The preservation of mineralised botanical remains in sediments depends upon other factors, such as environmental and geochemical processes, that need to be investigated. However, it can be assumed that a significant taphonomical bias exists due to the biomineralised nature of these botanical remains. This exceptional preservation permits the recovery of fruit remains from the mineral context of a site as old as Dmanisi. Taking into account the taphonomic bias, the carpological assemblage helps to reconstruct the local ecological conditions.

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