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Quaternary Research 65 (2006) 508–518
QUATERNARY RESEARCH
www.elsevier.com/locate/yqres

Suitability of biogenic carbonate of *Lithospermum* fruits for ^{14}C dating

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Received 9 November 2004

Abstract

Lithospermum (Boraginaceae) belongs to a small group of plant taxa that accumulate biogenic carbonate in their fruits. In this genus, carbonate incrustations form in the cells of the epidermis and sclerenchyma of the pericarp. Fossil *Lithospermum* fruits (nutlets) with well-preserved calcified tissues commonly occur in Quaternary sediments and cultural layers. We tested the suitability of biogenic carbonate of *Lithospermum* fruits for radiocarbon dating using a total of 15 AMS measurement results from four modern and 11 fossil samples. The ^{14}C data from modern samples suggest that *Lithospermum* utilises only atmospheric carbon to synthesise calcite in the nutlets. In general, the ages determined through ^{14}C dating of fossil fruitscorresponded well with the absolute-age intervals for archaeological sites over the last 5000 yr. Biogenic carbonate of *Lithospermum* fruits, like that of *Celtis*, represents a new source of chronological information for late Quaternary studies.

Keywords: Biogenic carbonate; *Lithospermum*; ^{14}C dating

Introduction

In arid climates, Quaternary sediments and soils are generally rich in calcium carbonate. It occurs in a variety of forms, such as primary lithogenic, pedogenic (nodules, concretions, coatings on clasts, etc.), and biogenic carbonate (mollusc shells, some plant seeds, etc.). Due to the abundance of carbonate and the general deficiency of organic carbon in deposits from arid regions, researchers have repeatedly attempted to discover whether different forms of $CaCO_3$ might be suitable for absolute age determination. Specifically, researchers have demonstrated that radiocarbon dating can be applied, with certain limitations, to carbonate of terrestrial mollusc shells (Evin et al., 1980; Goodfriend and Hood, 1983; Zhou et al., 1999; Pigati et al., 2004), to carbonate of egg shells (Haas and Haynes, 1980; Freundlich et al., 1989), to pedogenic carbonate (Chen and Polach, 1986; Amundson et al., 1994; Wang et al., 1996; Monger et al., 1998; Pustovoytov, 2002), to artificial lime mortars (Folk and Valastro, 1985), and to carbonate-rich endocarps (Wang et al., 1997). The latter study was carried out on modern and fossil fruits of the genus *Celtis*. Wang et al. (1997) concluded that biogenic carbonate in *Celtis* accurately records the ^{14}C content of the atmosphere and may be resistant to diagenetic alteration in the archaeological and geological record. An important advantage of ^{14}C dates on endocarp carbonate is that fruit formation occurs over a single growing season, which suggests that *Celtis* fruits are potentially suitable for high-resolution absolute dating (Wang et al., 1997).

Fossil *Celtis* fruits, though common in North America, are comparatively rare in Eurasia. However, other plant groups that accumulate calcium carbonate in their fruits, are well represented as fossils in the Old World and may function as proper candidates for ^{14}C dating. Carbonate-rich fruits of the genus *Lithospermum* (for some species the synonym *Buglossoides* is frequently used) are very common in late Pleistocene and Holocene deposits and cultural layers.

Testing whether radiocarbon dating can be applied to the carbonate of *Lithospermum* fruits is important for several reasons. Similar to *Celtis*, biogenic carbonate accumulates in fruits of *Lithospermum* within one vegetative period and thus may contain precise chronological information. Unlike the majority of plant macroremains (mostly carbonised) in late

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0033-5894/$ - see front matter © 2006 University of Washington. All rights reserved.
doi:10.1016/j.yqres.2006.02.011

Quaternary deposits of arid regions, fruits of *Lithospermum* can remain preserved in an uncharred state, i.e. without having fire as a pre-condition for fossilisation. In dry climates, fruit carbonate may remain unaltered through diagenetic-crystallisation after burial. In previous studies, we initially reported seven radiocarbon determinations on samples, which were problematic in their origins, from the carbonate in *Lithospermum* fruits from an early Bronze Age site (with the main occupation phase at 5050–4200 cal yr BP) in Jordan (Pustovoytov et al., 2004). We argued that radiocarbon determinations from samples of non-conjectural origin are necessary for determining the applicability of the ^{14}C method to nutlet biogenic carbonate. Here we present an extended set of ^{14}C dates on the carbonate fraction of *Lithospermum* fruits that includes such "reference" samples. The data suggest that biogenic carbonate from the fruits of *Lithospermum* represents suitable material for radiocarbon dating.

The genus *Lithospermum* and its presence in the fossil record

The genus *Lithospermum* from the Boraginaceae family includes 59 species that are annual or perennial herbs and subherbs with simple, alternate leaves and funnel- or silver-shaped flowers. They are distributed in different temperate regions of the world, with the exception of Australia (Hyam and Pankhurst, 1995). *Lithospermum* species inhabit mostly open grassy places, arable fields, scrubs and wood margins (Fig. 1). *L. arvense* L. (*Buglossoides arvensis* (L.) I.M. Johnson), *L. purpurocaeruleum* L. and *L. officinale* L. are the most common forms of the species from the genus found in Middle Europe. In the Mediterranean region, also *L. tenuiflorum* L. (*Buglossoides teniuflora* (L.f.) I.M. Johnson) is prevalent. Morphologically, fruits of *Lithospermum* are nutlets, ovoid-truncate in form, with a ridge on one side, a broad scar at the base and a mostly smooth and glossy surface (Martin and Barkley, 1973) (Figs. 1b and e). Calcium carbonate accumulates in the epidermal cells and in parts of the sclerenchyma[1] (Seibert, 1978).

As mentioned above, fossil *Lithospermum* fruits are widespread in some regions of particular palaeogeographical and archaeological interest. In the areas of the Mediterranean and the Near East, they are a typical component of the plant macroremains of Pleistocene cave deposits (Hansen, 2001) and are found in a wide spectrum of Holocene cultural layers and sediments (e.g., Riehl, 1999; Hillman et al., 2001; van Zeist, 2001; Savard et al., 2003). They have also been found in Tertiary (Gabel, 1987) and late Quaternary (Spencer, 2003) deposits of North America. Finds of *Lithospermum* fruits are interpreted as indicating semiarid (Spencer, 2003) or steppe (Hillman et al., 2001) environments, or as a product of past ruderal vegetation (van Zeist, 2001). In many archaeobotanical studies, however, *Lithospermum* fruits are considered as problematic plant remains. Since they are often uncharred, it is often difficult to determine whether they have been deposited as part of the sediment or introduced into the sediment later (for example, through soil fauna) (Miller, 1991; Melamed, 1996).

Materials and methods

All samples were obtained from seed collections and cultural layers of archaeological sites of known age. Particular attention was paid at minimising the possibility of admixture of *Lithospermum* fruits of unknown origin, i.e. through secondary intrusions into the sediment. In archaeobotanical studies, charred seeds at archaeological sites are assumed to be almost always deposited along with the cultural layer (Pearsall, 2000). If the fruits are not charred, the fact that they are artificially worked can serve as important proof for their authenticity as old nutlets. For example, it has been demonstrated that *Lithospermum* fruits were used in prehistory as pearls in necklaces (for this purpose the apex and hilum ends of the fruit were sanded off to produce two holes in the pericarp that turned the fruit into a pearl; Marinescu-Bilcu and Cârciumaru, 1992; Novikova et al., 2002). For this reason, we preferentially took charred or artificially worked examples from among the fossil nuts for the purposes of radiocarbon dating. The site of Hirbet ez-Zeraqon, for which we have 7 AMS measurements on biogenic carbonate, represents an exception as the carpological material from its cultural layer was especially rich in *Lithospermum* fruits.

The biogenic carbonate of the following nutlets listed below were dated by the radiocarbon method:

(1) Modern fruits, including that of *L. arvense* L. from the seed collection of the Botanical Garden of the University of Göttingen (sampled in 2001); *L. purpurocaeruleum* L., which we collected in 2003 in a broad-leaf forest in the vicinity of Kirchentellinsfurt, SW Germany (Figs. 1d–f); and *L. officinale* L., collected in the Botanical Garden of the University of Hohenheim in 2004. We also examined fruits of *L. tenuiflorum* L. that were collected in the early 19th century. According to the herbarium label, this *Lithospermum* exemplar was collected near Cagliary on Sardinia (Italy) in 1827 (the Herbarium of the University of Tübingen).

(2) The cultural layer of Troy (Turkey), phase IV–V, with an age of 2350–1760 BC (4300–3710 cal yr BP), provided a sample of *L. arvense* L. fruits, which displayed a black pigment through charcoal matter. The absolute chronology of Troy is based on abundant ceramic material and supported by more than 260 radiocarbon dates (Korfmann and Kromer, 1993; Kromer et al., 2003). Although the majority of radiocarbon measurements were performed on wood charcoal (including wiggle-matched dates on tree-rings), about twenty ^{14}C ages derived from seed and bone material were also determined.

(3) Two samples of *L. officinale* L. fruits from the Bronze Age burials of Kalmykia (Russia) from the time of the "catacomb culture" dated to 2600–2000 BC (4550–

[1] The fibrous or woody tissue in a plant that provides mechanical support for it (Allaby et al., 1998).