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ORIGINAL ARTICLE

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Radiocarbon age of carbonate in fruits of *Lithospermum* from the early Bronze Age settlement of Hirbet ez-Zeraqōn (Jordan)

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Abstract Uncarbonized fruits of the Boraginaceae occur widely in cultural layers of archaeological sites in the Mediterranean and the Near East. To date, interpreting their origin remains problematic. It is difficult for archaeobotanists to tell whether such fruits were deposited as part of the cultural layer or were introduced post-depositionally. In an attempt to answer this question for the early Bronze Age site of Hirbet ez-Zeraqon (Jordan), we used direct ^{14}C dating of biogenic carbonate from calcareous fruits of *Lithospermum*. The radiocarbon ages of seven fossil samples of the fruits suggest that they originate from plants that grew during or around the time of occupation.

Keywords Archaeobotany · *Lithospermum* · Biogenic carbonate · Radiocarbon dating · Near East · Early Bronze Age

Introduction

Fruits of the genus *Lithospermum* are, beside other members of the Boraginaceae, common in cultural layers of archaeological sites of the Mediterranean and the Near East (for example de Moulins 2000b; Hillman et al. 2001; van Zeist 2001, and for a summary of some earlier work see Miller 1991). They appear mostly uncharred and without endosperm. Charred nutlets, sometimes with carbonised endosperm, although they have also been found, are less common. The interpretation of the origin of the uncharred objects remains conjectural: they could have been deposited along with the cultural sediments or as later intrusions (Melamed 1996). To solve the problem, evidence of the absolute age of such fruits is required. Isotopic studies on fruits of *Celtis* sp. suggest that biogenic carbonate of fossil fruits can be successfully dated by the radiocarbon method (Wang et al. 1997). Similarly to *Celtis*, *Lithospermum* forms fruits rich in biogenic carbonate (Seibert 1978), which is as resistant to decomposition by microorganisms as charcoal, and has the potential to be dated. So far, radiocarbon dating has not been applied to fossil *Lithospermum* nutlets. We present here the results of ^{14}C dating of biogenic carbonate fruits of *Lithospermum* from the cultural layer of the Bronze Age settlement Hirbet ez-Zeraqōn, Jordan.

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Carbonate fruits of the Lithospermeae as an archaeobotanical phenomenon

Lithospermum species – taxonomy, ecology, and potential use

Amongst the subfamily of the Boraginoideae four main tribes are differentiated, the Eritrichieae, the Anchuseae, the Cynoglosseae and the Lithospermeae. Based on Johnston's contributions, appearing at regular intervals (1923–1959, for references see Seibert 1978), it is known that the tribe of the Lithospermeae contains 23 genera. The very frequent genera occurring in archaeological excavations *Lithospermum*/*Buglossoides*, *Echium*, *Arnebia* and *Alkanna* all belong to this tribe. The species of these genera are mostly bristly or stiffly hairy annual or perennial herbs, and while *Echium* and *Alkanna* are very rich in species, *Lithospermum*/*Buglossoides* consists only of a few species. We concentrate here on the latter, first because species of this genus were most numerous in our material, and second they contain biogenic calcium carbonate to be dated.

There are 5 species of *Lithospermum/Buglossoides* listed in "The Flora of Turkey" (Davis 1965–1988). *Lithospermum arvense* L. and *Lithospermum tenuiflorum* L. (syn. *Buglossoides tenuiflora* (L. fil.) Johnston) are the most commonly reported finds of the genus at archaeological sites. The two species are annuals with average growing heights between 6 and 30 cm, both grow as crop weeds, mainly on calcareous soils, on fallow fields or waste ground.

The roots of the species contain a purple dye, which was commonly used, as indicated in the German vernacular name "Bauernschminke" (peasant's make-up).

All organs of the *Lithospermum* plant are used in ethnomedicine, and the nutlets contain Lithosperm acid. The endocrinological effect of this acid was recently discussed again (Brinker 1990; Auf'mkolk et al. 1985).

Fruit anatomical and chemical properties

Detailed fruit anatomical and chemical investigation of the tribe Lithospermeae was conducted by Seibert (1978) for systematic reasons.

The pericarp of the Lithospermeae is structured into 4 layers which are from the outer to the inner (Fig. 1(3)): epidermis (p1), sclerenchymous layer (p2), pericarp parenchyma (p3) and a second pericarp parenchyma with thinner cell walls (p4). The inner testa (s) is structured into testa parenchyma and endosperm.

The presence of calcium carbonate in the pericarps of *Celtis* and *Lithospermum* was already mentioned by Molisch (1913), but not proved spectroscopically until by Seibert in 1978. Incrustation of the fruit wall with calcium carbonate within the Boraginaceae is restricted to the Lithospermeae, but not all genera contain it. Calcium carbonate in fruits of the Lithospermeae generally completely fills up the epidermal cells, and parts of the sclerenchymous layers. The intensity of deposition is in reverse proportion to the thickness of the cell layers.

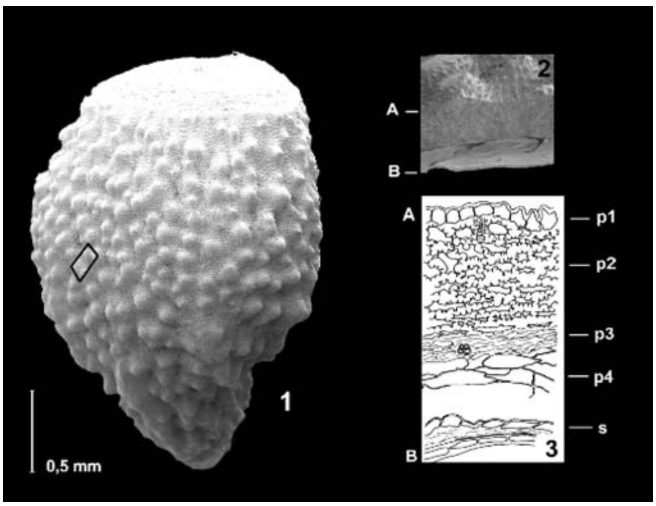

Fig. 1 Modern *Lithospermum arvense* L. nutlet and its fruit wall: (1) – the general view of the fruit; (2) - the fragment of fruit wall marked in (1) showing a section through pericarp (A – outermost layer, B—innermost layer); (3) – the structure of pericarp along the line A-B in (2) (after Seibert 1978, see text for details)

There are two main factors that should be taken into consideration to explain a good preservability of *Lithospermum* fruits in cultural layers. First is a remarkable hardness of the fruits wall in modern fruits, which is due to sclerenchymatisation (Seibert 1978). This property is undoubtedly essential to prevent mechanical destruction prior to sedimentation of the fruit or to a post-sedimentary introduction into the cultural layer. The second factor is represented by constituents of the pericarp tissues which are resistant to chemical (microbiological) alteration in the cultural layer. These are calcium carbonate and silicon dioxide. Calcium carbonate generally remains well-preserved in soils and sediments under arid climatic conditions (Pustovoytov 2002 and references therein). On the other hand, biogenic carbonate, which lines the cell luminae of the modern fruit walls, enhances fragility of the fruit (Seibert 1978) and theoretically should—in contrast to sclerenchymatisation—reduce the likelihood of preservation of the fruit. Carbonate of excavated *Lithospermum* fruits has been occasionally mistaken for SiO_2 (for example, van Zeist and Buitenhuis 1983), the latter being thus considered to be the main reason of the durability of fruits in archaeological deposits. Actually, SiO_2 comprises less than 10% of the mineral mass of fruits of *Lithospermum* (Svensson 1925; Jaretzky and Drimborn 1937/38), whereas the bulk of pericarp consists of biogenic carbonate. It is therefore most probably the carbonate that is responsible for the fruit durability in the archaeological record. However, the preservability of carbonate-free fruits (such as *Echium* spp., Seibert 1978) in cultural layers is very likely to be determined by silicon dioxide.

On the whole, the role of the three components of the pericarp tissues (sclerenchymous layers, biogenic carbonate and silicon dioxide) in preservation of *Lithospermum* fruits still remains to be explained.

Archaeological find situation and interpretation

Lithospermum fruits extracted from archaeological sediments can be optically very similar to modern comparative material appearing greyish or whitish in colour, and their real age cannot be recognised. The problem of potential contamination by modern material arises frequently, especially when the fruits are present in large numbers. This was the case at PPNB Can Hasan III, where thousands of *Lithospermum* fruits occurred in some samples (Hillman 1972). Similarly at PPNB Abu Hureyra 2 (de Moulins 2000a), Neolithic Erbaba (van Zeist and Buitenhuis 1983) and many other sites. These objects were either interpreted as modern intrusions or probable weeds of dry land cultivation. At late Bronze Age Kamid el-Loz millions of *Echium* fruits in a vessel were interpreted for their potential medicinal use (Baas 1980).

Table 1 Radiocarbon ages of one modern and seven prehistoric samples

Sample	Area, depth of the surface	No. of fruits dated	^{14}C (B.P.)	cal B.C. (1σ)	cal B.C. (2σ)	Lab. N°
Modern	-	15	Modern	-	-	Ua-21360
HZ91–688	Lower city, building 3, 127 cm	11	3020±55	1380–1330		
				1320–1210	1410–1110	Ua-19862
				1200–1190	1100–1080	
				1180–1160		
				1140–1130		
Z91–727	Upper city, building 11, 69 cm	12	3530±60	1940–1740	2030–1730	Ua-19863
					1720–1680	
HZ91–665	Lower city, building 3, 105 cm	25	3790±45	2290–2190	2410–2370	Ua-21404
				2180–2140	2350–2120	
					2100–2030	
HZ91–762	Upper city, building 2, 86 cm	9	3975±40	2570–2510	2580–2390	Ua-21371
				2500–2450	2380–2340	
HZ91–756	Upper city, building 8, 34 cm	12	4035±45	2620–2470	2860–2810	Ua-21409
					2680–2460	
HZ91–769	Upper city, altar, 152 cm	6	4059±90	2870–2800		
				2780–2770	2900–2450	Ua-19864
				2760–2560		
				2530–2490		
HZ91–683	Upper city, temple, 8 cm	20	4135±45	2870–2800	2880–2570	Ua-21410
				2780–2770		
				2760–2610		
				2610–2600		

At the early Bronze Age settlement of Hirbet ez-Zeraqōn, fruits of *Lithospermum tenuiflorum* L.f. occurred in large amounts mainly in the upper part and the northern lower part of the settlement (Riehl in press). If the fruits of *Lithospermum* were contemporary with the occupation of the city, they may most probably represent weeds. With regard to the overwhelming amounts in which the fruits occur, this would provide new perspectives of understanding the composition of ancient crop weed floras. But for this to happen the age of the fruits has first to be established.

Materials and methods

In our study, calcareous fruits of *Lithospermum* were collected at the site Hirbet ez-Zeraqōn in Jordan (Riehl in press). The site is situated on the top of a limestone ridge and consists of an upper and a lower city, both of which were excavated between 1984 and 1994 (Mittmann 1994). Hirbet ez-Zeraqōn was occupied during the Early Bronze Ages II (3100–2700 B.C.) and III (2700–2250/2300 B.C.) (Mittmann 1994; Kamlah 2000; Genz 2002). *Lithospermum* fruits represented more than 10% of the finds (n=1618) and were found both in the upper (27%) and the lower city (6%). The pericarp of the excavated *Lithospermum* fruits was rich in carbonate (hydrochloric acid test).

For radiocarbon dating, seven samples of fruits of *Lithospermum* were selected. Five of them originate from the upper city and two from the lower city (Table 1). Modern fruits of *Lithospermum* were obtained from the seed collections of the Botanical Garden of the University of Göttingen (Germany).

The AMS ^{14}C measurements were performed at the Angström Laboratory at the University of Uppsala (Sweden), the results were normalized to $\delta^{13}C$ = -25‰ and calibrated with the OxCal v3.5 program (Bronk Ramsey 2001). Prior to radiocarbon dating, X-ray patterns (CuKα-radiation) of biogenic carbonate of fossil and several modern *Lithospermum* fruits were investigated and the surface of the fossil fruits was examined with scanning electron microscopy (SEM: Zeiss DSM 940, coating Au(80%) and Pd(20%), working voltage 5000 V).

Results and discussion

The results of ^{14}C dating are presented in Table 1 and plotted in Fig. 2. The recent ^{14}C age of the modern sample suggests that calcium carbonate of fruits of *Lithospermum* – similarly to that of *Celtis* – may record the ^{14}C content of the atmosphere and thus serve as a chronological indicator. All dates of the excavated fruits fall within the Bronze Age range. Four radiocarbon ages from the upper city (HZ91–683, HZ91–756, HZ91–762 and HZ91–769) correlate perfectly with the assumed occupation phase at the site (Mittmann 1994). These fruits coincide with the duration of the settlement. The ^{14}C age range of one sample from the lower city (HZ91–665), while partially beyond the limit, still overlaps chronologically with the period of occupation. The rest of the samples (HZ91–688 and HZ91–727), are, however, too young, although prehistoric in ^{14}C age, and there are several theoretical possibilities to explain them.

1. Biogenic carbonate of the fruits of *Lithospermum* may be well-preserved, accurately reflecting the atmospheric radiocarbon content during the lifespan of the parent plant, but at least some of these fruits were introduced into the sediment during a post-occupational phase of the existence of the site (during the Middle and/or late Bronze Age).
2. The fruits might have been produced by *Lithospermum* during the occupation period but their biogenic car-

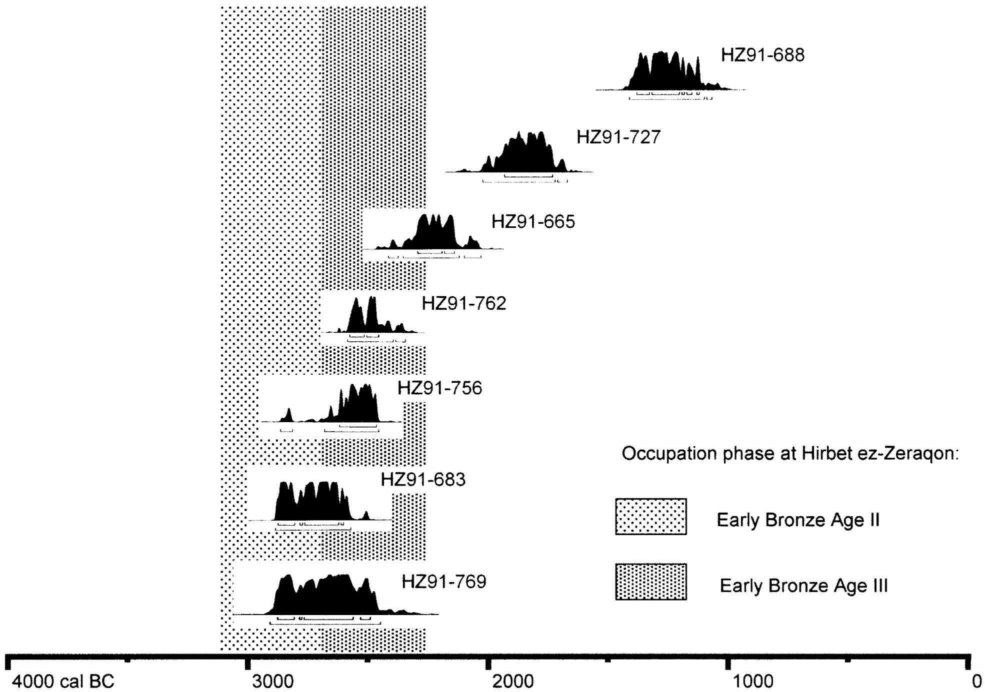

Fig. 2 Plot of the ^{14}C ages of fruits of *Lithospermum*. For fossil fruits calibrated ^{14}C dates are presented (see Table 1)

bonate was exposed to ^{14}C contamination within the cultural layer (Pendall et al. 1994).

3. A combination of these options.

At present, it is difficult to tell which of these versions holds true. However, it is clear that most of the biogenic carbonate of *Lithospermum* at Hirbet ez-Zeraqōn is of prehistoric origin with no or insignificant contribution from modern plants.

In this study we attempted to find out the degree of diagenetic alteration of biogenic carbonate of *Lithospermum*-fruits on the basis of the X-ray analysis and scanning electron microscopy (SEM). In their study on fruits of *Celtis*, Wang et al. (1997) used the X-ray analysis for this purpose. Modern *Celtis* fruits are made up of aragonite, which is a relatively unstable modification of calcium carbonate and converts to calcite if diagenetic alteration occurs. X-ray patterns of aragonite and calcite are distinctly different and thus in the case of *Celtis* are indicative of whether carbonate in fossil fruits was affected by diagenetic processes or not. However, the X-ray test turned out to be inappropriate for *Lithospermum* fruits. We examined X-ray reflections of 12 fossil and 10 modern samples of fruit carbonate of *Lithospermum*. All samples consisted of almost pure calcite and lacked any admixtures of aragonite (Fig. 3). The absence of aragonite in modern fruits renders detection of diagenetic alteration for this genus impossible.

SEM analysis can be considered as a reasonable alternative to X-ray diffraction, as although it probably provides a weaker test, it shows some promise for identifying well-preserved biogenic carbonate (Bezerra et al. 2000; Schleicher et al. 1998). Furthermore, it has been demonstrated that dissolution or re-precipitation of carbonate in soil results in specific types of micro-relief of the surface of carbonate material, which is visible under the electron microscope (Berrier et al. 1987). We observed a pronounced, intact micro-relief of the surface of fossil *Lithospermum* fruits, bearing no signs of corrosion or re-precipitation (Fig. 4), which testifies to the absence of intensive diagenetic processes in the cultural layer at the site. Further studies are needed, however, to clarify the sensitivity of SEM for detecting diagenesis of carbonate fruits. In doing this, comparative observations of the surface of modern and ancient *Lithospermum* seeds under the electron microscope should be a priority. Modern seeds of *Lithospermum* are covered by a cuticle and a waxy layer (Seibert 1978) which mask the microrelief of epidermis cells incrusted by biogenic carbonate (Fig. 1). For this reason, a special pre-treatment of modern seeds (possibly with organic solvents) is required to expose the surface of carbonate incrustations for comparative SEM investigations.

Future research

The seven ^{14}C dates in our study still do not give a final answer to the question of the origin of fruits of *Lithospermum* at Hirbet ez-Zeraqōn. However, they demonstrate that direct ^{14}C dating of fruit carbonate can be relevant to the problem in general. Dating of such fruits when they are abundant in archaeological excavations should be carried out. Future progress in our understanding the nature of *Lithospermum* fruits at archaeological sites will obviously depend on at least three research priorities:

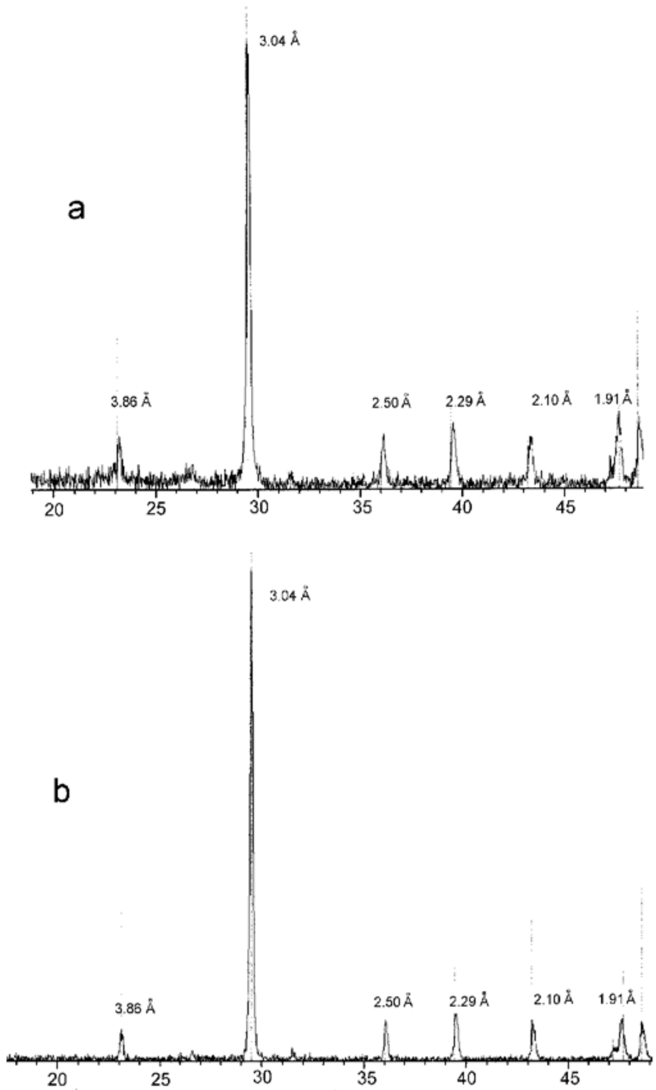

Fig. 3a,b X-ray diffraction patterns of a modern (**a**) and a fossil (HZ91–727) (**b**) *Lithospermum* fruit. Diffraction peaks of both are typical of calcite. Scale in °2d

1. [14]C dating of fossil carbonate "reference fruits", which clearly represent a constituent of the cultural layer (such as dark-greyish coloured *Lithospermum* fruits that were affected by fire);
2. exploration of factors affecting the radiocarbon age of carbonate materials in soils and sediments (Chen and Polach 1984; Pendall et al. 1994; Amundson et al. 1994);
3. elucidation of the role of different factors (such as carbonate, sclerenchyma, SiO_2) in preservation of carpological material in the archaeological record.

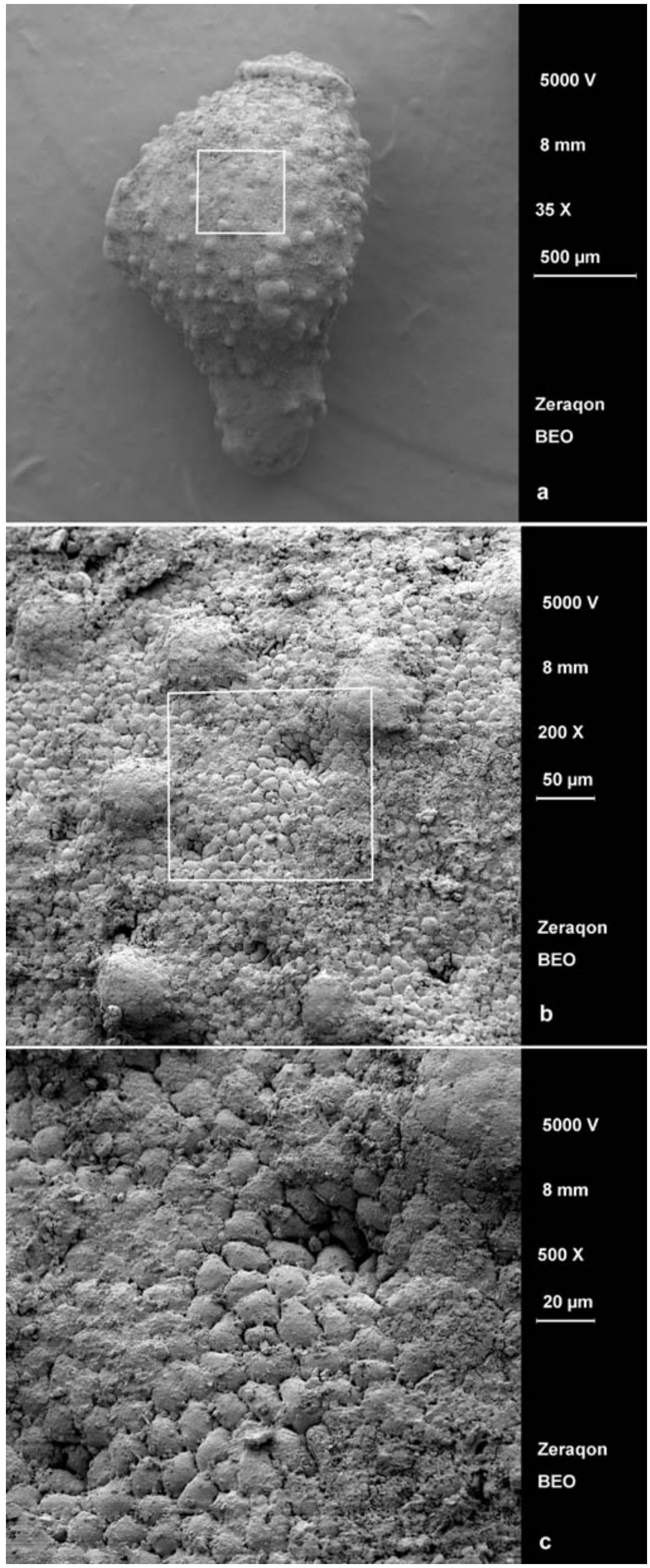

Fig. 4a–c SEM of a fossil fruit of *Lithospermum* (HZ91–727) at 35x (**a**), 200x (**b**) and 500x (**c**). Note the distinct cellular structures of the microrelief of the fruit surface (**b** and **c**)

Conclusions

The ^{14}C ages of biogenic fruit carbonate from Hirbet ez-Zeraqōn suggest that no or little modern contamination of the cultural layer by recent fruits of *Lithospermum* took place and most of their biogenic carbonate is of prehistoric origin. As with calcium carbonate of fruits of *Celtis*, that of *Lithospermum* may reflect the ^{14}C content of the atmosphere and thus represent a new material appropriate for radiocarbon dating. Carbonate of modern fruits of *Lithospermum* is represented by calcite, which implies that the X-ray test used for *Celtis* is not applicable in the case of *Lithospermum* for detecting diagenetic alteration of fossil fruits. However, SEM analysis should be taken into consideration as potential alternative to test preservation of carbonate fruits.

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