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Oxygen isotopic composition of fruit carbonate in Lithospermeae and its potential for paleoclimate research in the Mediterranean

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ABSTRACT

Calcareous pericarps of the tribe Lithospermeae (fam. Boraginaceae) are a common component of archaeobotanical macroremain assemblages in the Mediterranean region. In this study, the relationship between oxygen isotopic composition of fruit biogenic carbonate and climatic conditions was examined. $\delta^{18}O$ and $\delta^{13}C$ values of biogenic carbonate were measured in modern Lithospermeae fruits from seven Eurasian sites (Berlin, Kirchentellinsfurt, Göttingen, Athens, Ankara, Tbilisi, and Almaty) and in fossil fruits from three archaeological sites in the eastern Mediterranean (Troy, Kumtepe, and Hirbet ez-Zeraqon). Additionally, three ^{14}C measurements were performed on ancient fruit carbonate from Hirbet ez-Zeraqon. The $\delta^{18}O$ and $\delta^{13}C$ values varied from −9 to 5‰ PDB and between −35 and −7‰ PDB respectively. In modern fruits, $\delta^{18}O$ of biogenic carbonate was correlated to local summer precipitation amounts (inversely proportional) and summer air temperatures (proportional). In fossil fruits, the $\delta^{18}O$ values of carbonate from Troy and Kumtepe were significantly lower than that from Hirbet ez-Zeraqon (ca. −5 vs. 2‰ PDB respectively). The vertical distribution of stable isotopic values and ^{14}C dates in cultural layers of Hirbet ez-Zeraqon indicate that fruit biogenic carbonate can persist in sediment without appreciable diagenetic alteration. These findings suggest that biogenic carbonate of Lithospermeae fruits can be useful as a paleoclimate proxy at least in the Mediterranean.

1. Introduction

Variations in the oxygen isotopic composition of meteoric water with time are important baseline for paleoclimatic reconstructions in the Mediterranean (Bar-Matthews et al., 1997, 2003; Robinson et al., 2006 and references therein; Roberts et al., 2008 and references therein). In terrestrial environments, different types of carbonate materials can serve as archives of the $\delta^{18}O$ values of paleoprecipitation. Up to now, paleoenvironmental research in the Mediterranean used primarily oxygen isotopic signatures in carbonates of speleothems (Bar-Matthews et al., 1997; Burns et al., 2001; Bar-Matthews et al., 2003; McDermott, 2004; Drysdale et al., 2006; Mattey et al., 2008) and lacustrine sediments (Roberts et al., 2001, 2008 and references therein; Jones et al., 2006; Leng et al., 2006), whereas $\delta^{18}O$ records in other carbonate materials such as pedogenic (Magaritz, 1986; Pustovoytov et al., 2007) and biogenic carbonates (Quade et al., 1994; Goodfriend, 1999; Dufour et al., 2007) remained less explored. It is notable that in the Mediterranean, biogenic carbonates investigated as a paleoclime proxy have been restricted to animal remains.

In this study, we examine the oxygen isotope composition of plant biogenic carbonate, namely in fruits of tribe Lithospermeae (fam. Boraginaceae) and its potential for paleoclimate research. Previously, biogenic carbonate in fruits of flowering plants has been studied isotopically in the genus *Celtis* (Wang et al., 1997; Jahren et al., 1998, 2001). These works addressed the processes of biomineralization in fruit tissues (Jahren et al., 1998) as well as the radiocarbon content (Wang et al., 1997) and oxygen isotopic composition (Jahren et al. 2001) of fruit carbonate. It has been demonstrated that the $\delta^{18}O$ values of biogenic carbonate in *Celtis* fruits are correlated to $\delta^{18}O$ of local meteoric water and, for the studied ecological range, also to mean annual temperatures (Jahren et al., 2001).

Plants of the tribe Lithospermeae are common in the Mediterranean region. A characteristic feature of at least two Lithospermeae genera, *Lithospermum* and *Buglossoides*, is that they accumulate carbonate in the fruit pericarp during their lifetime (Seibert, 1978; Hilger et al., 1993; Pustovoytov et al., 2004). Under arid and semiarid climatic conditions, the pericarps of their fruits remain well-preserved as fossils in sediments–the oldest ones are known from the Ogallala

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series (Miocene) in North America (Gabel, 1987)–and cultural layers, thus representing a typical element of macroremain assemblages at archaeological sites of the Mediterranean and the Near East. It has been demonstrated that these plants use atmospheric carbon to synthesize carbonate in their fruits (Pustovoytov et al., 2004; Pustovoytov and Riehl, 2006). This implies that the biogenic carbonate of Lithospermeae is suitable for ^{14}C dating (Pustovoytov et al., 2004; Pustovoytov and Riehl, 2006), which makes it strongly relevant to paleoenvironmental studies.

2. Biology of Lithospermeae and its occurrence at Mediterranean archaeological sites

Tribe Lithospermeae consists mostly of perennial and, to a lesser extent annual herbs, some subshrubs (e.g., *Lithodora* s.l.) and very rarely shrubs (e.g., in *Lithospermum*) that inhabit mostly open grassy places, arable fields, scrubs and wood-margins. Fruits of Lithospermeae are dry schizocarps separating into four nutlets, usually ovoid-truncate in form, with a ridge on one side and a broad scar at the base (Fig. 1). The pericarp contains biogenic calcite that accumulates in the epidermal cells and parts of the sclerenchyma. The majority of the genera of the tribe occur in the Northern hemisphere and have colonized South America along the Andes with only 1 genus *Lithospermum* (most probably including genera such as *Onosmodium*, *Macromeria* etc.) and Africa along the East African mountains, but are completely absent in Australia and humid tropics. The largest generic diversity of the tribe is found from the Mediterranean region to the Near East (Irano-Turanian region). Some of Lithospermeae are common as weeds on arable fields, especially *Buglossoides arvense* s.l., also included in *Lithospermum* (Clermont et al., 2003), but are nowadays threatened. In many localities of middle Europe, the numbers of individuals of Lithospermeae declined over the last several centuries, probably due to application of herbicides. Beyond being categorized as weeds, they are also investigated for their endocrinologically active components (Auf'mkolk et al., 1985; Brinker, 1990; Yarnell and Abascal, 2006).

Fossil fruits of Lithospermum species are relatively rare in middle Europe. However, they occur in one third of all Eastern Mediterranean and Near Eastern archaeobotanically investigated sites dating from the Epipalaeolithic to historic times (Table 1). These are almost 30,000 seed records from 95 sites, where they occasionally reach frequencies of 100%. (Fig. 2) (Riehl and Kümmel, 2005). The often greyish–whitish fruits in an archaeobotanical sample of charred seeds attracted the attention of Near Eastern archaeobotanists, and have been frequently discussed for their authenticity within the archaeological context (van Zeist, 1999, 2001), which has been concluded as positive for most cases (Pustovoytov et al., 2004). In archaeological contexts they occur mostly together with other remains from crop-processing in cultural layers, and only sometimes in large concentrations (Baas, 1980). At the sites of provenience of our *Lithospermum* seeds, the frequencies were 33% at Kumtepe and Troy, and 64% at Hirbet ez-Zeraqon indicating a widespread occurrence across the excavation area.

Table 1
Occurrence of Lithospermeae fruits in the cultural layers of archaeological sites in the eastern Mediterranean and the Near East (Riehl and Kümmel, 2005).

Periods	No. of sites
Epipalaeolithic	4
PPNA	5
PPNB	19
PPN	28
Chalcolithic	26
Early Bronze Age	29
Middle Bronze Age	13
Late Bronze Age	16
Iron Age	24
Roman period	9
Medieval	9

3. Materials and methods

The series of modern Lithospermeae nutlets were obtained from the seed collections of botanical gardens of the Universities of Berlin, Göttingen and the herbaria of the Universities of Tübingen and Ankara. All fruits from collections originated from local, open-air grown plants. In addition, field sampling took place in Berlin and Kirchentellinsfurt (Table 2, Fig. 3).

There are several factors complicating substantial extension of this data set of modern fruits. First, formerly moderately common weeds, many species of Lithospermeae (primarily *Lithospermum arvense* and *L. officinale*) experienced a dramatic drop in numbers over the last several decades, most probably due to application of herbicides. It makes it difficult to find and collect them in the field, particularly in middle Europe but also in the Mediterranean. Second, when collecting plants for herbaria, botanists are usually interested in flowering exemplars. For this reason, it is much easier to find plants of the tribe at the blossom stage, i.e. without fruits or with weakly developed ones.

The fossil pericarps were obtained from three Mediterranean archaeological sites (Table 2, Fig. 3): Kumtepe (Chalcolithic) (Gabriel, 2000) and Troy (Bronze Age–Roman Time)(Korfmann and Kromer, 1993) in western Turkey and Hirbet ez-Zeraqon in Jordan (Early Bronze Age)(Kamlah, 2000; Genz, 2002).

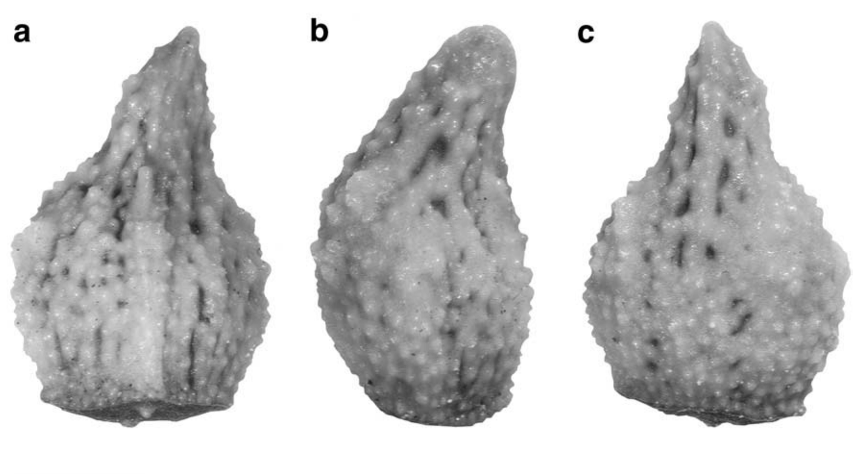

Fig. 1. Modern fruits of *Lithospermum arvense* L. (*Buglossoides arvensis* (L.) I.M. Johnst.) from the seed collection of the University of Göttingen. (a) — dorsal view, (b) — lateral view, (c) — ventral view. Scale bar: 1 mm.

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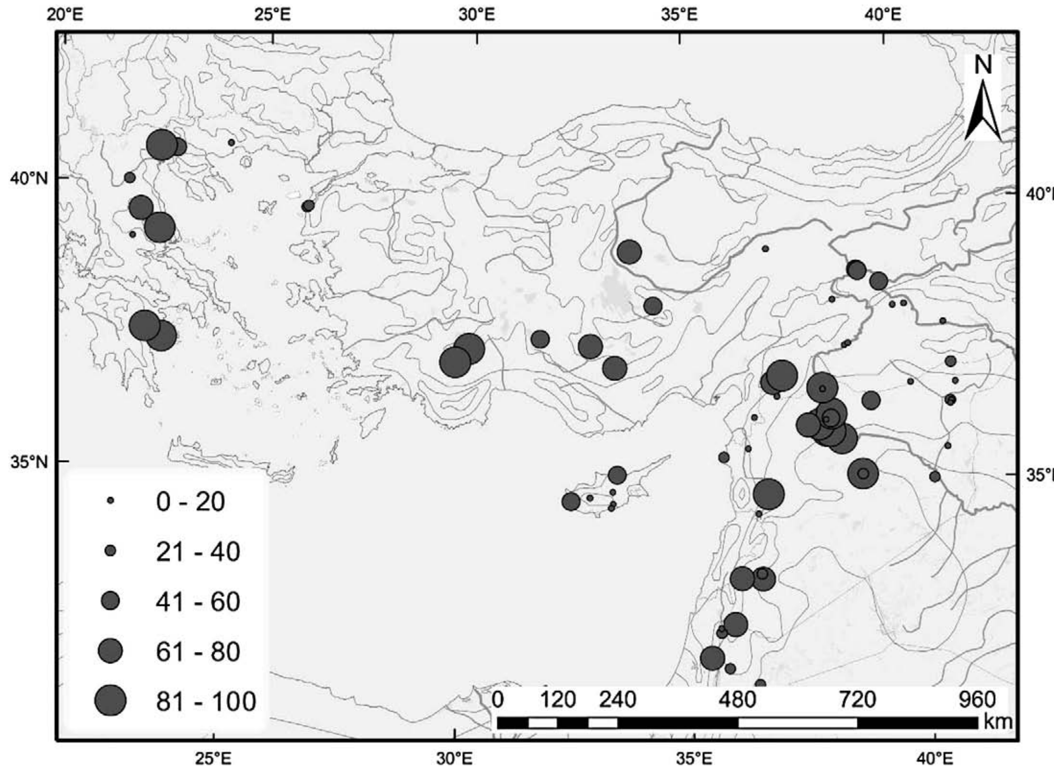

Fig. 2. Map of the eastern Mediterranean with locations of archaeological sites with findings of Lithospermeae fruits. The legend indicates the ubiquities (%) of the fruits in the archaeobotanical material.

The monthly air temperature and precipitation for the sites are given in Fig. 4. All sites have their temperature maximum in the midsummer months, but the climate at German sites is generally cooler. Almaty is characterized by a higher-contrast, continental temperature regime with summer temperatures similar to the Mediterranean sites but substantially lower winter temperatures. Regarding monthly precipitation, the sites can be divided into two groups: most of the sites receive maximum precipitation in summer or late spring, whereas the Mediterranean sites (Athens, Ankara, Troy, Kumtepe and Hirbet ez-Zeraqon) show a distinct precipitation maximum in winter. The monthly values of $\delta^{18}O$ of precipitation at study sites are similar to those of temperature (Fig. 5). The modern pericarps were separated from the endocarps by needle and surgical blade and placed into plastic vials prior to the laboratory analyses. The fossil nutlets were gained by water flotation from sediment samples. This standard method to extract ancient plant remains from cultural layers and other archaeological contexts makes use of the floatability of light objects, such as charred seed remains, roots, small molluscs etc. in relation to water. The plant remains were extracted and dried on-site and their identification was done in the archaeobotanical laboratory of the Center for Archaeological Science, University of Tübingen, with the help of a microscope and a comparative collection.

Measurements of $\delta^{18}O$ and $\delta^{13}C$ were carried out at the Institute of Geosciences of the University of Tubingen, Germany on a Finnigan MAT 252 gas source mass spectrometer with a ThermoFinnigan GasBench II/CTC Combi-Pal autosampler (Spötl and Vennemann, 2003). Prior to mass-spectrometric measurements, the pericarps were reacted with peroxide to reduce the content of organic fraction in biogenic carbonate.

$\delta^{18}O$ and $\delta^{13}C$ values of carbonate are reported in VPDB and $\delta^{18}O$ of meteoric water in VSMOW.

The $CaCO_3$ content in pericarp tissues was estimated by dissolution in phosphoric acid. The ^{14}C measurements (AMS) on pedogenic carbonate were performed at the Leibniz-Laboratory at the University of Kiel, Germany and at the Angström Laboratory at the University of Uppsala, Sweden.

For some of the sampling sites, the oxygen isotopic composition of local precipitation was available in the database of the IAEA (International Atomic Energy Agency) at www.iaea.org/water. This database provided both the $\delta^{18}O$ values of meteoric water at the sites and local climatic characteristics for our comparative considerations. For the other sampling sites, climatic data were taken from www.klimadiagramme.de. The *t*-tests as well as calculation of the Spearman's rank coefficients (r_s) and *p*-values were performed using SAS (9.2) (Dufner et al., 2004).

4. Results and discussion

4.1. Carbonate content of Lithospermeae fruits

The mean carbonate content in the fruits (Table 3) varied between 11 and 63% with an average of 49% in modern fruits. Fossil nutlets contained appreciably more carbonate: from 75 to 97% averaging 81%. This difference is most probably due to the fact that modern nutlets contain organic structural tissues (cell walls etc.), whereas in fossil ones organic matter is almost completely lost (Pustovoytov and Riehl, 2006). The source of variation in modern nutlets' carbonate content in Lithospermeae fruits is less clear. It is likely that one of them is organic matter, which can account for the greater spectrum in carbonate concentration in modern fruits. It is important to note that the samples from Kirchentellinsfurt with the lowest carbonate amounts, had also the hardest and thickest pericarps. Another source of variation in carbonate content both in modern and fossil samples could be silica, which is the second most important mineral component of Lithospermeae nutlets (Hilger et al., 1993).

4.2. General features of stable isotope composition of Lithospermeae fruit carbonate

All $\delta^{18}O$ and $\delta^{13}C$ values measured on biogenic carbonate of pericarps of Lithospermeae is presented in Fig. 6. $\delta^{18}O$ values showed ranges between −9 and 5‰, with most data gathered into two groups

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Table 2
Origin of samples of biogenic carbonate of *Lithospermum*/*Buglossoides* fruits with selected site characteristics.

Site[a]	Geographic coordinates	Mean annual/ June temperature (°C)	Mean annual/ June precipitation (mm)	Mean annual/June $\delta^{18}O$ of local precipitation (‰)	Age	Number of fruit pericarps studied	Species	Source of samples
Berlin, Germany	52°32′N 13°24′E	9.7/16.9	580/68	−7.92/−7.27	Modern	3	*Lithospermum purpurocaerulea* L. (*Buglossoides purpurocaeruleum* (L.) I.M. Johnson)	Field sampling
Kirchentellinsfurt, Germany (Stuttgart–Bad–Cannstatt)	48°32′N 9°09′E	9.8/16.7	646/87	−7.95/−6.30	Modern	3	*L. purpurocaerulea* L. (*Buglossoides purpurocaeruleum* (L.) I.M. Johnson)	Field sampling
Trieste, Italy	45°39′N 13°45′E	13.9/20.7	964/102	−6.99/−5.68	Modern	4	*L. officinale* L.	Botanical garden of the University of Berlin, seed collection
Athens, Greece	37°58′N 23°43′E	17.9/24.6	358/13	−5.75/−3.15	Modern	1	*L. tenuiflorum* L. (*Buglossoides teniuflora* (L.f.) I.M. Johnson)	Botanical garden of the University of Tubingen, herbarium
Ankara, Turkey	39°57′N 32°53′E	11.9/19.9	404/34	−7.99/−4.92	Modern	2	*L. arvense* L. (*Buglossoides arvensis* (L.) I.M. Johnson)	Herbarium of the University of Ankara
Göttingen, Germany	51°32′N 9°56′E	9.0/15.5	628/74	No data	Modern	4	*L. arvense* L. (*Buglossoides arvensis* (L.) I.M. Johnson)	Botanical garden of the University of Göttingen, seed collection
Almaty, Kazakhstan	43°17′N 76°56′E	9.1/20.5	645/57	No data	Modern	3	*L. officinale* L.	Botanical garden of the University of Berlin, seed collection
Tbilisi, Georgia	41°43′N 44°48′E	13.0/21.2	492/71	No data	Modern	1	*L. tenuiflorum* L. (*Buglossoides teniuflora* (L.f.) I.M. Johnson)	Herbarium of the University of Tubingen
Troy, Turkey (Çanakkale)	39°58′N 26°14′E	14.9/22.0	634/21	No data	Troy IV, about 2200–1900 BC	6	*L. arvense* L. (*Buglossoides arvensis* (L.f.) I.M. Johnson)	Cultural layers
Kumtepe, Turkey (Çanakkale)	39°58′N 26°11′E	14.9/22.0	634/21	No data	Kumtepe B, about 3200–3000 BC	3	*L. arvense* L. (*Buglossoides arvensis* (L.f.) I.M. Johnson)	Cultural layers
Hirbet ez-Zeraqon, Jordan (Irbit)	32°36′N 35°56′E	17.6/23.5	475/1	No data	Early Bronze Age II–III, about 3000–2200 BC	18	*L. tenuiflorum* L. (*Buglossoides teniuflora* (L.f.) I.M. Johnson)	Cultural layers

[a] If it differs from the name of site, the name of meteorological station is given in brackets.

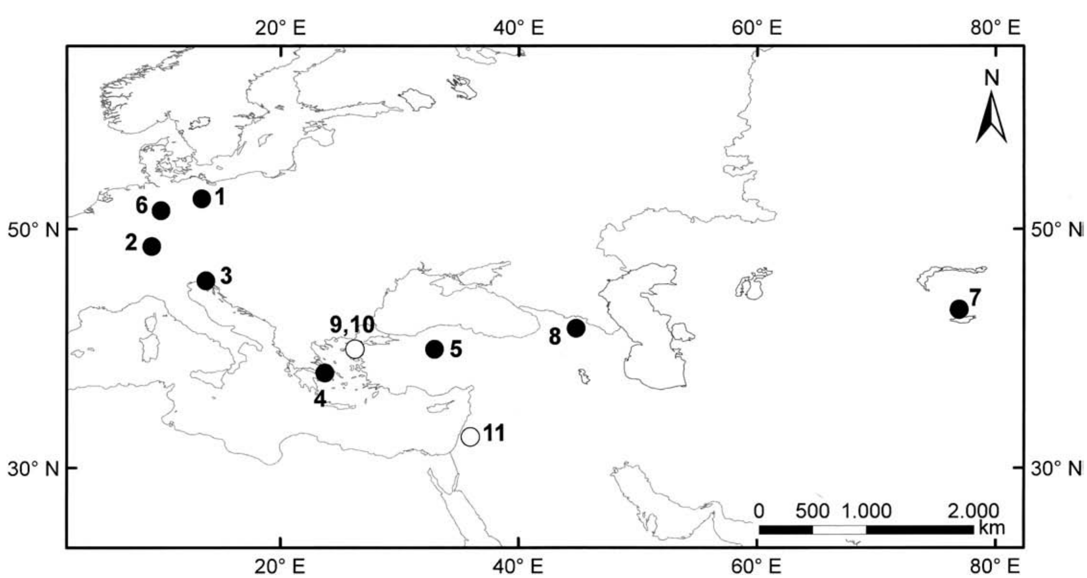

Fig. 3. Map of the locations of sampling sites. Modern samples (closed circles): 1 — Berlin, 2 — Kirchentellinsfurt, 3 — Trieste, 4 — Athens, 5 — Ankara, 6 — Göttingen, 7 — Almaty, 8 — Tbilisi; ancient samples (open circles): 9 — Kumtepe, 10 — Troy, 11 — Hirbet ez-Zeraqon.

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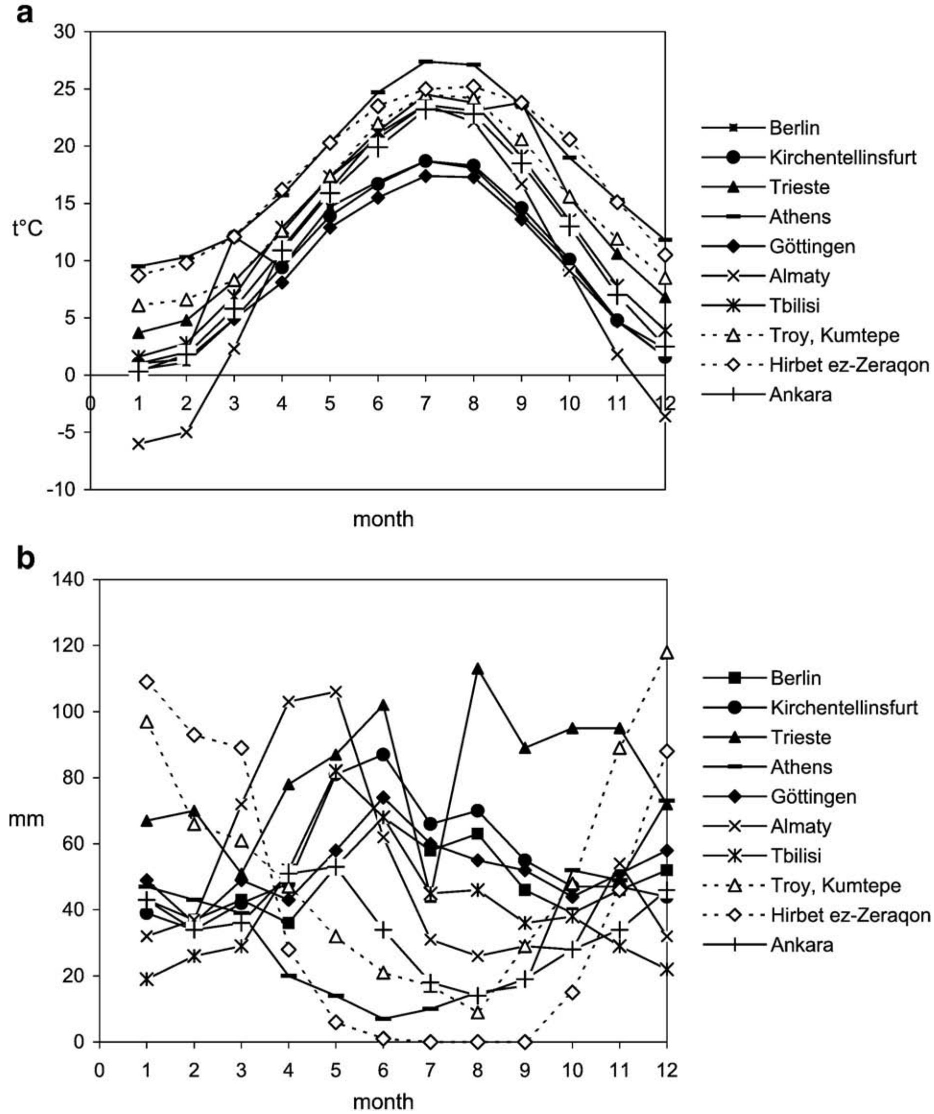

Fig. 4. Mean monthly air temperatures (a) and precipitation amounts (b) at sampling sites.

at approximately -6 ± 2‰ and 2 ± 2‰. The $\delta^{13}C$ values were scattered in a range from −35 to −7‰ with a somewhat higher concentration of around −10‰. The whole data set in the $\delta^{18}O$–$\delta^{13}C$ diagram can be divided into two clusters. The distinct cluster with highest ^{18}O- and ^{13}C-concentrations came into being most probably for the following reasons. (1) Hirbet ez-Zeraqon is the site with maximum amount of pericarps analysed. (2) This area today is distinctly the driest and one of the warmest among all the sites in this

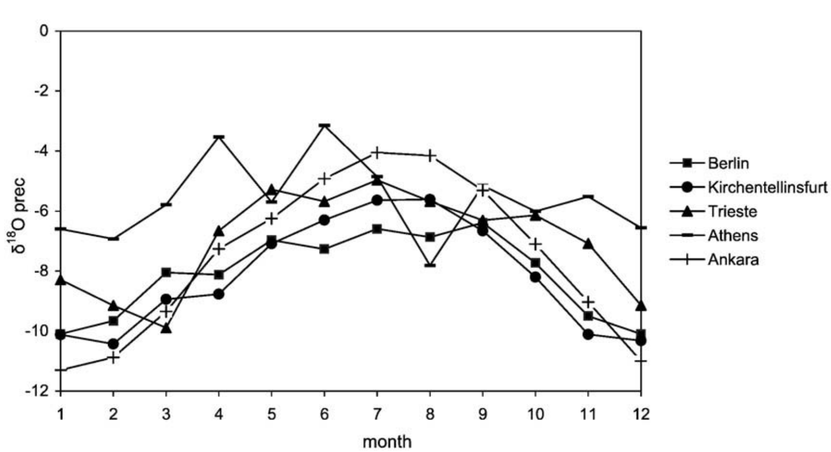

Fig. 5. Mean weighted monthly $\delta^{18}O$ values of precipitation at sampling sites of modern samples of Lithospermeae fruits.

Table 3
Summary statistics for $\delta^{18}O$ of fruit carbonate by site.

Site	Number of fruits analysed	$CaCO_3$ content (mean) (%)	$\delta^{18}O$					
			Mean	Median	Minimum	Maximum	Standard deviation	Variance
Berlin	3	43	−6.22	−6.20	−6.40	−6.05	0.18	0.03
Kirchentellinsfurt	3	11	−6.52	−6.47	−6.68	−6.41	0.14	0.02
Göttingen	4	59	−6.06	−5.99	−6.84	−5.42	0.61	0.37
Trieste	4	63	−6.33	−6.32	−7.10	−5.59	0.62	0.38
Athens	1	62	−3.08	–	–	–	–	–
Ankara	2	60	−1.45	−1.45	−1.53	−1.37	0.11	0.01
Almaty	3	57	−5.07	−5.12	−5.14	−4.94	0.11	0.01
Tbilisi	1	50	−4.78	–	–	–	–	–
Kumtepe	3	97	−5.12	−4.92	−5.99	−4.47	0.78	0.61
Troy	6	75	−5.33	−5.22	−8.61	−1.40	2.40	5.77
Hirbet ez-Zeraqon	19	80	1.74	1.8	0.12	4.55	1.28	1.64
Modern total	21	49	−5.42	−6.05	−7.10	−1.37	1.59	2.54
Ancient total	28	81	−0.51	0.60	−8.61	4.55	3.65	13.30
Total	49	68	−2.61	−4.71	−8.61	4.55	3.82	14.56

study. Taking into account its geographic position, it appears plausible that it might have been drier and warmer than the other sites also during the Mid-Holocene (see also below).

Another cluster has most of its $\delta^{18}O$ values of around −6‰ extends along the $\delta^{13}C$ axis roughly from −35 to −15‰. Generally, the $\delta^{13}C$ values are more positive for drier and warmer sites within the cluster. The reasons for that are unknown but it may be reasonably explained by the influence of water stress on the photosynthetic carbon isotope fractionation (Williams and Ehleringer, 1996; Ferrio et al., 2003). The very low ^{13}C concentrations in the biogenic carbonate of the mid-European samples is conspicuous and should be addressed in future research.

It should be emphasized that the $\delta^{18}O$ and $\delta^{13}C$ values were obtained for different Lithospermeae species, because no uniform carpological material for different geographical areas was available in botanical gardens and seed collections. The variation in isotopic composition of biogenic carbonate may involve some genetically specific biochemical properties of the plants. However, radiometric evidence strongly suggests that diverse species use a common mechanism of $CaCO_3$ synthesis in pericarp tissues (Pustovoytov and Riehl, 2006). Furthermore, we find more stable isotopic similarity between fruit carbonate in different species growing under similar climatic conditions than between fruit carbonate of the same species growing under different climatic conditions. As it can be seen from Fig. 6 and Table 4, *L. officinale* from Trieste is more similar in $\delta^{18}O$ to *L. arvense* and *L. purpurocaerulea* from German sites ($|t|=0.30$ to 0.62, $p=0.56$ to 0.78) than to *L. officinale* from Almaty ($|t|=3.42$, $p=0.02$), or *L. arvense* from Göttingen is centred closer to *L. purpurocaerulea* from Berlin ($|t|=0.43$, $p=0.69$) and Kirchentellinsfurt ($|t|=1.27$, $p=0.26$) than to *L. arvense* from Ankara ($|t|=10.08$, $p=0.00$). Nevertheless, it would be vital to explore the relation of oxygen and carbon isotopes in biogenic carbonate to climate within individual species, which should be a target for forthcoming research.

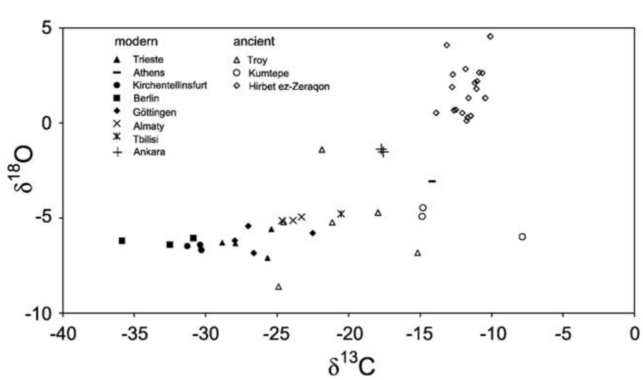

Fig. 6. $\delta^{18}O$ (‰) vs. $\delta^{13}C$ (‰) of biogenic carbonate in modern and fossil fruits of Lithospermeae.

4.3. $\delta^{18}O$ values of modern fruit carbonate vs. site characteristics

In the modern Lithospermeae fruits, the $\delta^{18}O$ values of biogenic carbonate ranged from ca. −8 to −3‰ (Fig. 6, Table 3). Within a single series, the value ranges were as high as 1.5‰ (samples from Trieste and Göttingen), a feature that may be explained in two ways. First, since every individual fruit on the same plant has its own ripening time, the spread of data may have been caused by fluctuations in isotopic composition of meteoric water, temperature or possibly other factors within one vegetative period. It can also be due to differences in $\delta^{18}O$ values of meteoric water or temperatures over a period of several years, if new material has been added to the already existing in a seed collection. Alternatively, this variation may reflect some minor local differences at the sites of plant growth within a botanical garden.

We compared the $\delta^{18}O$ values in fruit carbonate with the $\delta^{18}O$ values of local meteoric water, air temperature and precipitation for every month and a year (Table 5, Fig. 7). The climatic parameters (Fig. 7b and c) and to a lesser extent the $\delta^{18}O$ of precipitation at sites (Fig. 7a) displayed seasonality in their relationship with the $\delta^{18}O$ values of pericarp carbonate. In the course of a year, the correspondence between oxygen isotope composition of fruit carbonate and temperature as well as the amount of precipitation becomes significant (p-value$<\alpha=0.05$) in summer. The correlation is especially clear for the amount of precipitation, where the p-values are negligibly low in June through September, with R^2 and r_S reaching 0.6 and −0.7 respectively. Furthermore, precipitation amount also appears to be the only characteristic, whose mean annual values show correlation to $\delta^{18}O$ of pericarp carbonate. For temperature, the general seasonal pattern was similar, however there was a pronounced maximum of the degree of correlation falling on June (R^2 and r_S around 0.4 and 0.6 respectively with a p-value of 0.01). These dependences can be best explained by the fact that the fruit ripening generally takes place in summer months, although the exact time of formation of biogenic carbonate may vary from site to site.

The relationships between the $\delta^{18}O$ values of fruit carbonate and June oxygen isotopic values of atmospheric water, air temperatures and precipitation amounts are given in Fig. 8. For this month, isotopic fractionation results in the following $\delta^{18}O$ differences between fruit carbonate (vs. PDB) and precipitation water (vs. SMOW): −0.65‰ (Trieste), −0.22‰ (Kirchentellinsfurt), +0.07‰ (Athens), +0.99‰

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Table 4
T-tests for δ^{18}O values of pericarp carbonate from the study sites (numerator: |*t*|, denominator: *p*-value).[a]

	Hirbet ez-Zeraqon	Troy	Kumtepe	Tbilisi	Almaty	Göttingen	Ankara	Athens	Trieste	Kirchentellinsfurt
Berlin	10.55/0.00	0.62/0.56	2.36/0.08	14.22/0.00	9.62/0.00	0.43/0.69	33.41/0.00	31.02/0.00	0.30/0.78	2.35/0.08
Kirchentellinsfurt	10.96/0.00	0.83/0.43	3.05/0.04	21.29/0.00	14.03/0.00	1.27/0.26	42.13/0.00	42.04/0.00	0.52/0.63	
Trieste	12.16/0.00	0.80/0.47	2.29/0.07	5.03/0.02	3.42/0.02	0.62/0.56	10.49/0.00	10.53/0.00		
Athens	16.43/0.00	2.30/0.07	4.52/0.05		31.29/0.00	9.82/0.00	21.09/0.03			
Ankara	3.45/0.00	2.17/0.07	6.26/0.01	43.05/0.01	36.09/0.00	10.08/0.00				
Göttingen	11.76/0.00	0.59/0.57	1.80/0.13	4.22/0.02	2.73/0.04					
Almaty	9.03/0.00	0.18/0.86	0.12/0.91	4.55/0.05						
Tbilisi	22.22/0.00	0.56/0.60	0.76/0.53							
Kumtepe	8.92/0.00	0.14/0.89								
Troy	9.49/0.00									

[a] For Athens and Tbilisi; where only one value result was available, the one sample *t*-test was applied. For all other sites, the independent samples t-test was carried out.

(Berlin) and +3.47‰ (Ankara). The δ^{18}O values of fruit carbonate show correlation trends with δ^{18}O of atmospheric water (direct) (Fig. 8a), temperature (direct) (Fig. 8b) and precipitation amount (reverse) (Fig. 8c). The dependence of pericarp carbonate δ^{18}O on rainfall is the strongest, followed by that on the ^{18}O content of precipitation and on temperature. It should be noted that although the R^2 is relatively low for June, it is accompanied by the annual maximum of the Spearman's coefficient and the lowest *p*-value. These relationships show that plant biogenic carbonate in Lithospermeae is sensitive to climatic parameters in a very similar fashion as other continental oxygen isotopic archives.

The question arises as to why the degree of correlation between δ^{18}O values of fruit carbonate and δ^{18}O of atmospheric water is less distinct when compared to precipitation amounts or air temperature. Especially enigmatic appear the maximum of R^2 and r_s and the minimum of *p*-value in September. The ^{18}O-enrichment of meteoric water is determined by multiple factors such as temperature, amount of precipitation, source of precipitation and altitude (Rozanski et al., 1993; Gat, 1996; Bowen and Wilkinson, 2002; Darling et al., 2006). Specifically, in the present-day Mediterranean the sum effect of these factors results in a gradual decrease of δ^{18}O of precipitation eastward and northward from approximately −4 to −10‰ (Roberts et al., 2008). The factors governing this pattern are still in question. Precipitation amounts in the Mediterranean are temperature-dependent and it is difficult to say which factor is leading in formation of $^{18}O/^{16}O$ ratios of atmospheric water (Bar-Matthews et al., 1997; Jones and Roberts, 2008). As mentioned above, the seasonality of δ^{18}O values in atmospheric water at sites shows a similar character as the air temperatures (Fig. 5).

At least two possible reasons for the relatively low correlation degrees of oxygen isotope ratios in fruit carbonate and in meteoric water come into consideration. One could be the more limited data set for δ^{18}O of precipitation at sites (5 stations vs. 8 for air temperatures and rainfall amounts). Another possible explanation is that in summer, especially at the Mediterranean sites, the biological fractionation of oxygen isotopes may be complicated by non-equilibrium evaporative ^{18}O-enrichment. Evaporation would strengthen the climatic effect of dry and hot summer on the oxygen isotopic fingerprint in biogenic carbonate but at the same time would introduce more complexity into the seasonality of isotopic fractionation (see also below).

Considering the relation of fruit $CaCO_3$ to climate, it should be remembered that we were unaware of the real dynamics of fruit

Table 5
Correlation between δ^{18}O of pericarp carbonate ($\delta^{18}O_{fr}$) and mean monthly and annual site characteristics: δ^{18}O of meteoric water ($\delta^{18}O_{prec}$), air temperature (*t*) and precipitation (prec) (R^2 — Pearson product–moment coefficient, r_s — Spearman's rank correlation coefficient).

Month	$\delta^{18}O_{fr}$–$\delta^{18}O_{prec}$			$\delta^{18}O_{fr}$–*t*			$\delta^{18}O_{fr}$–prec		
	R^2	r_S	*p*-value	R^2	r_S	*p*-value	R^2	r_S	*p*-value
1	0.00	−0.08	0.79	0.00	−0.34	0.13	0.07	−0.31	0.17
2	0.01	−0.08	0.79	0.00	−0.17	0.46	0.08	0.13	0.56
3	0.04	0.10	0.75	0.02	−0.32	0.16	0.05	−0.16	0.48
4	0.16	0.41	0.16	0.12	0.35	0.11	0.00	0.17	0.47
5	0.01	0.30	0.32	0.14	0.33	0.15	0.11	−0.13	0.58
6	0.44	0.49	0.09	0.22	0.49	0.02	0.65	−0.75	0.00
7	0.46	0.51	0.08	0.26	0.41	0.07	0.66	−0.70	0.01
8	0.16	−0.01	0.98	0.28	0.33	0.14	0.50	−0.80	0.00
9	0.86	0.71	0.01	0.05	0.22	0.35	0.47	−0.77	0.00
10	0.04	0.41	0.16	0.09	−0.22	−0.05	0.17	−0.60	0.00
11	0.02	0.41	0.16	0.03	−0.22	−0.05	0.19	−0.26	0.26
12	0.01	−0.08	0.79	0.00	−0.05	0.08	0.04	−0.24	0.29
Year	0.00	−0.08	0.79	0.09	0.05	0.83	0.41	−0.59	0.00

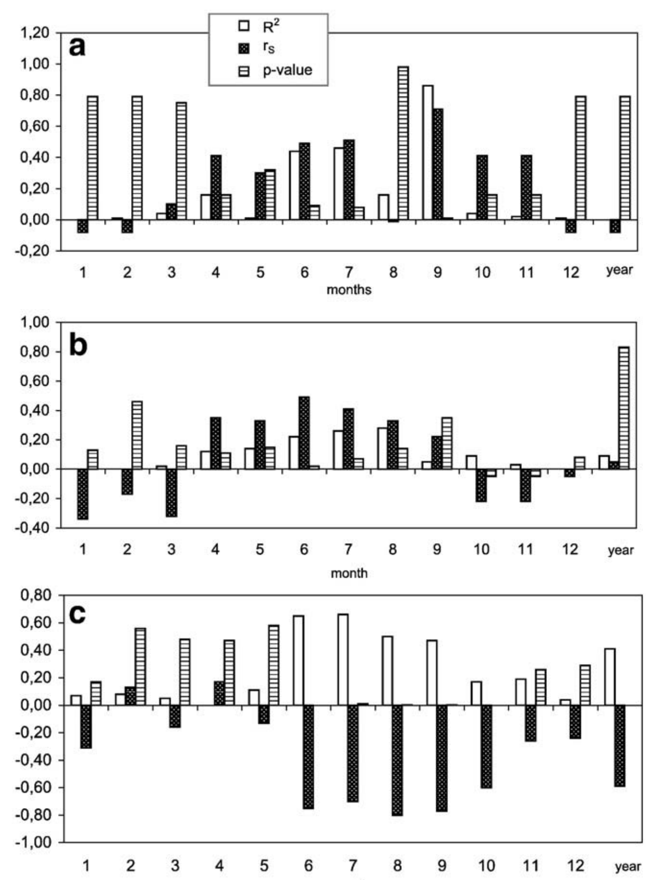

Fig. 7. Correlation (R^2, r_s and *p*-value) between δ^{18}O of pericarp carbonate and mean monthly and annual δ^{18}O of meteoric water (a), δ^{18}O of pericarp carbonate and mean monthly and annual air temperatures (b), δ^{18}O of pericarp carbonate and mean monthly and annual precipitation amounts (c) at study sites; see Table 5 for figure data and abbreviations.

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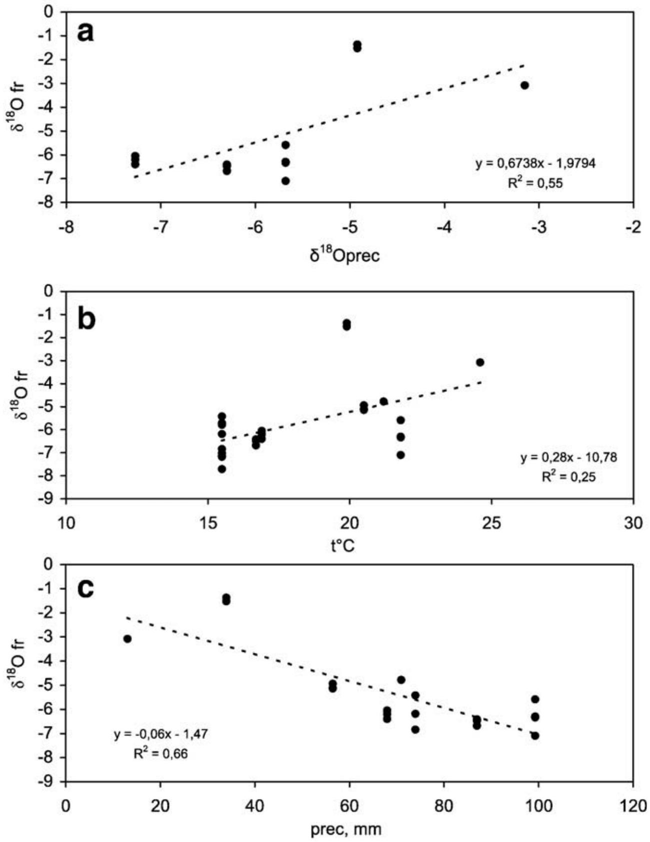

Fig. 8. Relationship between the $\delta^{18}O$ (‰) values of modern fruit biogenic carbonate ($\delta^{18}O_{fr}$) and site characteristics: (a) — $\delta^{18}O$ (‰) of local precipitation ($\delta^{18}O_{prec}$), (b) — mean local air temperatures of June in degrees centigrade (t, °C) and (c) — mean local June precipitation amount in mm (prec, mm).

ripening and seasonality at sites. The degree of correlation between $\delta^{18}O$ of plant biogenic carbonate and climatic characteristics may be higher than the one based on parameters for June. To exemplify this, we compared temperatures calculated on the basis of mean $\delta^{18}O$ of fruit biogenic carbonate and monthly $\delta^{18}O$ values of precipitation with measured temperatures for April through July on the basis of the equilibrium precipitation equation (Leng and Marshall, 2004) (Table 6). In contrast to the rest of sample sets, the samples from Ankara displayed an obvious inconsistency between the calculated and measured temperature values. We hypothesise that this is due to evaporative effects, which can either affect the oxygen isotopic composition of already precipitated meteoric water or cause non-equilibrium precipitation of carbonate in fruits. Oxygen isotopic fractionation in the other samples can be well described by the equilibrium precipitation equation, however the sites differ regarding the months when the calculated temperatures approximate the measured ones most closely. The samples from Kirchentellinsfurt provided the best fit between calculation and measurement, which fall on June and May. A reasonably good consistency is seen also in the temperature data for Trieste (the whole period considered) and Berlin (April and May), whereas the latter site provided for some reason less agreement between calculated and measured temperatures in summer months. The sample from Athens differed from the other samples displaying a perfect data fit for April but an obvious discrepancy for June and July. As a working hypothesis, we explain this fact by a different seasonality pattern at the collection sites. It is very likely that the fruit ripening and formation of biogenic calcite in pericarp in Athens, a typical Mediterranean site, starts relatively early in a year in order to fulfil the vegetative cycle before the onset of summer dryness. By contrast, there is no water stress during the warm season at the two German sites and the north-Italian one, which all have a much more uniform distribution of precipitation in the course of a year with a maximum in summer.

Table 6
Comparison of temperatures °C calculated on the basis of $\delta^{18}O$ of biogenic carbonate (t(c)) with measured ones (t(m)) for five sites.

Site	Month							
	April		May		June		July	
	t(c)	t(m)	t(c)	t(m)	t(c)	t(m)	t(c)	t(m)
Berlin, Germany	5.4	9.5	10.4	14.7	9.1	16.9	12.1	18.7
Kirchentellinsfurt, Germany	3.9	9.4	11.2	13.9	14.8	16.7	17.9	18.7
Trieste, Italy	12.3	12.5	18.7	17.3	16.8	20.7	20.2	23.6
Athens, Greece	11.8	15.7	2.3	20.3	13.5	24.7	5.9	27.4
Ankara, Turkey	−10.1	10.4	−6.3	15.9	−1.1	19.9	2.4	23.2

4.4. $\delta^{18}O$ values of ancient fruit carbonate

As stated above, ancient nutlets of Lithospermeae are common at archaeological sites of the Mediterranean. We examined isotopic signatures of fossil fruit carbonate from the cultural layers of three sites differing significantly in geographical position: two of them were in north-western Turkey and one in Jordan (Table 2, Fig. 3). Although we cannot rule out the possibility of diagenetic alteration of carbonate in sediment, radiocarbon dates suggest that biogenic carbonate of pericarps can remain in cultural layers for millennia without appreciable re-crystallization (Pustovoytov et al., 2004; Pustovoytov and Riehl, 2006). In particular, fruit carbonate from Kumtepe and Troy provided ^{14}C dates 4155 ± 60 bp (4840–4520 cal BP, 2σ) and 3600 ± 45 bp (4090–3720 cal BP, 2σ) respectively, which perfectly fits the period chronology of sites (Pustovoytov and Riehl, 2006). For Hirbet ez-Zeraqon, seven radiocarbon dates were available, five of which were between 4135 ± 45 and 3790 ± 45 bp (4830–4520 to 4360–3980 cal BP, 2σ) and corresponded well with the estimated age of archaeological contexts but two were of somewhat younger age interpreted as either a result of admixture of younger fruits after the deposition of cultural layers or diagenetic alteration of carbonate (Pustovoytov et al., 2004). However, no microscopic evidence for dissolution of fruit biogenic carbonate could be found (Pustovoytov et al., 2004; Pustovoytov and Riehl, 2006). In the following section, we also address the problem of preservation of carbonate material in cultural layers of Hirbet ez-Zeraqon by considering the vertical distribution of its stable isotopic and ^{14}C values, showing no clear signs of carbonate re-crystallization.

The samples from Troy and Kumtepe show very similar average $\delta^{18}O$ values of around −5‰ (−5.33‰ and −5.12‰ respectively), whereas the samples from Hirbet ez-Zeraqon have a significantly higher mean value, 1.74‰ (Table 3, Fig. 6). This difference is well understandable in terms of the isotopic geography of modern precipitation in the eastern Mediterranean. At a regional scale, the position of Troy is identical to Kumtepe (less than 10 km distance), whereas Hirbet ez-Zeraqon is situated almost 1500 km to the southeast at a much lower latitude. Oxygen isotopic data are not available for areas around the three archaeological sites, but the generalized map of $\delta^{18}O$ of modern Mediterranean precipitation (Roberts et al., 2008) indicates that Troy and Kumtepe are in a zone with mean weighted $\delta^{18}O$ of precipitation ranging from −6 to −8‰, whereas Hirbet ez-Zeraqon is a −4 to −6‰ zone. Although isotopic ratios of local meteoric waters at the sites most probably have not been stable in time, it seems entirely possible that the territories of today's Jordan and north-western Turkey received atmospheric precipitation with distinctly different oxygen isotopic signatures in the Mid-Holocene. A comparison of Troy and Kumtepe shows a much

Table 7
Radiocarbon ages of fruit biogenic carbonate from Hirbet ez-Zeraqon.

Sample	Area, depth of the surface (cm)	No. of fruits dated	^{14}C age (yrs BP (uncal.))	^{14}C age (yrs BC (cal., 1σ))[a]	^{14}C age (yrs BC (cal., 2σ))[a]	Lab. no.
HZ91-723-724	Upper city, building 3, 120	4	2845 ± 120	1200–890 870–850	1400–800	Ua-21369
HZ91-741	Upper city, building 3, 124	4	4745 ± 100	3640–3490 3450–3370	3800–3300 3250–3100	Ua-21368
HZ91-233	Lower city, gateway, 241	6	3100 ± 80	1460–1260	1530–1120	Ua-21367

[a] Calibration with OxCal (Ramsey, 2001).

greater scattering of $\delta^{18}O$ values in samples from Troy (Table 3, Fig. 6). This might be a result of different catchment areas around these sites. Kumtepe represented a homestead on a small peninsula with subsistence based on resources from a very restricted area, whereas the resource exploitation in Troy involved relatively large areas with a broad spectrum of environments from lowlands to mountains (Riehl, 1999; Riehl and Marinova, 2008).

In this study, we were dependent on a relatively small set of archaeobotanical samples, which did not allow us to consider the evolution of $\delta^{18}O$ of plant biogenic carbonate with time at sites. Thus, we were unable to compare it with other paleoclimate archives in the eastern Mediterranean, especially existing oxygen isotope records. Another important aspect of investigation of ancient biogenic carbonate species would be a comparison with their modern counterparts from the same geographic locations. However, up to now we could not find appropriate modern botanical material in herbariums or seed collections and it should be one of the priorities for future research.

4.5. Vertical profile distribution of stable isotope composition and ^{14}C ages of fruit carbonate

The isotopic signatures in carbonates can be used as paleoclimate proxies only if the geochemical system remained continuously closed. Theoretically, carbonate materials in sediments can be digenetically altered. It has been demonstrated that in terrestrial ecosystems the vertical distribution of $CaCO_3$ isotopic characteristics ($\delta^{18}O$, $\delta^{13}C$, and ^{14}C) can serve as a test of geochemical integrity of carbonate in a soil profile (Pendall et al., 1994). The theory suggests that in the course of soil formation, the process of carbonate re-crystallization progresses vertically into sediment, gradually modifying the oxygen and carbon isotopic ratios and introducing new portions of ^{14}C into carbonate (Pendall et al., 1994).

We used this approach to assess the possibility of diagenetic modification of biogenic carbonate in fossil pericarps of Lithospermeae. We analysed the relationship between the isotope characteristics of fruit carbonate, namely, ^{18}O, ^{13}C and ^{14}C content and depth below the soil surface at Hirbet ez-Zeraqon. This site was chosen, because it provided especially high numbers of ancient pericarps. In addition to stable isotope data, we extended the ^{14}C data set of seven ages of fruit biogenic carbonate reported earlier (Pustovoytov et al., 2004; Pustovoytov and Riehl, 2006) by three additional dates (Table 7). No systematic changes in $\delta^{18}O$ or $\delta^{13}C$ with depth have been observed (Fig. 9). Similarly, the ^{14}C ages did not show any decrease towards the soil surface (Fig. 10). The ^{14}C dates display, in fact, even a slight increasing trend with decreasing depth. The vertical distribution of the isotopic characteristics in the cultural layer of the site suggests that no appreciable diagenesis of pericarp carbonate took place. The variation in ^{14}C ages at ca. 120 cm depth, is in our view better to explain by later additions of seeds rather than processes of carbonate re-crystallization. Generally, the vertical functions of $\delta^{18}O$, $\delta^{13}C$ and ^{14}C ages imply that biogenic carbonate in Lithospermeae fruits can retain isotopic signals from its contemporary environment over millennia.

There are two questions about the fossil of Lithospermeae fruits that remain open though. One is how to interpret the fact that some of the dates are younger than expected on the basis of the age of cultural layer. It can be explained by intrusion of younger material into depth, possibly through the activity of soil mesofauna. Secondly, it still appears puzzling, why the preservation of carbonate can be so good in cultural layers exposed to weathering for thousands of years. An

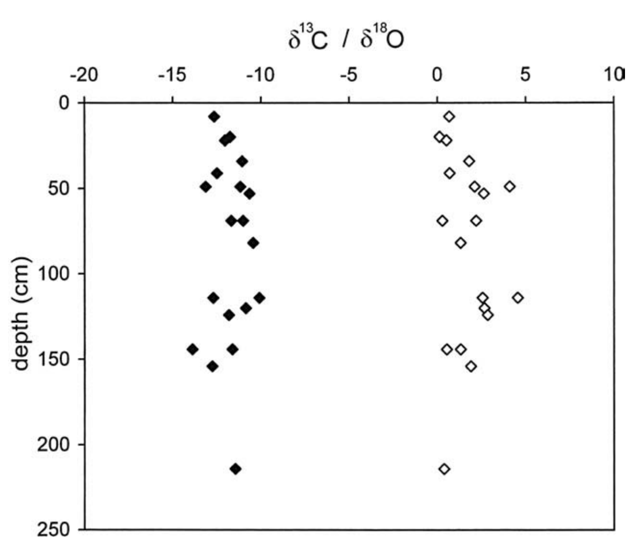

Fig. 9. The vertical distribution of $\delta^{18}O$ (‰) (open diamonds) and $\delta^{13}C$ (‰) (closed diamonds) of ancient fruit carbonate in cultural layers of Hirbet ez-Zeraqon.

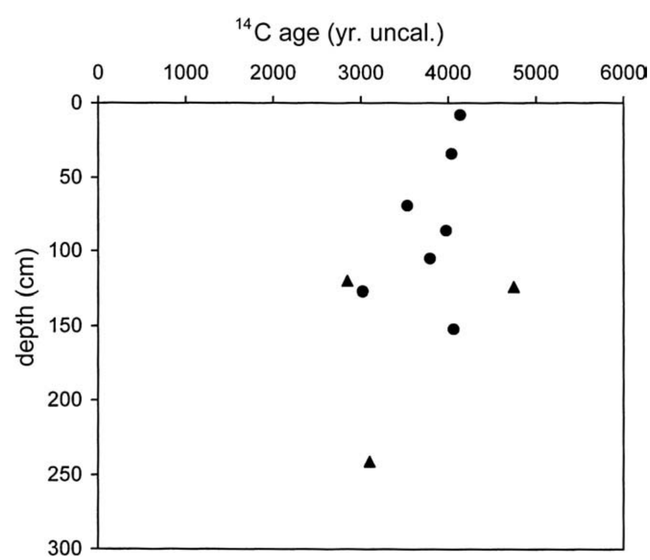

Fig. 10. The vertical distribution of the mid-points of uncalibrated ^{14}C ages of fruit biogenic carbonate in cultural layers of Hirbet ez-Zeraqon; triangles — radiocarbon dates from this study, circles — ^{14}C dates from Pustovoytov et al., 2004.

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answer to this question will require considerably more empirical data and comparative investigation from a large spectrum of sites.

5. Conclusions

The biogenic carbonate in pericarps of fruits of the tribe Lithospermeae (Boraginaceae) may be useful in paleoclimate research, at least in the Mediterranean region. The $\delta^{18}O$ values of modern fruit carbonate from a number of Eurasian collection sites show correlation to summer mean monthly temperatures of vegetative period (proportional) and the precipitation amount (reversely proportional). Carbonate of Mid-Holocene pericarps from cultural layers in north-western Turkey and Jordan provided distinctly different $\delta^{18}O$ values, demonstrating its potential implication for fossil samples. The vertical distribution of $\delta^{18}O$, $\delta^{13}C$, and ^{14}C of ancient pericarps does not indicate measurable recrystallization of biogenic carbonate. Although the set of modern and ancient fruits of Lithospermeae in this work was limited, the findings provide promising evidence that the fruit carbonate can potentially serve as an adequate indicator of climatic changes in the past.

Some problems of isotopic research on plant biogenic carbonate still remain to be solved. Two central of them are: (1) the isotopic variability of modern fruit carbonate within a single Lithospermeae species under different climatic conditions and (2) the stable isotopic composition of modern plant biogenic carbonate from the areas around archaeological sites where ancient carbonate pericarps of Lithospermeae have been found. Furthermore, investigation of samples from an array of cultural layers with a wide geographical and chronological range represents a desideratum.

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