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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).

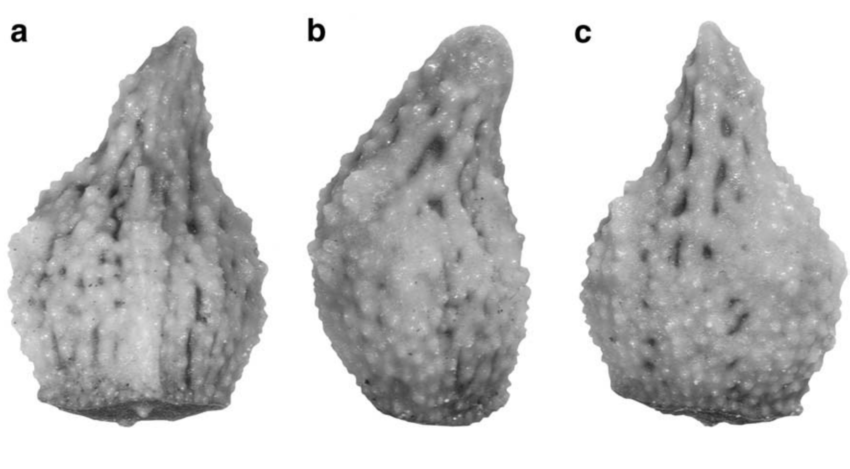

Fig. 1. Modern fruits of *Lithospermum arvense* L. (*Buglossoides arvensis* (L.) I.M. Johnst.) from the seed collection of the University of Göttingen. (a) — dorsal view, (b) — lateral view, (c) — ventral view. Scale bar: 1 mm.