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Chemotaxonomy in some Mediterranean plants and implications for fossil biomarker records

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Abstract

The increasing utilization of *n*-alkanes as plant-derived paleo-environmental proxies calls for improved chemotaxonomic control of the modern flora in order to calibrate fossil sediment records to modern analogues. Several recent studies have investigated long-chain *n*-alkane concentrations and chain-length distributions in species from various vegetation biomes, but up to date, the Mediterranean flora is relatively unexplored in this respect. Here, we analyse the *n*-alkane concentrations and chain-length distributions in some of the most common species of the modern macchia and phrygana vegetation in south western Peloponnese, Greece. We show that the drought adapted phrygana herbs and shrubs, as well as some of the sclerophyll and gymnosperm macchia components, produce high concentrations of *n*-alkanes, on average more than double *n*-alkane production in local wetland reed vegetation. Furthermore, the chain-length distribution in the analysed plants is related to plant functionality, with longer chain lengths associated with higher drought adaptive capacities, probably as a response to long-term evolutionary processes in a moisture limited environment. Furthermore, species with relatively higher average chain lengths (ACL) showed more enriched carbon isotope composition in their tissues ($\delta^{13}C_{plant}$), suggesting a dual imprint from both physiological and biochemical drought adaptation. The findings have bearings on interpretation of fossil sedimentary biomarker records in the Mediterranean region, which is discussed in relation to a case study from Agios Floros fen, Messenian plain, Peloponnese. The 6000 year long *n*-alkane record from Agios Floros (ACL, $\delta^{13}C_{wax}$) is linked to the modern analogue and then evaluated through a comparison with other regional-wide as well as local climate and vegetation proxy-data. The high concentration of long chain *n*-alkanes in phrygana vegetation suggests a dominating imprint from this vegetation type in sedimentary archives from this ecotone.

Keywords: Biomarkers; *n*-alkanes; Leaf wax; Chemotaxonomy; Carbon isotope composition; ACL; Phrygana; Macchia; Greece; Mediterranean

1. INTRODUCTION

The isotope composition of organic biomarkers in sediment cores is increasingly used as a proxy for past climate and environmental change. The carbon and hydrogen

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isotopic composition in plants and their leaf wax derived *n*-alkanes, have proven to reflect parameters strongly related to climate factors, such as source water isotope composition (Sachse et al., 2012, and references therein) and mean annual precipitation (Diefendorf et al., 2010; Diefendorf and Freimuth, 2017). In Greece, paleo-environmental reconstructions using biomarkers have been performed on marine sediments (Triantaphyllou et al., 2009; Kouli et al., 2012; Grauel et al., 2013; Gogou et al., 2016), and occasionally on lacustrine sediments, applying an isotope approach (Schemmel et al., 2016). A complicating factor for the interpretation of fossil *n*-alkane records is the sometimes high variability in *n*-alkane distribution and isotope composition between, and even within, plant functional types (Diefendorf et al., 2011; Bush and McInerney, 2013; Eley et al., 2014). Although *n*-alkane isotope studies on sediment cores preferably should be paralleled and confined by paleo-vegetation studies using e.g. fossil pollen analysis (e.g. Feakins, 2013; Norström et al., 2014), the interpretation may also be strengthened by increased knowledge on chemotaxonomy of the most abundant plants producing and depositing *n*-alkanes at the studied site. The Mediterranean flora is unique in its species composition with high number of endemic plants, but so far, few studies with a paleo-environmental perspective have focused on lipid chemotaxonomy of the Mediterranean vegetation. Here, we have analysed the *n*-alkane distribution and concentration in some of the most abundant macchia and phrygana species in SW Peloponnese, Greece. We also discuss the implications of this new chemotaxonomic information on paleo-environmental studies using a biomarker approach in this specific ecotone. We exemplify this by presenting new fossil *n*-alkane abundance and carbon isotope data from a site located in Peloponnese, south-western (SW) Greece.

2. MEDITERRANEAN VEGETATION

The basic types of Mediterranean vegetation ecosystems represented in SW Greece are the macchia (*syn.* maquis), Aegean phrygana (*syn.* garrigue) and the Mediterranean conifer woodlands. The macchia vegetation represents evergreen sclerophyllous shrubs and trees that are hard-leaved, adapted to dry and hot conditions and sensitive to frost (Margaris, 1981). These plants are physiologically most active during the spring, autumn and winter, while photosynthesis during summer is lower, although reaching ca 50–70% of the average spring net photosynthesis (Rotondi et al., 2003). In SW Peloponnese the dense thickets of macchia vegetation grows from coastal areas up to an altitude of ca 350 m a.s.l. (Margaris, 1981). The Aegean phrygana vegetation is represented by shrubs and herbs that are seasonally dimorphic, meaning that they adapt to harsh climate conditions by adjusting leaf and stem properties between summer and winter months (Margaris and Vokou, 1982). The phrygana shrublands are characterized by high species diversity and drought resistance (European Environmental Agency, EUNIS, 2012), and are sometimes regarded as an indicator of degraded land (Jahns, 1993). Phrygana annuals are dormant during summer months, while the woody and perennial phrygana adjust their leaves and stems according to season. The larger wet-season leaves are formed after the first autumn rains and these leaves are photosynthesizing with a rate double that of the sclerophyll macchia (Margaris and Vokou, 1982). In the end of the wet season the winter-season leaves fall off, leaving place for the smaller summer leaves as well as thicker xylem cell walls in the stem (Margaris, 1976). Although both macchia and phrygana vegetation are highly adapted to moisture stress, the phrygana is generally associated with drier growth environments (Margaris and Vokou, 1982).

3. CASE STUDY, AGIOS FLOROS FEN, MESSENIA, GREECE

A sediment section was retrieved from a fen close to Agios Floros village, c. 18 km north-west of Kalamata, Messenia. The fen site (N 37°10′ 05.25″ E 22°01′ 05.61″, 13 m a.s.l.) is part of the upper drainage system of Pamisos River on the Messenian plain, supplied by water from nearby groundwater aquifer springs that are productive all year round. The continuous water supply has allowed accumulation of highly organic sediment in this otherwise dry environment, and favored its preservation throughout the late Holocene period. Recent in-depth studies of diatom assemblages and sedimentological properties on the sediment sequence, suggest that the site experienced limnic conditions and dramatic water depth variations between ca. 6000–4500 cal yrs BP (Katrantsiotis et al., 2016a). After 4500 cal yrs BP conditions became locally drier and the site developed into a terrestrial-dominated environment with a slow but relatively continuous accumulation of organic-rich sediments (Katrantsiotis et al., 2016a).

The local fen vegetation is dominated by emergent semi-aquatic plants such as *Arundo donax* (Mediterranean reed), *Phragmites australis* (common reed), *Typha latifolia* (bulrush), *T. angustifolia* (lesser bulrush), *Equisetum telmateia* (great horsetail), *Carex* spp. (sedges), *Juncus acutus* (spiny rush), *Cyperus* spp. (sedges) and *Ajuga orientalis* (bugleweed). Characteristic trees in the area surrounding the fen are *Olea europea* (olive), *Pistacia lentiscus* (mastic), *Ceratonia siliqua* (carob), *Quercus coccifera* (kermes oak), *Phillyrea latiflia* (Green olive), *Myrtus communis* (myrtle), *Rhamnus alaternus* (buckthorn), *Smilax aspera* (common smilax), *Ruscus aculeatus* (butcher's broom), *Pistacia terebinthus* (terebinth tree), *Salix fragilis* (brittle willow), *S. alba* (white willow), *Platanus orientalis* (Plane), *Nerium oleander* (Oleander) (Horvat et al., 1974; Polunin, 1980; Papazisimou et al., 2005). The majority of these trees are sclerophyll evergreen species, although some are deciduous (e.g. *Salix* sp., *Platanus orientalis*). Phrygana vegetation in the Agios Floros area is represented by herbs and shrubs such as *Sarcopoterium spinosum* (thorny burnet), *Coridothymus capitatus* (Spanish oregano/thyme), *Calicotome villosa* (spiny broom), *Salvia triloba* (Greek sage) and *Helichrysum* spp. (Papazisimou et al., 2005). The Agios Floros site has been described in detail by Katrantsiotis et al. (2016a, 2016b).

Climate in the study area is typical Mediterranean with mild, wet winters and hot, dry summers. Precipitation is strictly seasonal, with winter precipitation between October and April representing ca 90% of the annual rains. Annual