



## Evaluating the use of amber in palaeoatmospheric reconstructions: The carbon-isotope variability of modern and Cretaceous conifer resins

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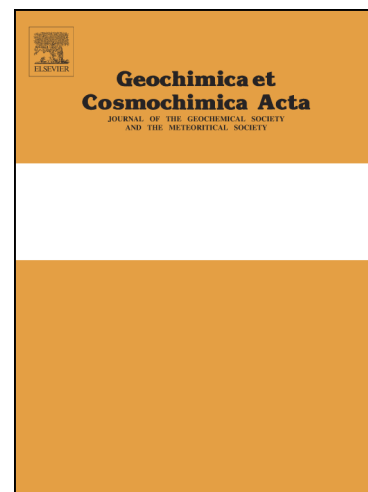
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**1 Evaluating the use of amber in palaeoatmospheric reconstructions: The carbon-isotope  
2 variability of modern and Cretaceous conifer resins**

3

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6

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23 **ABSTRACT**

24 Stable carbon-isotope geochemistry of fossilized tree resin (amber) potentially could be a very  
25 useful tool to infer the composition of past atmospheres. To test the reliability of amber as a  
26 proxy for the atmosphere, we studied the variability of modern resin  $\delta^{13}\text{C}$  at both local and  
27 global scales. An amber  $\delta^{13}\text{C}$  curve was then built for the Cretaceous, a period of abundant  
28 resin production, and interpreted in light of data from modern resins. Our data show that  
29 hardening changes the pristine  $\delta^{13}\text{C}$  value by causing a  $^{13}\text{C}$ -depletion in solid resin when  
30 compared to fresh liquid-viscous resin, probably due to the loss of  $^{13}\text{C}$ -enriched volatiles.  
31 Modern resin  $\delta^{13}\text{C}$  values vary as a function of physiological and environmental parameters in  
32 ways that are similar to those described for leaves and wood. Resin  $\delta^{13}\text{C}$  varies between plant  
33 species and localities, within the same tree and between different plant tissues by up to 6‰,  
34 and in general increases with increasing altitudes of the plant-growing site. We show that, as  
35 is the case with modern resin, Cretaceous amber  $\delta^{13}\text{C}$  has a high variability, generally higher  
36 than that of other fossil tissues. Despite the high natural variability, amber shows a negative  
37 2.5–3‰  $\delta^{13}\text{C}$  trend from the middle Early Cretaceous to the Maastrichtian that parallels  
38 published terrestrial  $\delta^{13}\text{C}$  records. This trend mirrors changes in the atmospheric  $\delta^{13}\text{C}$   
39 calculated from the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of benthic foraminiferal tests, although the magnitude of  
40 the shift is larger in plant material than in the atmosphere. Increasing mean annual  
41 precipitation and  $p\text{O}_2$  could have enhanced plant carbon-isotope fractionation during the Late  
42 Cretaceous, whereas changing  $p\text{CO}_2$  levels seem to have had no effect on plant carbon-  
43 isotope fractionation. The results of this study suggest that amber is a powerful fossil plant  
44 material for palaeoenvironmental and palaeoclimatic reconstructions. Improvement of the  
45 resolution of the existing data coupled with more detailed information about botanical source  
46 and environmental growing conditions of the fossil plant material will probably allow a more  
47 faithful interpretation of amber  $\delta^{13}\text{C}$  records and a wider understanding of the composition of  
48 the past atmosphere.

49 **Keywords:** Conifer resin, amber, carbon isotopes, palaeoclimate, Cretaceous

50

## 51 1. INTRODUCTION

52

53 Since C3 plants take up atmospheric CO<sub>2</sub> during photosynthesis and record its carbon-isotope  
54 signature, fossil plant remains (such as leaves and wood) can be used to reconstruct the  
55 palaeoatmosphere (e.g. Gröcke, 2002; Arens *et al.*, 2000; Bechtel *et al.*, 2008; Diefendorf *et*  
56 *al.*, 2010). Plants discriminate against <sup>13</sup>C during photosynthesis, and the degree of <sup>13</sup>C  
57 fractionation ( $\Delta^{13}\text{C}_\text{P}$ ) depends not only on plant physiology but also on a number of  
58 environmental factors and post-photosynthetic  $\Delta^{13}\text{C}_\text{P}$  processes, which determine the  $\delta^{13}\text{C}$  of  
59 plant tissues (Arens *et al.*, 2000; Diefendorf *et al.*, 2010; Schubert and Jahren 2012). The  
60 pristine carbon-isotope composition of wood and leaves, the most commonly used tissues in  
61 chemostratigraphic analysis, is further changed by diagenesis, through which moieties with  
62 different  $\delta^{13}\text{C}$  signatures are selectively removed (e.g. van Bergen and Poole, 2002; Bechtel *et*  
63 *al.*, 2002). Natural variability and diagenesis make the reconstructions of past atmospheric  
64 carbon-isotope composition based on plant  $\delta^{13}\text{C}$  analysis difficult because, particularly in  
65 deep-time studies, it is often impossible to separate the physiological and environmental  
66 effects from atmospheric signals and evaluate the diagenetic effect (Diefendorf *et al.*, 2010).  
67 The  $\delta^{13}\text{C}$  of fossil wood and leaves ( $\delta^{13}\text{C}_\text{WOOD}$  and  $\delta^{13}\text{C}_\text{LEAF}$ ) has been successfully used to  
68 infer changes in the carbon-isotope composition of past atmosphere–ocean systems, an  
69 approach supported by the evidence of  $\delta^{13}\text{C}$  excursions synchronously recorded in both  
70 terrestrial organic matter and marine carbonates (e.g. Gröcke, 2002; Strauss and Peters-Kottig,  
71 2003; Dal Corso *et al.*, 2011). Records of  $\delta^{13}\text{C}_\text{WOOD}$  and  $\delta^{13}\text{C}_\text{LEAF}$  parallel those of marine  
72 carbonates and can record global long- and short-term perturbations of the carbon cycle, such  
73 as the Middle–early Late Triassic 3‰ positive  $\delta^{13}\text{C}$  long-term trend (Dal Corso *et al.*, 2011),

74 and the Jurassic and Cretaceous positive and negative shifts associated with oceanic anoxic  
75 events (OAEs; e.g. Gröcke, 2002; Hesselbo *et al.*, 2007).

76

77 As a biochemical product of terrestrial plants, amber (fossil tree resin) is expected to record  
78 the same  $\delta^{13}\text{C}$  shifts recorded by other plant compounds and tissues. Amber is an  
79 extraordinary medium for the preservation of animals, plants and fungi that are otherwise rare  
80 in the fossil record. It is resistant to diagenesis and can maintain its original chemical and  
81 isotopic composition and for this reason is thought to be a very powerful tool for  
82 reconstruction of the palaeoatmosphere and the palaeoenvironment (Murray *et al.*, 1998;  
83 McKellar *et al.*, 2011; Dal Corso *et al.*, 2011, 2013; Aquilina *et al.*, 2013; Tappert *et al.*,  
84 2013). It has been shown that amber  $\delta^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{AMBER}}$ ) falls in the range of typical modern C3  
85 plants and may reveal information about climate and environment at the time of resin  
86 exudation, for example changes in plant carbon-isotope discrimination linked to  
87 environmental stresses such as insect infestation or water availability (Murray *et al.*, 1994,  
88 1998; Nissenbaum & Yakir, 1995; McKellar *et al.*, 2008, 2011; Dal Corso *et al.*, 2011, 2013;  
89 Tappert *et al.*, 2013). However, contrary to that of wood and leaf, less research has focused on  
90 developing amber as a palaeoatmosphere proxy (Tappert *et al.*, 2013). In addition, the lack of  
91 sufficient data on the carbon-isotope geochemistry of modern resin, i.e. on the variation of  
92  $\delta^{13}\text{C}_{\text{RESIN}}$  (resin  $\delta^{13}\text{C}$ ) under different environmental conditions, renders interpretation of  
93  $\delta^{13}\text{C}_{\text{AMBER}}$  problematic.

94

95 Here, as a test case, we explore the value of  $\delta^{13}\text{C}_{\text{AMBER}}$  as a proxy for the Cretaceous  
96 atmosphere. We studied the variability of modern  $\delta^{13}\text{C}_{\text{RESIN}}$  using samples produced by extant  
97 conifers from different temperate to tropical environments in order to understand whether  
98 resin carbon-isotope behaviour is similar to that of plant tissues. We do not aim to explain the  
99 biological and biochemical reasons behind the observed behaviour of modern  $\delta^{13}\text{C}_{\text{RESIN}}$  but

rather to highlight the patterns and variability that could hamper palaeoclimatic reconstructions and chemostratigraphy. New Cretaceous  $\delta^{13}\text{C}_{\text{AMBER}}$  data, coupled with a compilation of published data, were compared in order to combine terrestrial and marine  $\delta^{13}\text{C}$  records, and interpreted in light of both present-day isotopic variability and the Cretaceous climate.

## 2. MATERIAL AND METHODS

### 2.1 Methodical background: Factors controlling the $\delta^{13}\text{C}$ of modern C3 plants

The  $\delta^{13}\text{C}$  of C3 plants ( $\delta^{13}\text{C}_{\text{PLANT}}$ ) was calculated according to the model of Farquhar *et al.* (1989) [eq.1] and depends on the  $\delta^{13}\text{C}_{\text{ATM}}$  ( $\delta^{13}\text{C}$  of the atmosphere) and on the ratio between the  $p\text{CO}_2$  inside the leaves and the atmospheric  $p\text{CO}_2$  ( $c_i/c_a$ ):

$$\delta^{13}\text{C}_{\text{PLANT}} = \delta^{13}\text{C}_{\text{ATM}} - a - (b - a) * c_i/c_a$$

where  $a$  is the fractionation during diffusion of the  $\text{CO}_2$  from the atmosphere into leaves and is fixed at 4.4‰;  $b$  is the fractionation during ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) carboxylation and has values of 26–30‰ (e.g. Farquhar *et al.*, 1989; Arens *et al.*, 2000; Schubert and Jahren, 2012); and  $c_i/c_a$  is the ratio between intercellular and atmospheric  $p\text{CO}_2$ . The  $c_i/c_a$  usually varies between 0.65 and 0.8 with a maximum range between 0.3 and 0.9 (e.g. Farquhar *et al.* 1989; Arens *et al.*, 2000).

Post-photosynthetic fractionation also occurs during the biosynthesis of plant compounds, which consequently have different  $\delta^{13}\text{C}$  signatures (Badeck *et al.*, 2005). In general, non-

125 photosynthetic tissues are more  $^{13}\text{C}$ -enriched by 1–3‰ than photosynthetic tissues such as  
 126 leaves (Cernusak *et al.*, 2009).  
 127  
 128 Studies suggested that the  $\delta^{13}\text{C}_{\text{PLANT}}$  is primarily controlled by  $\delta^{13}\text{C}_{\text{ATM}}$  (Arens *et al.*, 2000).  
 129 However, additional strong dependence of  $\Delta^{13}\text{C}_\text{P}$  upon other factors complicates the  $\delta^{13}\text{C}_{\text{PLANT}}$   
 130 -  $\delta^{13}\text{C}_{\text{ATM}}$  relationship (e.g. Nordt *et al.*, 2016). The  $c_i/c_a$  ratio in [eq.1] is regulated by  
 131 stomatal conductance, which is governed by the closing or opening of the stomata. Stomatal  
 132 conductance can be influenced by many environmental factors, particularly water availability  
 133 and  $p\text{CO}_2$ . For example, Diefendorf *et al.* (2010) and Kohn (2010) showed that  $\Delta^{13}\text{C}_\text{P}$  is  
 134 strongly correlated to mean annual precipitation (MAP) and plant functional types. Both these  
 135 studies found an increase of  $\Delta^{13}\text{C}_\text{P}$  with increase of MAP. This dependence was modelled and  
 136 tested in the fossil record (Diefendorf *et al.*, 2015; Kohn, 2016). Schubert and Jahren (2012)  
 137 gave evidence that  $\Delta^{13}\text{C}$  by C3 plants grown in environmentally controlled chambers  
 138 hyperbolically increases with increasing ambient  $p\text{CO}_2$  levels. The model of Schubert and  
 139 Jahren (2012) was tested against ice-core records and used to reconstruct  $p\text{CO}_2$  during the  
 140 Palaeocene–Eocene Thermal Maximum (PETM) (Schubert and Jahren 2013, 2015). In  
 141 contrast to this model, recent studies found no or negligible  $p\text{CO}_2$  dependence over long time  
 142 scales (Kohn 2016), keeping open the question as to whether MAP or  $p\text{CO}_2$  predominantly  
 143 control  $\Delta^{13}\text{C}_\text{P}$ . Moreover, Berner *et al.* (2000) and Beerling *et al.* (2002) experimentally  
 144 demonstrated an increase of plant  $\Delta^{13}\text{C}$  with increase in  $p\text{O}_2$  levels. Subsequently, Tappert *et*  
 145 *al.* (2013) proposed the use of fossil plant  $\delta^{13}\text{C}$  to reconstruct palaeo- $p\text{O}_2$ , assuming that, in  
 146 ambient air, plant  $\Delta^{13}\text{C}$  is proportional to  $p\text{O}_2$  and that physiological adaptations did not occur  
 147 through time. Although there is no agreement as to which factor is most important in  
 148 determining the carbon-isotope composition of modern plants, all these factors must be taken  
 149 into account to correctly interpret the carbon-isotope shifts registered by fossil plant material  
 150 in the geological record (Diefendorf *et al.*, 2010; Schubert and Jahren, 2012; Kohn, 2016).



151

152 **2.2 Modern and Cretaceous resin samples**

153

154 Modern resin samples from USA and New Caledonia were collected by A. R. Schmidt and L.  
155 J. Seyfullah in 2005, 2010 and 2011 (USA) and in 2006 and 2011 (New Caledonia). J. Dal  
156 Corso, G. Roghi and E. Ragazzi collected resins from different conifers growing at the  
157 Botanical Gardens of the University of Padova in 2010. In Padova, *Araucaria heterophylla*  
158 resin, leaves and wood were also collected at different heights from the base of the tree. Both  
159 liquid-viscous and solid resins were sampled. Carbon-isotope data, plant species, altitude and  
160 geographic provenance are summarized in Fig. 1 and Supplementary Table 1.

161

162 The Cretaceous amber analysed for this study derive from different deposits in Spain (25  
163 samples), France (10 samples), and from the Grassy Lake deposit (5 samples) in Canada (Fig.  
164 1). Their origin and ages are summarized in Supplementary Table 2 and Supplementary  
165 Figure 1. Spanish amber samples were collected by X. Delclòs and are stored at Universitat  
166 de Barcelona, Spain. They derive from several Aptian–Maastrichtian deposits from the  
167 Central Asturian Depression, the West and East areas of the Basque-Cantabrian Basin, the  
168 Maestrazgo (=Maestrat) Basin and the Castilian Platform. The age of these deposits is mainly  
169 constrained by pollen and spores and includes uncertainties from ~1 up to ~18 Myrs (see  
170 Table 2 and references therein; Peñalver & Delclòs, 2010; Barrón *et al.*, 2015). Samples of  
171 French amber come from the collection of D. Néraudeau stored at the Université de Rennes,  
172 France. The Late Albian-Early Cenomanian and Santonian ages of amber samples from  
173 different localities in France are well constrained by pollen, spores, dinoflagellates,  
174 foraminifers, ostracods and rudists (Peyrot *et al.*, 2005; Batten *et al.*, 2010), with uncertainties  
175 of ~1 up to ~3 Myrs (see Table 2). Grassy Lake amber was collected and provided by A.  
176 Wolfe (University of Alberta) and is Campanian in age, according to McKellar *et al.* (2008)

177 and Tappert *et al.* (2013).  $\delta^{13}\text{C}_{\text{AMBER}}$  data of Cretaceous amber were coupled with previously  
 178 published  $\delta^{13}\text{C}_{\text{RESIN}}$  data from Nissenbaum & Yakir (1995), Dal Corso *et al.* (2013) and  
 179 Tappert *et al.* (2013). The ages of some of these deposits, namely the Levantine amber from  
 180 Israel and Lebanon and the San Just amber from Spain, have been revised according to recent  
 181 stratigraphic data. The Lebanese amber-bearing deposits with bioinclusions (entrapped  
 182 fossilized organisms) are from the Lower Cretaceous: Ante-Jezzinian (Maksoud *et al.* 2014),  
 183 i.e., ante Lower Bedoulian (Bedoulian being Upper Barreman–Lower Aptian). Deposits of  
 184 Cretaceous Lebanese amber with bioinclusions are situated in the Chouf Sandstone Formation  
 185 (= Grès de Base or C1 in older usages), under the recently defined Jezzinian Regional-Stage  
 186 (uppermost Barremian–lower Aptian). The lower boundary of the Jezzinian is probably within  
 187 the uppermost Barremian (Maksoud *et al.* 2014). According to new biostratigraphical data,  
 188 the oldest Lebanese amber deposits with bioinclusions are Early Barremian and the youngest  
 189 are intra-Barremian (Maksoud *et al.*, 2016). The San Just amber outcrop is located in the  
 190 Maestrazgo Basin and is included in the Escucha Fm. of the Utrillas Group (SSS – Superior  
 191 Sedimentary Succession; Rodríguez-López *et al.*, 2009). It was dated as Middle-Upper Albian  
 192 by Villanueva-Amadoz *et al.* (2010), based on the palynological fossil record and it is now  
 193 constrained to the Upper Albian by comparison with similar deposits in the Basque–  
 194 Cantabrian Basin with similar fossil content (Barrón *et al.* 2015).

195

### 196 **2.3 $\delta^{13}\text{C}_{\text{RESIN}}$ analysis**

197

198 Clean sub-millimetric fragments of the collected modern resins were separated under the  
 199 microscope to perform  $\delta^{13}\text{C}$  analysis. Close attention was paid in order to select clear resin  
 200 portions to avoid the presence of inclusions. The  $\delta^{13}\text{C}$  analysis was performed on a Thermo  
 201 Scientific Delta V Advantage Isotope Ratio Mass Spectrometer in continuous flow mode,  
 202 coupled with a Flash 2000 Elemental Analyser and a ConFlo IV interface. 0.03–0.05 mg of

resin were weighed in a tin capsule and fed to the Elemental Analyser. The Mass Spectrometer analysed CO<sub>2</sub> gas resulted from high temperature combustion. On the basis of a long-term mean of >30 tin-cap analyses, a blank correction was applied to the raw data and the results were calibrated against repeated analyses of IAEA-CH6 and IAEA-CH7 international standards, whose  $\delta^{13}\text{C}$  is respectively -10.449‰ and -32.151‰ (Coplen *et al.*, 2006). The long-term internal reproducibility was estimated on repeated analyses of an internal standard (C3 plant sucrose) and is better than 0.15‰ (1 $\sigma$ ).

Samples of Cretaceous amber were first crushed with an agate mortar to obtain a fine powder. Repeated analyses on different portions of single Cretaceous amber specimens have shown that the  $\delta^{13}\text{C}$  is remarkably homogeneous within the same piece (Dal Corso *et al.*, 2013). We thus consider the measured  $\delta^{13}\text{C}$  as representative of the entire amber sample. The amber powder was placed in a polypropylene tube and treated with 3M HCl to remove possible residual carbonates from the sediments where the amber had been embedded. Samples were then rinsed with deionized water until neutrality was reached and were oven-dried at 50°C. 1.5–2 mg of amber powder were weighed in tin capsules and fed into the Elemental Analyzer.  $\delta^{13}\text{C}$  analysis was performed using a Carlo Erba NA 1108 Elemental Analyzer coupled to a SERCON Geo 20/20 IRMS running in continuous flow mode with a He carrier gas (flow rate 100ml per min). The reproducibility of the analyses was estimated using an internal standard (alanine) routinely checked against international standards IAEA-CH-6 and IAEA-CH-7 and traceable back to the VPDB standard. All results are accurate to better than  $\pm 0.15\text{‰}$  (1 $\sigma$ ).

#### 2.4 Meta-analysis of terrestrial and marine carbon-isotope data

The amber data generated in this study have been coupled with the published  $\delta^{13}\text{C}_{\text{AMBER}}$  data of Tappert *et al.* (2013), Nissenbaum & Yakir (1995) and Dal Corso *et al.* (2013), allowing improved resolution of the  $\delta^{13}\text{C}_{\text{AMBER}}$  record. To compare the variability of  $\delta^{13}\text{C}_{\text{AMBER}}$  with

229 other Cretaceous C3 plant material we used the recently compiled ISOORG database (Nordt  
 230 *et al.*, 2016). ISOORG comprises  $\delta^{13}\text{C}$  data ( $\delta^{13}\text{C}_{\text{ISOORG}}$ ) of plant material including wood,  
 231 leaf, charcoal, coal, and bulk terrestrial organic matter from various geographical locations.  
 232 We also built a low-resolution wood  $\delta^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{WOOD}}$ ) record coupling the Lower Cretaceous  
 233 wood data extracted from ISOORG (Nordt *et al.*, 2016) with the Maastrichtian data of  
 234 Salazar-Jaramillo *et al.* (2016). Before processing data we excluded from ISOORG all  
 235  $\delta^{13}\text{C}_{\text{AMBER}}$  data, all of which were already included in our compilation. Some of the amber  
 236 deposits described here have age uncertainties of several millions of years, especially in the  
 237 case of the mid-Cretaceous Spanish ambers (Table 2 and Supplementary Figure 1). These  
 238 uncertainties depend on the fact that Cretaceous amber is commonly found in continental  
 239 (fluvial sediments, coal deposits) or coastal (brackish estuarine/lagoonal) deposits that lack  
 240 age-significant fossils. For this reason and to allow comparison with the ISOORG database,  
 241  $\delta^{13}\text{C}_{\text{AMBER}}$  data were placed into 5 Myrs-age bins following the criteria used by Nordt *et al.*  
 242 (2016). Amber with age uncertainty larger than the bin was excluded. The same procedure  
 243 was used also for  $\delta^{13}\text{C}_{\text{WOOD}}$  from Salazar-Jaramillo *et al.* (2016). Box-and-whiskers plots for  
 244  $\delta^{13}\text{C}_{\text{AMBER}}$ ,  $\delta^{13}\text{C}_{\text{WOOD}}$  and  $\delta^{13}\text{C}_{\text{ISOORG}}$  data were built for each age bin with a sample size of at  
 245 least 5 (Krzywinski and Altman, 2014). To compare the terrestrial  $\delta^{13}\text{C}$  signal to the marine  
 246  $\delta^{13}\text{C}$  signal we took marine carbonate data from the database compiled by Prokoph *et al.*  
 247 (2008) and Bodin *et al.* (2015). We used  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  data from benthic and planktonic  
 248 foraminifera and belemnites. Terrestrial  $\delta^{13}\text{C}$  data were also compared to the  $\delta^{13}\text{C}_{\text{ATM}}$ , which  
 249 was estimated from the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of benthic foraminifera using the equations proposed  
 250 by Tipple *et al.* (2010). A third-degree polynomial curve was fitted to the data to compare the  
 251 terrestrial and marine carbonate  $\delta^{13}\text{C}$  records. Prediction intervals for individual observations  
 252 hold about 95% of data. Polynomial curve fitting by the least-squares method and prediction  
 253 intervals were obtained with JMP software, version 10 (SAS Institute Inc., Cary, NC, USA).  
 254

### 3. RESULTS

#### 3.1 Modern resin $\delta^{13}\text{C}$

The  $\delta^{13}\text{C}$  of all the analysed modern resins varies from -31.6‰ to -22.8‰ (mean  $\pm$  SD = -26.7  $\pm$  1.8‰, n=84; Table 1).  $\delta^{13}\text{C}_{\text{RESIN}}$  values obtained in this study show a normal distribution with a mean of -26.7‰ (Fig. 2). The mean  $\delta^{13}\text{C}_{\text{RESIN}}$  is more  $^{13}\text{C}$ -enriched than the mean global leaf  $\delta^{13}\text{C}$  (-28.5‰ calculated from data of Diefendorf *et al.*, 2010; Fig. 3A). A statistically significant difference ( $p$  value = 0.001) exists between liquid-viscous resin and solid resin, the former having more  $^{13}\text{C}$ -enriched values (mean -25.9‰) than the latter (mean -27.1‰) (Fig. 3A). Resin has  $\delta^{13}\text{C}$  values systematically more  $^{13}\text{C}$ -enriched by 1–2.3‰ than those of bulk leaf and wood samples collected from the same branch at the same tree height in *Araucaria heterophylla*, *Picea abies* and *Cupressus arizonica* (Fig. 3B). Resin, wood and leaves collected from a single tree of *Araucaria heterophylla* at different heights also possess variable  $\delta^{13}\text{C}$  signatures (Fig. 3C). Differences of up to 6‰ exist between the mean  $\delta^{13}\text{C}$  of resins from different plant species (Table 1). The  $\delta^{13}\text{C}_{\text{RESIN}}$  from different tree genera growing at the same altitude in the same locality (Padova, Italy) differs by about 2–5‰ (Fig. 3B). Liquid-viscous and solid resin  $\delta^{13}\text{C}$  of *Pinus* and *Araucaria* significantly increases with increasing altitude of the sampling site (Fig. 4; liquid-viscous resin,  $R = 0.527$ ,  $p$  value < 0.001; Solid resin of *Pinus* and *Araucaria*,  $R = 0.603$ ,  $p$  value < 0.001). Similar correlation was also observed between  $\delta^{13}\text{C}_{\text{LEAF}}$  and altitude ( $R=0.59$ ; Körner *et al.*, 1988). The  $\delta^{13}\text{C}_{\text{RESIN}}$  values for the most represented genera show that *Pinus* resin is statistically indistinguishable from *Araucaria* resin ( $p$  value = 0.6, Students'  $t$ -test; Table 1).

#### 3.2 Cretaceous amber $\delta^{13}\text{C}$

The  $\delta^{13}\text{C}$  of amber from Spain varies between  $-17\text{‰}$  and  $-24.2\text{‰}$  (mean =  $-20.1 \pm 1.8\text{‰}$ ) in the range expected for C3 plant resins (Table 2). Similarly,  $\delta^{13}\text{C}$  of amber from France and Canada ranges from  $-18.5\text{‰}$  to  $-23.5\text{‰}$  (mean =  $-21.1 \pm 1.9\text{‰}$ ) and from  $-21.4\text{‰}$  to  $-23.4\text{‰}$  (mean =  $-22.7 \pm 0.8\text{‰}$ ), respectively (Table 2). The compiled Cretaceous amber and ISOORG  $\delta^{13}\text{C}$  values show a normal distribution (Fig. 5A). On average, amber is more  $^{13}\text{C}$ -enriched (mean =  $-22.3\text{‰} \pm 1.9\text{‰}$ ) than Cretaceous C3 plant material (mean =  $-24.2\text{‰} \pm 1.3\text{‰}$ ) and wood (mean =  $-23.1\text{‰} \pm 1.3\text{‰}$ ) (Fig. 5B). Cretaceous  $\delta^{13}\text{C}_{\text{AMBER}}$  data are more dispersed than  $\delta^{13}\text{C}$  values of C3 plant material: the box-and-whisker plots (Fig. 5B) show the interquartile range (IQR) of  $\delta^{13}\text{C}_{\text{AMBER}}$  to be much larger ( $2.5\text{‰}$ , Table 2) than  $\delta^{13}\text{C}_{\text{ISOORG}}$  ( $1.4\text{‰}$ ). F-test for the equality of variances indicates that the variances of  $\delta^{13}\text{C}_{\text{AMBER}}$  and  $\delta^{13}\text{C}_{\text{ISOORG}}$  are significantly different ( $p < 0.0001$ ). SD and IQR were calculated for each age bin (Table 2) and show that  $\delta^{13}\text{C}_{\text{AMBER}}$  is generally more dispersed than the  $\delta^{13}\text{C}_{\text{ISOORG}}$  and  $\delta^{13}\text{C}_{\text{WOOD}}$ . Amber, wood and ISOORG data show that latest Cretaceous (Maastrichtian)  $\delta^{13}\text{C}$  values are more  $^{13}\text{C}$ -depleted than those of the Early Cretaceous (Hauterivian–Barremian) by  $2.5\text{--}3\text{‰}$  (Fig. 6). The marine  $\delta^{13}\text{C}$  record from whole rock, belemnite, and foraminifera (Prokoph *et al.*, 2007; Bodin *et al.*, 2015) shows a pattern that only partially matches the terrestrial records (Fig. 6). The  $\delta^{13}\text{C}_{\text{ATM}}$  calculated from benthic foraminifera shows a decrease of approx.  $1\text{‰}$  from the Aptian to the Maastrichtian that mirrors the decrease ( $2.5\text{--}3\text{‰}$ ) shown by terrestrial plants (Fig. 7).

## 4. DISCUSSION

### 4.1 Modern resin

#### 4.1.2 Effect of resin hardening on the $\delta^{13}\text{C}_{\text{RESIN}}$

To obtain reliable information on the physiology of plants and the environmental conditions under which they grow from the carbon-isotope geochemistry of resin, it is necessary to understand whether the measured  $\delta^{13}\text{C}_{\text{RESIN}}$  values actually represent the pristine composition at the time of resin biosynthesis. After exudation, resin is composed of up to 50% of volatile fraction (mainly monoterpenes and sesquiterpenes). The volatile fraction is lost rapidly on exposure of resin to air and sunlight, whereas the non-volatile fraction (mainly diterpene acids in conifer resin) undergoes polymerization (cross-linking and isomerization) with the formation of high-molecular-weight polymers (Langenheim, 1990; Scalarone *et al.*, 2003; Lambert *et al.*, 2008; Ragazzi and Schmidt, 2011). This selective removal of moieties points to a possible change of the bulk  $\delta^{13}\text{C}_{\text{RESIN}}$  during resin hardening (Dal Corso *et al.*, 2011). Our dataset comprises both liquid-viscous resins sampled shortly after exudation and solid resins that already had hardened at the site of exudation. A statistically significant difference ( $p = 0.001$ ) is observed between liquid-viscous (mean = -25.9‰) and solid resin (-27.1‰), with an overall 1.2‰  $^{13}\text{C}$ -enriched values in the former (Fig. 3A). We conclude that volatile mono- and sesquiterpenes released by resin during hardening are more  $^{13}\text{C}$ -enriched than the non-volatile diterpenoid and triterpenoid acids. Consequently, changes in the pristine  $\delta^{13}\text{C}_{\text{RESIN}}$  occur soon after resin exudation. Future organic geochemical studies should precisely determine the magnitude of these isotopic changes in different resin types by studying the pattern of volatile loss during hardening, and the specific carbon-isotope signature and the relative abundance of the different resin compounds. Such a study would probably allow correction of the measured  $\delta^{13}\text{C}$  of solid resin back to the pristine signature at the time of exudation in order to faithfully interpret the data.

#### 4.1.2 Differences between the $\delta^{13}\text{C}_{\text{RESIN}}$ and the $\delta^{13}\text{C}$ of other plant tissues

Post-photosynthetic fractionation in plants results in differences in the  $\delta^{13}\text{C}$  of plant tissues (Badeck *et al.*, 2005). In general, non-photosynthetic tissue tends to be more  $^{13}\text{C}$ -enriched than photosynthetic tissue: leaves were found to have isotopically lighter values than wood and roots, and above-ground organs are more  $^{13}\text{C}$ -depleted than below-ground material (Badeck *et al.*, 2005; Cernusak *et al.*, 2009). Several biochemical causes have been invoked to explain this widespread isotopic behaviour and are still a topic of debate (review by Cernusak *et al.*, 2009).

$\Delta^{13}\text{C}_\text{P}$  during resin biosynthesis is evident from our data when comparing the  $\delta^{13}\text{C}_\text{RESIN}$  with the  $\delta^{13}\text{C}$  of other plant tissues. Our dataset shows that the mean  $\delta^{13}\text{C}_\text{RESIN}$  of fresh liquid-viscous resin (-25.9‰) is more  $^{13}\text{C}$ -enriched by 2.6‰ than the mean  $\delta^{13}\text{C}_\text{LEAF}$  from a published compilation of data of C3 leaves (-28.5‰; Fig. 3A, Diefendorf *et al.*, 2010), as expected from a non-photosynthetic plant compounds. Solid resin (-27.1‰), as previously described, is more  $^{13}\text{C}$ -depleted than liquid-viscous resin, but remains more  $^{13}\text{C}$ -enriched than mean leaf  $\delta^{13}\text{C}$ , so that carbon-isotope changes due to hardening do not overshadow post-photosynthetic  $\Delta^{13}\text{C}_\text{P}$  between resin and leaf. This difference is also evident from samples taken from the same trees and branches. Solid resin of *Araucaria heterophylla*, *Picea abies* and *Cupressus arizonica* sampled at the Botanical Garden in Padova (Italy) has higher  $\delta^{13}\text{C}$  values than leaves from the same branch by approx. 1–2‰ (Fig. 3B and C). This difference should be corrected for the loss of volatiles and was likely larger by 1–2‰ at the time of resin exudation (see 4.1.1).

Similar differences exist also between resin and wood  $\delta^{13}\text{C}$  signatures. In *Picea abies* and *Araucaria heterophylla*, resin is more  $^{13}\text{C}$ -enriched than wood, which, in turn, shows very small  $\delta^{13}\text{C}$  differences compared to leaf carbon-isotope signatures (Fig. 3B and C). As shown by the trees sampled for this study, fractionation during resin biosynthesis does occur and



results in a very  $^{13}\text{C}$ -enriched  $\delta^{13}\text{C}_{\text{RESIN}}$  signature (by approx. 2–4‰) when compared to the  $\delta^{13}\text{C}$  of other organs from the same plant branch. On the contrary,  $\delta^{13}\text{C}_{\text{WOOD}}$  and  $\delta^{13}\text{C}_{\text{LEAF}}$  show little difference (<1‰) within the same branch (Fig. 3B and C). Other studies show that on average stem wood and roots are more  $^{13}\text{C}$ -enriched by 1–1.9‰ than is leaf material (Badeck *et al.*, 2009). Our results suggest that the post-photosynthetic  $\Delta^{13}\text{C}_\text{P}$  is larger for resin than for other bulk plant tissues. Such patterns are visible also after resin hardening, meaning that both volatile (monoterpenes and sesquiterpenes), and non-volatile (diterpene acids) are affected.

#### 4.1.3 Environmental and physiological effects on $\delta^{13}\text{C}_{\text{RESIN}}$

Our results show that the carbon-isotope signature of resin records the environmental and physiological effects of C3 plant  $^{13}\text{C}$  discrimination, as do other plant tissues. The  $\delta^{13}\text{C}_{\text{RESIN}}$  varies by up to 2‰ within the same tree (Fig. 3C) and on average  $\delta^{13}\text{C}_{\text{RESIN}}$  differs by up to 6‰ between plant species and genera, and between different localities (Table 1 and Supplementary Table 1). This high variability in resin carbon-isotope composition is likely related to the local climatic and growing conditions, and plant physiology that regulate  $^{13}\text{C}$  discrimination in plants [eq. 1].

Several studies have explored the dependence of plant  $^{13}\text{C}$  discrimination in response to environmental gradients, which control the stomatal aperture and thus determine the  $c_i/c_a$  in [eq. 1] (see Cernusak *et al.*, 2013 for a summary). As previously described, C3 plants fractionate carbon isotopes depending on a number of factors: mean annual precipitation,  $p\text{CO}_2$ , soil moisture, nutrient availability, irradiation, etc., and can explain most of the  $\delta^{13}\text{C}$  variability of plant biomass (e.g. Diefendorf *et al.*, 2010; Kohn, 2010; Schubert and Jahren, 2012; Cernusak *et al.*, 2013). Here we consider the variability of  $\delta^{13}\text{C}_{\text{RESIN}}$  within the same

tree, with altitude of the growing site and between plant species, and show that  $\delta^{13}\text{C}_{\text{RESIN}}$  varies in ways that are similar to other tissues depending on the environmental conditions under which the plant grew.

Solid resin  $\delta^{13}\text{C}$  varies within an individual *Araucaria heterophylla* by approx. 2‰ (depending on different heights along the trunk), as also observed for leaf and wood  $\delta^{13}\text{C}$  (Fig. 3C). This difference suggests that either seasonality and/or physiological factors can considerably change the  $\delta^{13}\text{C}_{\text{RESIN}}$  within an individual plant. This phenomenon has also been observed in leaf  $\delta^{13}\text{C}$ , which varies by approx. 1–4‰ along vertical canopy profiles among conifers (e.g. Duursma and Marshall, 2006 and references therein).  $\delta^{13}\text{C}_{\text{LEAF}}$  generally increases from the bottom to the top of the crown due to hydraulic conductance or irradiation variations (Koch *et al.*, 2004; Duursma and Marshall, 2006; Cernusak *et al.*, 2013). Our resin, leaf and wood  $\delta^{13}\text{C}$  data from *Araucaria heterophylla* appear to show a similar pattern (Fig. 3C).

The  $\delta^{13}\text{C}$  of fresh liquid–viscous resin (Fig. 4A) increases with altitude from sea level to 3050m (Fig. 4B). This effect is also evident by plotting solid and liquid–viscous resin of *Pinus* and *Araucaria*, the most representative genera. In both cases  $\delta^{13}\text{C}_{\text{RESIN}}$  increases linearly with altitude ( $p < 0.001$ ; Fig. 4). These results contradict a previous study on  $\delta^{13}\text{C}_{\text{RESIN}}$ , which found a general  $^{13}\text{C}$ -depletion along altitudinal transects in the UK to a maximum altitude of 550m (Stern *et al.*, 2008). The dataset of  $\delta^{13}\text{C}_{\text{RESIN}}$  values presented in this study comprises a sample from altitudes up to approx. 3000m and is more comparable to the existing  $\delta^{13}\text{C}$  data from C3 leaves and wood from localities around the world of altitudes up to 5600m (Körner *et al.*, 1988; Warren *et al.*, 2001). Decreasing  $^{13}\text{C}$  discrimination with altitude has been extensively observed in conifer leaves and wood (e.g. Körner *et al.*, 1988; Hultine and Marshall, 2000; Warren *et al.*, 2001; Cernusak *et al.*, 2013). The net effect of

altitude on plant  $\delta^{13}\text{C}$  is, however, considered negligible compared, for example, to MAP  
 (Kohn, 2016). Indeed, the mechanism by which the discrimination-altitude correlation  
 operates is unclear: many authors have invoked changes in leaf morphology, water  
 availability, leaf nitrogen content, temperature, decrease of  $p\text{CO}_2$  with elevation,  $p\text{O}_2$  and  
 irradiance as possible causes (e.g. Hultine and Marshall, 2000; Diefendorf *et al.*, 2010;  
 Cernusak *et al.*, 2013). The strong dependence of plant  $\delta^{13}\text{C}$  towards very different  
 environmental factors (e.g. Arens *et al.*, 2000; Diefendorf *et al.*, 2010), points to a possible  
 combined effect of these factors on  $\delta^{13}\text{C}_{\text{RESIN}}$  with altitude. Additional  $\delta^{13}\text{C}_{\text{RESIN}}$  analyses  
 along altitudinal transects coupled with precise data about the environmental conditions  
 (moisture levels, temperature, irradiance, etc.) will elucidate the  $\delta^{13}\text{C}_{\text{RESIN}}$ -altitude correlation  
 found in this study and permit a greater understanding of the relative contribution of these  
 effects on the final carbon-isotope signature of the resin. The significant correlation between  
 $\delta^{13}\text{C}_{\text{RESIN}}$  and altitude, similar to the correlation found using other plant substrates, means that  
 environmental effects on plant  $\Delta^{13}\text{C}$  are recorded by resin despite fractionation during  
 biosynthesis, which determines the differences between its  $\delta^{13}\text{C}$  and that of other tissues (Fig.  
 3B and C), and during hardening (Fig. 3).

Several authors have reported high  $\delta^{13}\text{C}$  variability (e.g. up to 6‰ in lowland rainforest  
 stands; Bonal *et al.*, 2000) among plant species under the same environmental conditions (e.g.  
 Leavitt and Long, 1986; Zhang and Clegg, 1996; Schubert and Cui, 2016 and references  
 therein). These inter-specific differences in the  $\delta^{13}\text{C}$  of plants are related to differences in  
 $\Delta^{13}\text{C}$  regulated by the morphology of leaf and stomata that control efficiency of water use and  
 the  $c_i/c_a$  ratio (Murray *et al.*, 1998). The  $\delta^{13}\text{C}$  of resins sampled at the same altitude in the  
 same locality (Padova, Italy) from different tree genera differs by about 2–5‰ (Fig. 3B).  
 Overall, the  $\delta^{13}\text{C}_{\text{RESIN}}$  varies by up to 6‰ between plant species (Table 1). These findings  
 suggest that variations in  $^{13}\text{C}$  discrimination linked to plant physiology are recorded also by

resin. Interestingly, when resins are grouped at a high taxonomic level, the  $\delta^{13}\text{C}$  differences are not statistically significant ( $p = 0.598$ ) and their mean calculated  $\delta^{13}\text{C}_{\text{RESIN}}$  values (*Araucaria* =  $-27.1\text{‰}$ ; *Pinus* =  $-26.9\text{‰}$ ) approach that of the mean of our worldwide resin samples.

## 4.2 Cretaceous $\delta^{13}\text{C}_{\text{AMBER}}$ data

As hypothesised in the introduction, amber could potentially be used to reconstruct the carbon-isotope composition of the palaeoatmosphere, as is the case with other plant tissues such as leaf and wood. Our data on modern material show that the  $\delta^{13}\text{C}_{\text{RESIN}}$  can record changes in  $^{13}\text{C}$  discrimination by C3 plants as seen in leaves and wood. Records of the  $\delta^{13}\text{C}$  from fossil wood and bulk leaves or cuticles, despite their natural variability within each stratigraphic interval, parallel those of marine carbonates and can record global long- and short-term perturbations of the carbon cycle (e.g. Gröcke *et al.*, 1999; Gröcke, 2002; Dal Corso *et al.*, 2011). It is therefore reasonable to expect amber to record the same carbon-isotope changes. In the following sections we will discuss the potential of amber as a chemostratigraphic tool and as a proxy for Cretaceous palaeoatmosphere in the light of present-day resin carbon-isotope geochemistry.

### 4.2.1 Carbon-isotope signature of Cretaceous amber vs other C3 fossil plant material: pristine differences and diagenetic effects

On average, Cretaceous  $\delta^{13}\text{C}_{\text{AMBER}}$  (mean =  $-22.3\text{‰} \pm 1.9\text{‰}$ ) is  $^{13}\text{C}$ -enriched by  $1.6\text{‰}$  ( $p < 0.0001$ ) relative to other C3 plant material (mean =  $-24.2\text{‰} \pm 1.3\text{‰}$ ) and wood (mean =  $-23.1\text{‰} \pm 1.3\text{‰}$ ) (Fig.5). Amber is always more  $^{13}\text{C}$ -enriched than wood by  $1.5\text{--}2\text{‰}$  for each age bin present here (Table 2, Fig. 6). A similar offset was also observed for Upper Triassic conifer amber and wood from Italy ( $+2.5\text{‰}$ ) (Dal Corso *et al.*, 2011), and for Upper

462 Cretaceous gymnosperm-derived coals and associated resinites from Australia (+2.6‰)  
 463 (Murray *et al.*, 1998). A recent compilation of plant  $\delta^{13}\text{C}$  data for all the Phanerozoic shows  
 464 amber is on average the most  $^{13}\text{C}$ -enriched plant tissue (Nordt *et al.*, 2016). The differences  
 465 between resin and plant tissues (leaf and wood) observed in our modern material (Fig. 3) can  
 466 explain amber  $^{13}\text{C}$ -enriched values, showing that fossil material can retain the same patterns  
 467 observed in modern samples, that is, with the differences being generated by fractionation  
 468 during resin biosynthesis. Moreover, the dispersion of  $\delta^{13}\text{C}$  data is larger in amber (SD =  
 469 1.95‰; IQR = 2.5‰) than in other C3 plant material (SD = 1.31‰; IQR = 1.4‰) (Table 2).  
 470 This difference is evident also when considering separately different plant tissues with a  
 471 sample size similar to the size of our amber database and with the same age. In general, amber  
 472  $\delta^{13}\text{C}$  values are more scattered than those of Cretaceous wood (SD = 1.31‰; IQR = 1.47‰),  
 473 charcoal (SD = 1.55‰; IQR = 2‰) and coal (SD = 1.43‰; IQR = 1.23‰). In the  
 474 Hauterivian–Barremian (age bin = 130 Ma) and Maastrichtian (age bin = 70 Ma)  $\delta^{13}\text{C}_{\text{AMBER}}$   
 475 has a greater spread in values than wood  $\delta^{13}\text{C}$ ; and in the Turonian (90 Ma) and in the  
 476 Maastrichtian (70 Ma) the amber carbon-isotope signature is more variable than in other plant  
 477 substrates (Fig. 6; Table 2).  
 478  
 479 Comparison with modern material (Fig. 5B) points to an original high plant  $\delta^{13}\text{C}$  variability  
 480 for amber but less in other fossil plant remains (Dal Corso *et al.*, 2011). Taphonomical and  
 481 diagenetic processes could enhance the original  $\delta^{13}\text{C}$  discrepancies between tissues and  
 482 accentuate the spread in  $\delta^{13}\text{C}$  data. The carbon-isotope signature of plant tissue changes  
 483 towards more negative values during diagenesis (Spiker & Hatcher, 1987), a fact also  
 484 confirmed here for conifer resin (Fig. 3A). As previously discussed (section 4.1.2), solid resin  
 485 becomes more depleted by 1.2‰ when altered from fresh liquid–viscous resin, probably  
 486 because of the loss of  $^{13}\text{C}$ -rich volatiles during hardening (Fig. 3A). Subsequently, resin  
 487 maturation causes polymerization of non-volatile components accompanied by cross-linking

and isomerization, but no significant diagenetic changes of the carbon-isotope composition take place (Dal Corso *et al.*, 2013; Tappert *et al.*, 2013). In support of this assumption, Dal Corso *et al.* (2013) observed that altered and unaltered areas within the same Lower Cretaceous amber pieces from the San Just deposit show no  $\delta^{13}\text{C}$  differences despite oxidation and degradation, as revealed by infra-red spectroscopic and thermogravimetric analyses. This observation indicates that amber is a closed system with respect to C-isotopes as soon as it hardens. By contrast, other plant remains can experience a more pervasive diagenetic overprint. Charcoalification and coalification can severely change the pristine  $\delta^{13}\text{C}$  of tissues (e.g. Gröcke, 1998; Yans *et al.*, 2010 and references therein). Pyrolysis experiments have shown the  $\delta^{13}\text{C}$  of wood to become either more  $^{13}\text{C}$ -enriched or depleted depending on the temperature of combustion reached (Jones and Chaloner, 1991; Hall *et al.*, 2008). Upon burial, the preferential degradation of hemicellulose (average  $\delta^{13}\text{C}$  of about -23‰) and cellulose (average  $\delta^{13}\text{C}$  of about -25‰) over lignin (average  $\delta^{13}\text{C}$  of about -28‰) can change the pristine bulk wood  $\delta^{13}\text{C}$  by several ‰ towards more negative values (e.g. Spiker & Hatcher, 1987; van Bergen and Poole, 2002). As pointed out by Dal Corso *et al.* (2011), these diagenetic processes could be responsible not only for changing the average  $\delta^{13}\text{C}$  of plant tissue but also for narrowing  $\delta^{13}\text{C}$  variability of Triassic fossil wood and leaves compared with amber. Similarly, the Cretaceous  $\delta^{13}\text{C}_{\text{AMBER}}$  is consistently more variable than the  $\delta^{13}\text{C}$  of other plant substrates (Fig. 5 and 6, Table 2). Despite these complicating factors, data show that amber is very resistant to diagenesis and can preserve the pristine carbon-isotope signature of resin better than other plant tissues and, consequently, can retain information about past environments and climate.

#### **4.2.2 Interpreting $\delta^{13}\text{C}_{\text{AMBER}}$ record through the Cretaceous and comparison with terrestrial organic matter and marine carbonate carbon-isotope records**

514 Excluding the Barriasian–Valanginian interval for which the  $\delta^{13}\text{C}_{\text{AMBER}}$  data available are  
 515 indeed very scarce, the most remarkable feature shown by the Cretaceous  $\delta^{13}\text{C}_{\text{AMBER}}$  record is  
 516 an approx. 2.5‰ negative trend from the Hauterivian–Barremian (130 Ma) to the  
 517 Maastrichtian (70 Ma). Similarly, Late Cretaceous wood  $\delta^{13}\text{C}$  is more  $^{13}\text{C}$ -depleted than Early  
 518 Cretaceous wood  $\delta^{13}\text{C}$  (Fig. 6). Maastrichtian C3 plant  $\delta^{13}\text{C}$  data from ISOORG compiled by  
 519 Nordt *et al.*, 2016 (various types of fossil C3 plant remains minus amber data) are  
 520 approximately 3‰ more  $^{13}\text{C}$ -depleted than the Hauterivian–Barremian  $\delta^{13}\text{C}$  data (Fig. 6). In  
 521 the earliest Cretaceous, ISOORG  $\delta^{13}\text{C}$  rises from the Jurassic–Cretaceous boundary to the  
 522 early Albian (125 Ma). The  $\delta^{13}\text{C}$  changes shown by ISOORG, wood, and amber records  
 523 during the Cretaceous are very similar to or smaller than their carbon-isotope variability  
 524 within each age bin (Table 2 and Fig. 6). Moreover, the resolution of the data is very low and  
 525 long intervals of the Cretaceous are not covered. This drawback obviously hampers a correct  
 526 interpretation of the trends because the non-homogeneous distribution of data through time  
 527 biases the fitting. However, the overall 2.5–3‰ negative depletion towards the end of the  
 528 Cretaceous is in clear agreement among the global compilation of plant substrates. On the  
 529 contrary, the marine carbonate carbon-isotope records seem only to partially parallel the  
 530 terrestrial long-term signal. In the Early Cretaceous belemnite  $\delta^{13}\text{C}$  record, a long-term  
 531 positive trend from the late Berriasian–early Valanginian to the middle Aptian is followed by  
 532 a long-term negative trend, which ends in the middle Albian (Prokoph *et al.*, 2008; Bodin *et*  
 533 *al.*, 2015). For subsequent intervals, belemnite  $\delta^{13}\text{C}$  data are sparse but become overall more  
 534  $^{13}\text{C}$ -enriched in the Late Cretaceous (Fig. 6). Data from planktonic and benthic foraminifera  
 535 are available only from the early Albian onwards:  $\delta^{13}\text{C}$  declines by approx. 1‰ from the early  
 536 Albian to the Albian–Cenomanian boundary then rises by the same magnitude until the  
 537 Cenomanian–Turonian boundary and remains stable until the end of the Cretaceous (Fig. 6;  
 538 Prokoph *et al.*, 2008). The schematic curve of whole-rock carbonate  $\delta^{13}\text{C}$  analyses compiled  
 539 by Erba *et al.* (2004) mirrors the belemnite and foraminiferal records (Fig. 6). Despite the

540 offset in the carbon-isotope signature of the different proxies, which depends on the water  
 541 mass in which the carbonate was precipitated or secreted (Prokoph *et al.*, 2008), marine  
 542 carbonates show the same general carbon-isotope trends during the Cretaceous (Fig. 6). Using  
 543 the equation proposed by Tipple *et al.* (2010), we calculated the  $\delta^{13}\text{C}$  of the Cretaceous  
 544 atmosphere ( $\delta^{13}\text{C}_{\text{ATM}}$ ) from the available  $\delta^{13}\text{C}$  data of benthic foraminifera compiled by  
 545 Prokoph *et al.* (2008). The polynomial curve fitted to the inferred  $\delta^{13}\text{C}_{\text{ATM}}$  data points shows a  
 546 small long-term decline from approx. 125 Ma to the end of the Cretaceous (Fig. 7). The  
 547  $\delta^{13}\text{C}_{\text{ATM}}$  trend seems to mimic the 2.5–3‰ negative trend described by C3 plant material,  
 548 although with much smaller magnitude (1‰) (Fig. 7). This general relationship suggests that  
 549  $\delta^{13}\text{C}$  from Cretaceous amber and other plant tissues, despite high variability within each age  
 550 bin, can record changes in the carbon-isotope composition of the atmosphere. The relatively  
 551 small atmospheric shift, however, cannot alone explain the changes in plant  $\delta^{13}\text{C}$   
 552 records. These data, however, also suggest  $\Delta^{13}\text{C}_\text{P}$  increased towards the end of the Cretaceous  
 553 along with decreasing  $\delta^{13}\text{C}_{\text{ATM}}$  values. It is thus necessary to account for changes in climate  
 554 and floral community structure, upon which plant  $\Delta^{13}\text{C}$  is strongly dependent, to faithfully  
 555 interpret Cretaceous plant  $\delta^{13}\text{C}$  data (e.g. Diefendorf *et al.*, 2010; Schubert and Jahren, 2013).  
 556  
 557 Given the different provenances of Cretaceous amber, some of the changes in its  $\delta^{13}\text{C}$  through  
 558 time and the large variability within each age bin (Fig. 6) can be attributed to local plant  
 559 growing conditions, which are hardly constrainable for amber deposits, given the fact that  
 560 amber is rarely found *in situ* and is mostly reworked. The altitude of the Cretaceous resin-  
 561 producing trees, seemingly an important control on modern resin carbon-isotope signature  
 562 (see section 3), is relatively well known for those examples situated close to former sea level,  
 563 namely the Albian amber deposits (Peñacerrada, El Soplao), Albian-Cenomanian amber  
 564 deposits (Archingeay-Les Nouillers, Cadeuil, Fouras, Ile d'Aix, La Buzinie: Néraudeau *et al.*,



565 2009; Girard *et al.*, 2008) and the Santonian amber deposits (Belcodène, Piolenc: Gomez *et*  
 566 *al.*, 2003; Saint-Martin *et al.*, 2013). However, for other deposits the palaeo-altitude is  
 567 unknown and presumably variable. The depleted  $\delta^{13}\text{C}$  values of Campanian amber from  
 568 Canada could be partially related to a particularly high palaeo-latitudinal location of the  
 569 deposits (Fig. 1) and possibly from a different climatic regime (see compilation by Scotese  
 570 2002). Insect infestation has been shown to have substantially  $^{13}\text{C}$ -enriched the  $\delta^{13}\text{C}$  of part of  
 571 the Turonian New Jersey ambers analysed by McKellar *et al.* (2011), which are also included  
 572 in our dataset (Fig. 6). At a micro-environmental scale, the height at which the Cretaceous  
 573 amber was produced within the tree trunk is impossible to determine, and this factor has been  
 574 previously shown to affect the  $\delta^{13}\text{C}$  of modern resin by several ‰ (see section 3). Different  
 575 fractionation pathways of different plant functional type through time could also be  
 576 responsible for the  $\delta^{13}\text{C}_{\text{AMBER}}$  changes (Diefendorf *et al.*, 2010). In fact, the species  
 577 composition responsible for the amber production differed through the Cretaceous, even  
 578 though the number of species remained the same (1–2) for each time interval (see, e.g.,  
 579 Tappert *et al.*, 2013; Nohra *et al.*, 2015). As previously described, modern  $\delta^{13}\text{C}_{\text{RESIN}}$  varies by  
 580 up to 6‰ between plant species from different localities (Table 1), and the  $\delta^{13}\text{C}$  of resins  
 581 sampled in the same locality from different tree species differs by about 2–5‰ (Fig. 3B). To  
 582 avoid this problem it is recommended to use a plant substrate that averages the inter-specific  
 583 carbon-isotope differences for palaeo-atmosphere reconstructions (e.g. Arens *et al.*, 2000).  
 584  
 585 Significantly, the Cretaceous Period was a time of rapid taxonomic diversification and  
 586 ecological radiation of Angiosperms, starting from the Aptian–Albian and continuing to the  
 587 Campanian (McElwain *et al.*, 2005). Angiosperm tissue  $\delta^{13}\text{C}$  is generally more depleted than  
 588 conifer tissue  $\delta^{13}\text{C}$  (Arens *et al.*, 2000; Diefendorf *et al.*, 2010), something reflected in the  
 589 isotopic composition of modern resin (Murray *et al.*, 1998). The decline in the carbon-isotope  
 590 composition of plant material, of which the botanical affinity is unknown, from the Early to

the latest Cretaceous (Fig. 6) could be related to an increase in the relative abundance of Angiosperms. This factor could lie behind the ISOORG trends, where tissues from different sources are lumped together (charcoal, coal, leaf, wood and bulk terrestrial organic matter), but Cretaceous amber considered in this study comes only from conifers (e.g. Tappert *et al.*, 2013). Therefore, micro-environmental conditions, different plant functional type discrimination, and diagenesis (see 4.2.1) are all factors that could have modified the Cretaceous plant  $\delta^{13}\text{C}$  signature and determined the high variability for each age bin, but such factors are difficult to constrain for the fossil record and thus their relative effect on plant  $\delta^{13}\text{C}$  cannot be calculated. On the other hand, the similar general long-term  $\delta^{13}\text{C}$  patterns shown by ISOORG, wood, and amber suggest there is a global dominant factor that regulated plant discrimination throughout the long time scale of the Cretaceous (from 145 Ma to 66 Ma; Gradstein *et al.*, 2012).

Today, MAP accounts for more than the 50% of the variations observed in plant  $\Delta^{13}\text{C}$ , implying that stomatal conductance ( $c_i/c_a$  in eq.1) is primarily driven by water availability: The  $\Delta^{13}\text{C}_p$  increases with increasing MAP (Diefendorf *et al.*, 2010; Kohn 2010). Diefendorf *et al.* (2015) shows that  $\Delta^{13}\text{C}_p$  in Palaeogene plants responded to water availability in a way similar to modern plants. MAP calculated from compact-corrected depth to calcic horizon in palaeosols in the Colorado Plateau (Retallack, 2009) indicates Late Cretaceous MAP was higher (approx. 600–650 mm on average) than the Early Cretaceous MAP (approx. 450 mm on average) in the study area (Fig. 7). According to the general  $\Delta^{13}\text{C}_p$ –MAP relationship calculated for modern leaves (Diefendorf *et al.*, 2010), such increase of MAP would increase the  $\Delta^{13}\text{C}_p$  by approx. 1–2‰. Consequently, plant carbon-isotope composition would become more  $^{13}\text{C}$ -depleted, suggesting that Cretaceous plant  $\delta^{13}\text{C}$  data record changes in the global hydrological cycle, as predicted by the relationships found by Diefendorf *et al.* (2010) and Kohn (2010) for modern leaf  $\delta^{13}\text{C}$ . Calculation of Cretaceous MAP from  $\delta^{13}\text{C}_{\text{PLANT}}$

compilations using the proposed relationships is not possible. Information to compute the data (plant functional type, altitude and latitude of growing site) is either missing or very vague, and the plant substrate is mixed, i.e. derives from different plant tissues (amber, wood, charcoal, coal, leaf, bulk terrestrial organic matter) for which the botanical affinity is largely unknown.

Schubert and Jahren (2012) found a strong relationship between  $\Delta^{13}\text{C}_\text{P}$  and  $p\text{CO}_2$  for plants grown in chambers with controlled environmental conditions. According to their model, plant  $\Delta^{13}\text{C}_\text{P}$  hyperbolically increases with increasing  $p\text{CO}_2$  levels. This relationship was validated against ice-core  $p\text{CO}_2$  data for the Last Glacial Maximum and used to reconstruct the  $p\text{CO}_2$  at the Palaeocene–Eocene Thermal maximum (Schubert and Jahren, 2013, 2015). In contrast to these studies, Cretaceous  $\delta^{13}\text{C}_\text{AMBER}$  and  $\delta^{13}\text{C}_\text{ISOORG}$  shows the most  $^{13}\text{C}$ -enriched values in intervals of predicted high  $p\text{CO}_2$  and the most  $^{13}\text{C}$ -depleted values in intervals of predicted low  $p\text{CO}_2$  (Fig. 7, see also Wang *et al.*, 2014), as also previously noted by Tappert *et al.* (2013). Precise calculation of  $\Delta^{13}\text{C}_\text{P}$  is not possible for our dataset, given the age uncertainties of the samples and thus the difficulty in assigning to each  $\delta^{13}\text{C}_\text{PLANT}$  data point a precise value of  $\delta^{13}\text{C}_\text{ATM}$ . However, as previously described, comparison of the magnitude of the long-term negative trend of  $\delta^{13}\text{C}_\text{ATM}$  with the magnitude of amber and similar ISOORG  $\delta^{13}\text{C}$  trend suggests that  $\Delta^{13}\text{C}_\text{P}$  increased in the Late Cretaceous. This result suggests that either  $p\text{CO}_2$  has no effect on plant  $\delta^{13}\text{C}$  during the Cretaceous or that the  $p\text{CO}_2$  reconstructions made via biogeochemical modelling are incorrect. Similar to what was found in this study, Diefendorf *et al.* (2015) found that  $\Delta^{13}\text{C}_\text{P}$  does not increase in correspondence with intervals of high  $p\text{CO}_2$  in the Palaeogene. Kohn (2016) found no or negligible  $p\text{CO}_2$  dependence of  $\delta^{13}\text{C}_\text{PLANT}$  in selected Cenozoic case studies. This phenomenon is explained by the ability of plants to evolve within decadal–centurial timescales in response to changing  $p\text{CO}_2$  by adjusting their physiology to maintain an ideal  $c_i/c_a$  ratio (Diefendorf *et al.*, 2015; Kohn *et al.*, 2016 and

643 references therein). By contrast, on shorter timescales (<1 year chamber growth experiments),  
 644 plants respond to changing  $p\text{CO}_2$  through the stomata, thus changing the  $c_i/c_a$  (eq.1;  
 645 Diefendorf *et al.*, 2015).  
 646  
 647 The  $\delta^{13}\text{C}$  of amber and plant tissues seems to decrease with increasing  $p\text{O}_2$  levels, as  
 648 independently inferred by biogeochemical modelling (Berner 2009) and charcoal abundance  
 649 (Glasspool and Scott, 2010) (Fig. 7). Such a relationship is in line with theoretical  
 650 expectations and the results obtained in controlled chamber experiments, which show plant  
 651  $\Delta^{13}\text{C}$  increases by 1.5–3.5‰ in high (35%)  $p\text{O}_2$  (Berner *et al.*, 2000; Beerling *et al.*, 2002). As  
 652 previously described, Tappert *et al.* (2013) proposed the use of  $\delta^{13}\text{C}_{\text{AMBER}}$  to reconstruct  
 653 palaeo- $p\text{O}_2$ , assuming that, at ambient air, the  $\Delta^{13}\text{C}_p$  is proportional to  $p\text{O}_2$  and that  
 654 physiological adaptations did not occur through time. The Cretaceous  $p\text{O}_2$  model proposed by  
 655 Tappert *et al.* (2013) fails to reproduce the  $p\text{O}_2$  trends calculated by other authors (Fig. 7) and  
 656 contradicts plant  $\delta^{13}\text{C}$  data compiled in this study. This difference could be related to the  
 657 difficulty in calculating past  $\delta^{13}\text{C}_{\text{ATM}}$  and the use of mean  $\delta^{13}\text{C}_{\text{AMBER}}$ , which are terms in the  
 658 equations proposed by Tappert *et al.* (2013) to infer  $p\text{O}_2$  from  $\delta^{13}\text{C}_{\text{AMBER}}$ . Indeed, small  
 659 variations in growing conditions, such as light exposure, nutrient, and water levels, can mask  
 660 the  $p\text{O}_2$  effect on plant  $\delta^{13}\text{C}$ , as shown during controlled chamber experiments (Beerling *et al.*, 2002). Therefore, accurate reconstruction of past atmospheric  $p\text{O}_2$  from mean  $\delta^{13}\text{C}$  of  
 661 ambers is fraught with difficulties, given that the  $\delta^{13}\text{C}$  of resin varies enormously, even at the  
 662 scale of a single tree (see section 3). Moreover, Tappert *et al.* (2013) assumed in their model  
 663 that physiological adaptations did not occur but, as discussed above, on long timescales plants  
 664 do evolve to maintain an ideal leaf–gas exchange optimum. The observed correspondence  
 665 between biogeochemical modelling and charcoal  $p\text{O}_2$  records, and  $\delta^{13}\text{C}_{\text{PLANT}}$  (both amber and  
 666 other tissues) points to a possible  $p\text{O}_2$  effect on Cretaceous C3  $\Delta^{13}\text{C}_p$  that definitely deserves  
 667 further exploration.

669

## 670 5. CONCLUSIONS

671

672 Our carbon-isotope analysis of modern conifer resin and associated plant tissues showed that  
673 Hardening after exudation causes an overall  $^{13}\text{C}$ -enrichment in the bulk carbon-isotope  
674 signature of resin. This is evident comparing the  $\delta^{13}\text{C}$  of liquid-viscous (mean =  $-25.9\text{‰}$ ) to  
675 the  $\delta^{13}\text{C}$  of solid resins (mean =  $-27.1\text{‰}$ ) and is explained by selective loss of  $^{13}\text{C}$ -depleted  
676 volatiles. Carbon-isotope fractionation during resin biosynthesis occurs and results in a more  
677  $^{13}\text{C}$ -enriched  $\delta^{13}\text{C}_{\text{RESIN}}$  signature (by approx.  $2\text{--}4\text{‰}$ ) than the  $\delta^{13}\text{C}$  of other tissues sampled  
678 from the same plant branch. By contrast, wood and leaf  $\delta^{13}\text{C}$  show little difference ( $<1\text{‰}$ )  
679 within the same branch. Results of this study suggest post-photosynthetic  $\Delta^{13}\text{C}$  is larger in  
680 resin than in other plant tissues. Furthermore, the variability of the  $\delta^{13}\text{C}_{\text{RESIN}}$  is high (approx.  
681  $8\text{‰}$ ), from  $-30.6\text{‰}$  to  $-22.8\text{‰}$ .  $\delta^{13}\text{C}_{\text{RESIN}}$  shows differences of up to  $6\text{‰}$  between plant  
682 species, locality and within a single tree.  $\delta^{13}\text{C}_{\text{RESIN}}$  of different tree genera growing in the  
683 same locality and at the same altitude shows differences of about  $2\text{--}5\text{‰}$   $\delta^{13}\text{C}_{\text{RESIN}}$ .  $\delta^{13}\text{C}_{\text{RESIN}}$   
684 seems to become more  $^{13}\text{C}$ -enriched with increasing altitude. The environmental variability of  
685  $\delta^{13}\text{C}$  of resin is similar to that reported for leaf and wood, suggesting the potential to record  
686 changes in  $\Delta^{13}\text{C}$  by C3 plants. Therefore, resin appears to be a valuable substrate for carbon-  
687 isotope studies in modern plant ecology and physiology.

688

689 Our meta-analysis of new and published Cretaceous  $\delta^{13}\text{C}_{\text{PLANT}}$  (amber, wood and mixed  
690 substrates) revealed that Cretaceous  $\delta^{13}\text{C}_{\text{AMBER}}$  (mean =  $-22.3\text{‰} \pm 1.9\text{‰}$ ) is more  $^{13}\text{C}$ -enriched  
691 than other C3 plant material  $\delta^{13}\text{C}$  (mean =  $-24.2\text{‰} \pm 1.3\text{‰}$ ) and wood (mean =  $-23.1\text{‰} \pm 1.3\text{‰}$ ),  
692 as observed in modern plants. Therefore, fossil material can retain the same patterns observed  
693 in modern samples, i.e. the differences being generated by  $\Delta^{13}\text{C}$  during resin biosynthesis. In  
694 the Cretaceous,  $\delta^{13}\text{C}_{\text{AMBER}}$  has variability similar to modern resin, but the scatter of  $\delta^{13}\text{C}_{\text{AMBER}}$

data is larger than the scatter of  $\delta^{13}\text{C}$  data of other fossil C3 plant material, which is attributed to diagenesis. Amber has been shown to become a closed system with respect to carbon isotopes soon after hardening, whereas other plant remains can experience a more pervasive diagenetic overprint (both  $^{13}\text{C}$  enrichment or depletion). Diagenetic processes could be responsible also for narrowing  $\delta^{13}\text{C}$  variability by selectively removing specific compounds. These observations suggest amber can preserve the pristine  $\delta^{13}\text{C}$  signature better than other plant tissues and, consequently, the original high  $\delta^{13}\text{C}$  variability as shown by modern plants. Thus, amber can retain faithful information about past environments and climate. Despite the large variability, amber, wood, and mixed plant (ISOORG) record similar long-term trends during the Cretaceous. In particular, plant material record a 2.5–3‰ negative trend from the Hauterivian–Barremian to the Maastrichtian that mirrors a similar but smaller (1‰) shift in the  $\delta^{13}\text{C}$  of the atmosphere calculated from benthic foraminifera  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  data compilation. Increasing mean annual precipitation and/or  $p\text{O}_2$  levels could have increased  $\Delta^{13}\text{C}$  of plants during the Cretaceous, thus increasing the magnitude of the negative trend. Comparing the isotopic records with  $p\text{CO}_2$  trends suggests that  $p\text{CO}_2$  did not affect plant  $\Delta^{13}\text{C}$  on the long-time scales considered in this study.

Our study thus shows that in the deep past the interpretation of the  $\delta^{13}\text{C}_{\text{AMBER}}$  curve and, by extension, the  $\delta^{13}\text{C}$  of terrestrial plants, is ambiguous to some extent due to the difficulty in constraining the environmental and physiological factors that control the natural variability of  $\delta^{13}\text{C}_{\text{RESIN}}$  and the uncertainties in determining the age of some of the analysed material. However, meta-analysis of marine and terrestrial  $\delta^{13}\text{C}$  records coupled to the amber record reveals isotopic variations that seem ascribable to changes in the composition of the Cretaceous atmosphere–ocean system and climate. Improvement of the resolution of the existing data and collection of information about botanical source and environmental growing

conditions of the fossil plant material will undoubtedly improve our understanding of amber  $\delta^{13}\text{C}$  records and allow more faithful reconstruction of the past atmosphere.

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# 995 FIGURE CAPTIONS

996

**Figure 1.** Location of the sampling sites of modern resins (A) and Cretaceous amber (B) analysed for carbon isotopes. Red dots = this study; orange dots = previous studies (Nissenbaum & Yakir, 1995; Dal Corso *et al.*, 2013; Tappert *et al.*, 2013).

**Figure 2.** Distribution of modern resin  $\delta^{13}\text{C}$  (orange histogram) and range of variability of modern C3 plants from Cerling & Harris (1999) and Tippie & Pagani (2007).

**Figure 3.** A) Carbon-isotope composition of liquid-viscous vs solid modern resin (Students' *t*-test *p* value = 0.001). Resin data are compared to a compilation of leaf data taken from Diefendorf *et al.* (2010). Data are represented as box-and-whiskers plots in order to highlight differences in distribution. The bars represent the first and fourth quartile, the box represents the second and third quartile, and the mid-line is the median. All investigated species of both genera are considered. Variation of the carbon-isotope composition (B) of solid resin, wood and leaves from different trees (two trees of *Araucaria heterophylla*, a *Picea abies* tree and a *Cupressus arizonica* tree) and (C) of solid resin collected from a single tree of *Araucaria heterophylla* at different heights. Samples in boxes (B) and (C) were collected in the botanical gardens of the University of Padova.

**Figure 4.** Carbon-isotope data of (A) modern liquid-viscous resin, and (B) *Pinus* and *Araucaria* resin plotted against altitude of the plant-growing site.

**Figure 5.** (A) Comparison of the  $\delta^{13}\text{C}$  data distribution of Cretaceous C3 plant material from the ISOORG database (Nordt *et al.*, 2016) with amber. (B) Box-and-whiskers plots of  $\delta^{13}\text{C}$  data of modern leaves (Diefendorf *et al.*, 2010) and resin (this study), and Cretaceous ISOORG plants (Nordt *et al.*, 2016), wood (Nordt *et al.*, 2016; Salazar-Jaramillo *et al.*, 2016)

1022 and amber (this study; Nissenbaum & Yakir, 1995; Dal Corso *et al.*, 2013; Tappert *et al.*,  
1023 2013).

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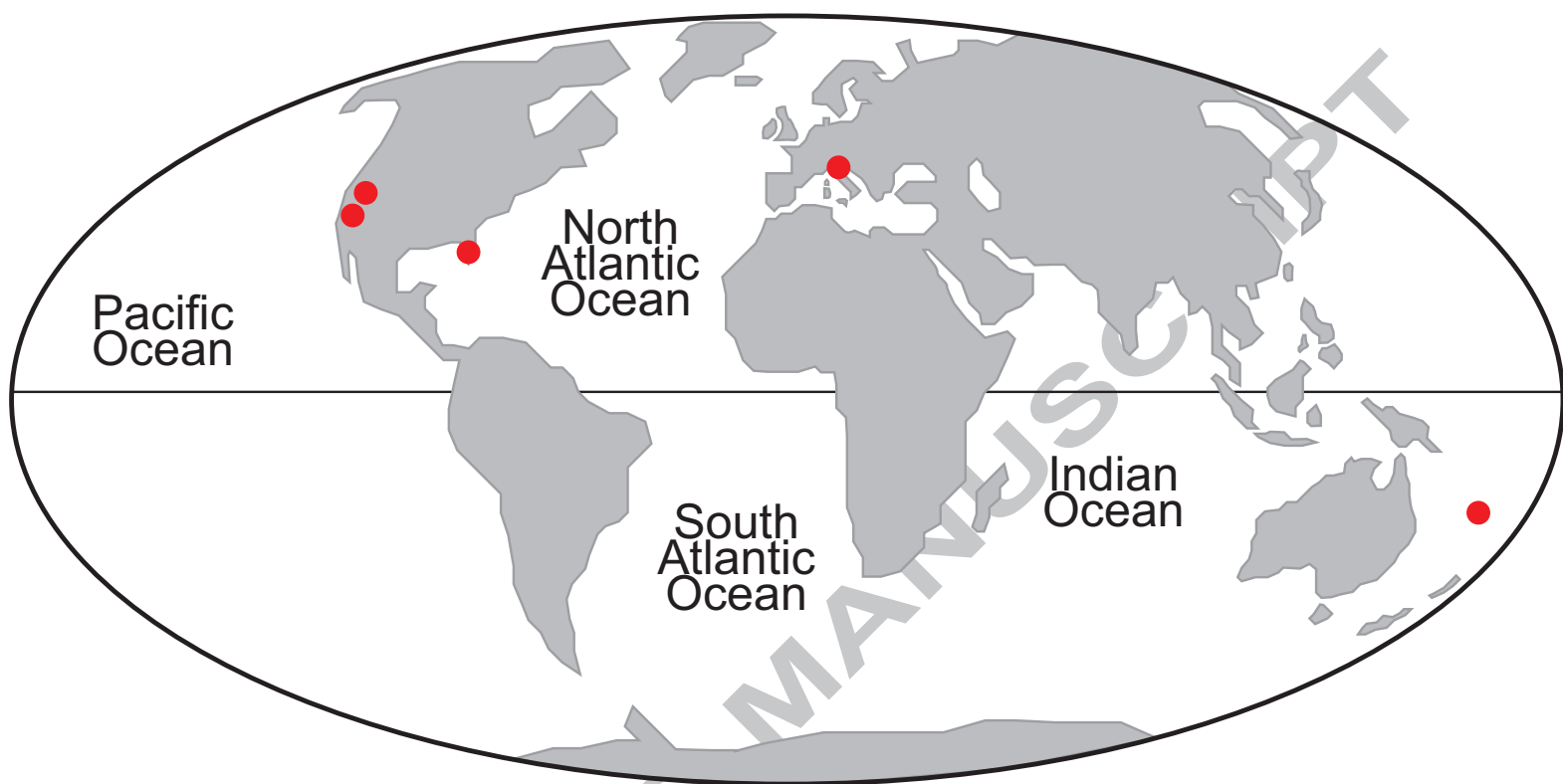
1025 **Figure 6.** Carbon-isotope ( $\delta^{13}\text{C}$ ) curves from Cretaceous amber, terrestrial organic matter,  
1026 marine carbonate.  $\delta^{13}\text{C}$  data from plant material was grouped in 5Myrs bins following the  
1027 method used by Nordt *et al.* (2016) and a third-degree polynomial curve was fit to the plant  
1028 data to highlight the main trends shown through the Cretaceous (see text for further  
1029 explanation). (A) Compilation of Cretaceous amber carbon-isotope data from this study and  
1030 Nissenbaum & Yakir (1995), Dal Corso *et al.* (2013) and Tappert *et al.* (2013). (B) Wood  $\delta^{13}\text{C}$   
1031 data from Nordt *et al.* (2016) and Salazar-Jaramillo *et al.* (2016). (C) ISOORG  $\delta^{13}\text{C}$  data from  
1032 Nordt *et al.* (2016). ISOORG database comprises isotopic data from wood, leaf, charcoal,  
1033 coal, palaeosols, bulk terrestrial organic matter. (D) Marine carbonate carbon-isotope data  
1034 from planktonic and benthic foraminifera, and belemnites (Prokoph *et al.*, 2008 and Bodin *et*  
1035 *al.*, 2015). Whole-rock general carbonate curve (black line) replotted from Erba (2004). The  
1036 arrows represent the main carbonate  $\delta^{13}\text{C}$  trend during the Cretaceous. Time scale after  
1037 Gradstein *et al.* (2012).

1038

1039 **Figure 7.** Plant (amber and other tissues from the ISOORG database)  $\delta^{13}\text{C}$  trends during the  
1040 Cretaceous compared with the carbon-isotope composition of the atmosphere ( $\delta^{13}\text{C}_{\text{ATM}}$ )  
1041 calculated from benthic foraminifera  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  (from Prokoph *et al.*, 2008), the Mean  
1042 Annual Precipitation (MAP) as reconstructed from compact-corrected depth to calcic horizon  
1043 in palaeosols in the Colorado Plateau (Retallack, 2009), the  $p\text{CO}_2$  calculated by different  
1044 biogeochemical models, and the  $p\text{O}_2$  inferred from charcoal abundance (Glasspool and Scott,  
1045 2010), biogeochemical modelling (Berner, 2009), and amber  $\delta^{13}\text{C}$  (Tappert *et al.*, 2013).

1046

## Modern Resins



## Cretaceous (Albian - Cenomanian) resins

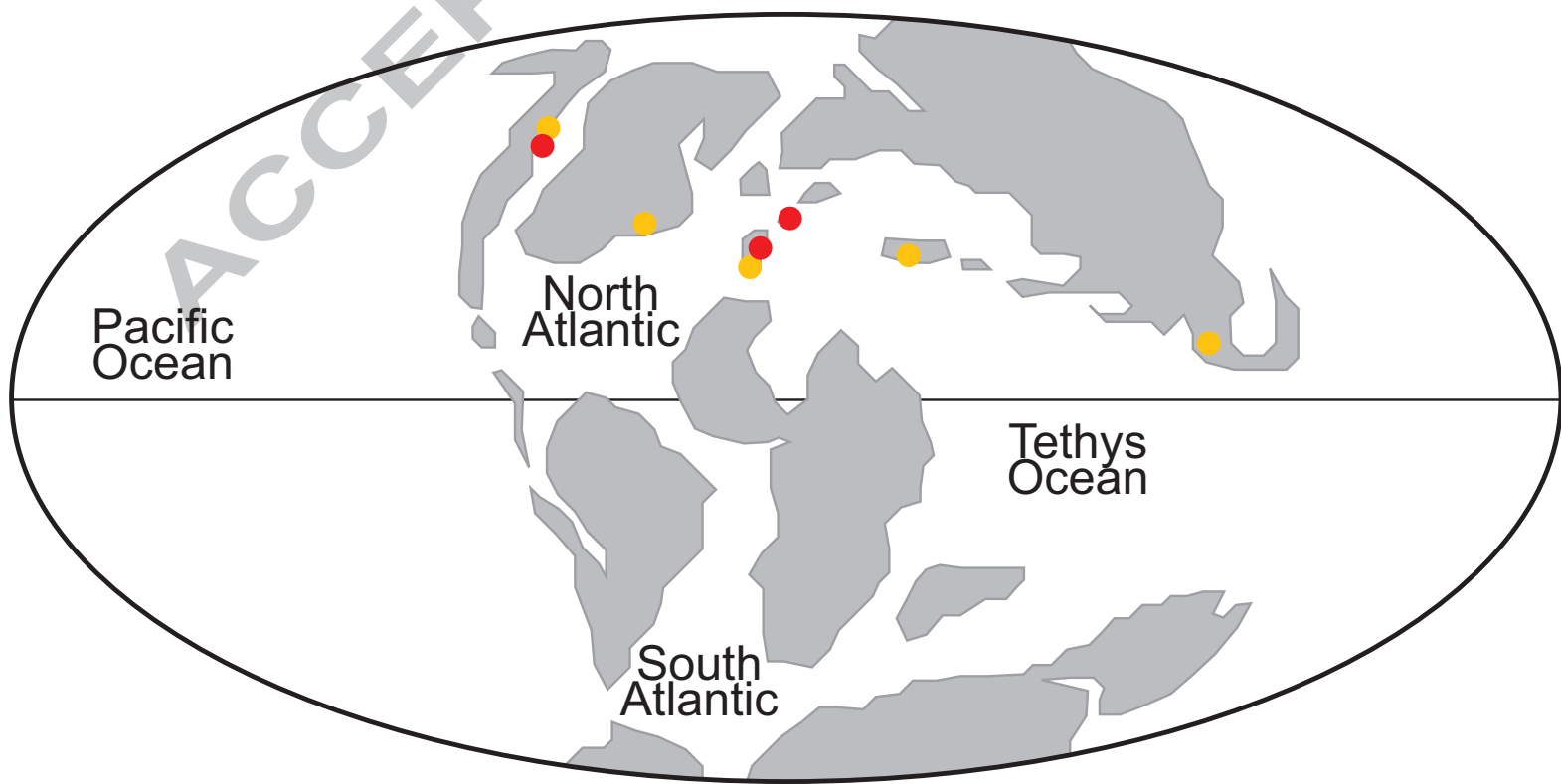


Figure 2

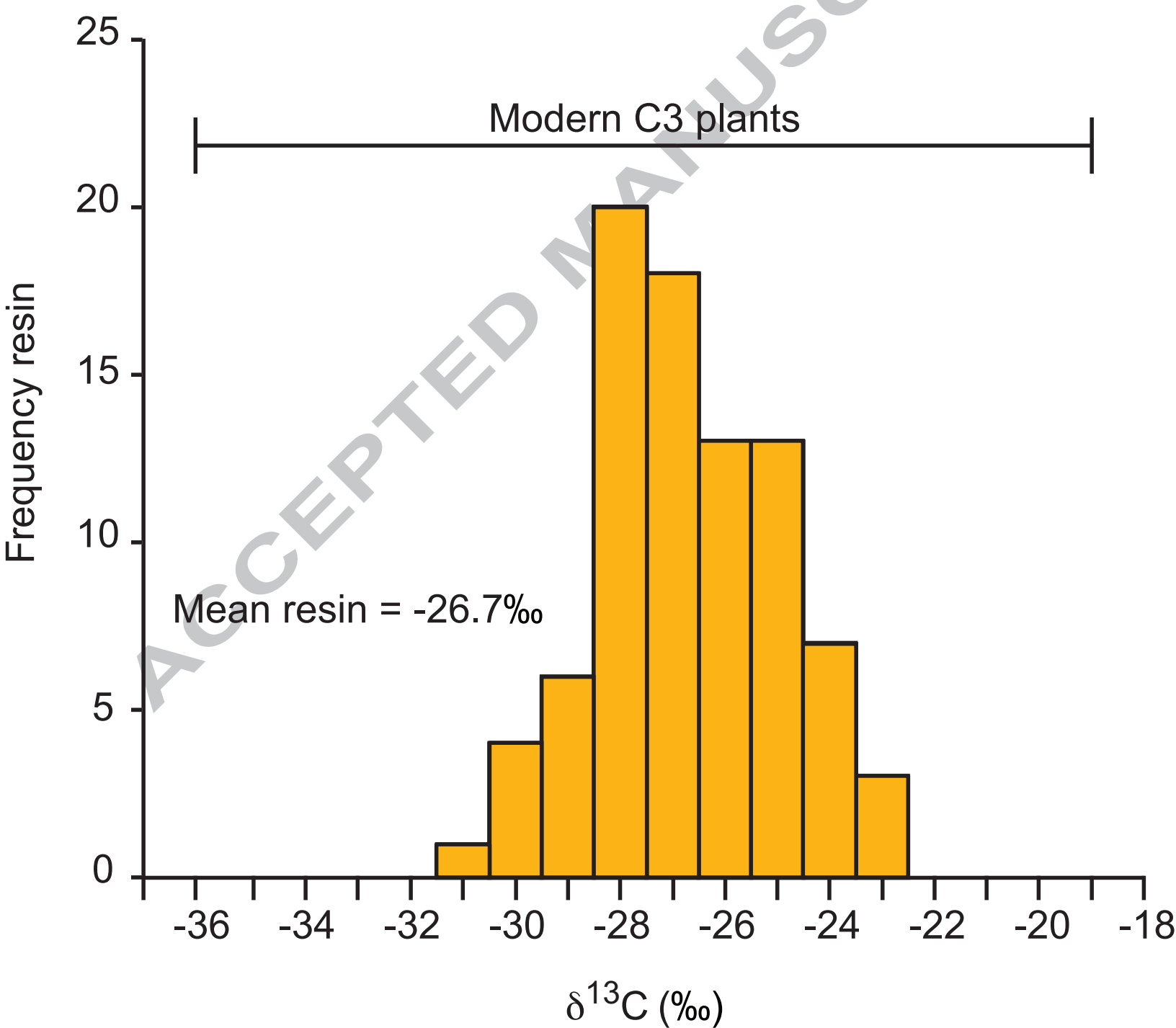
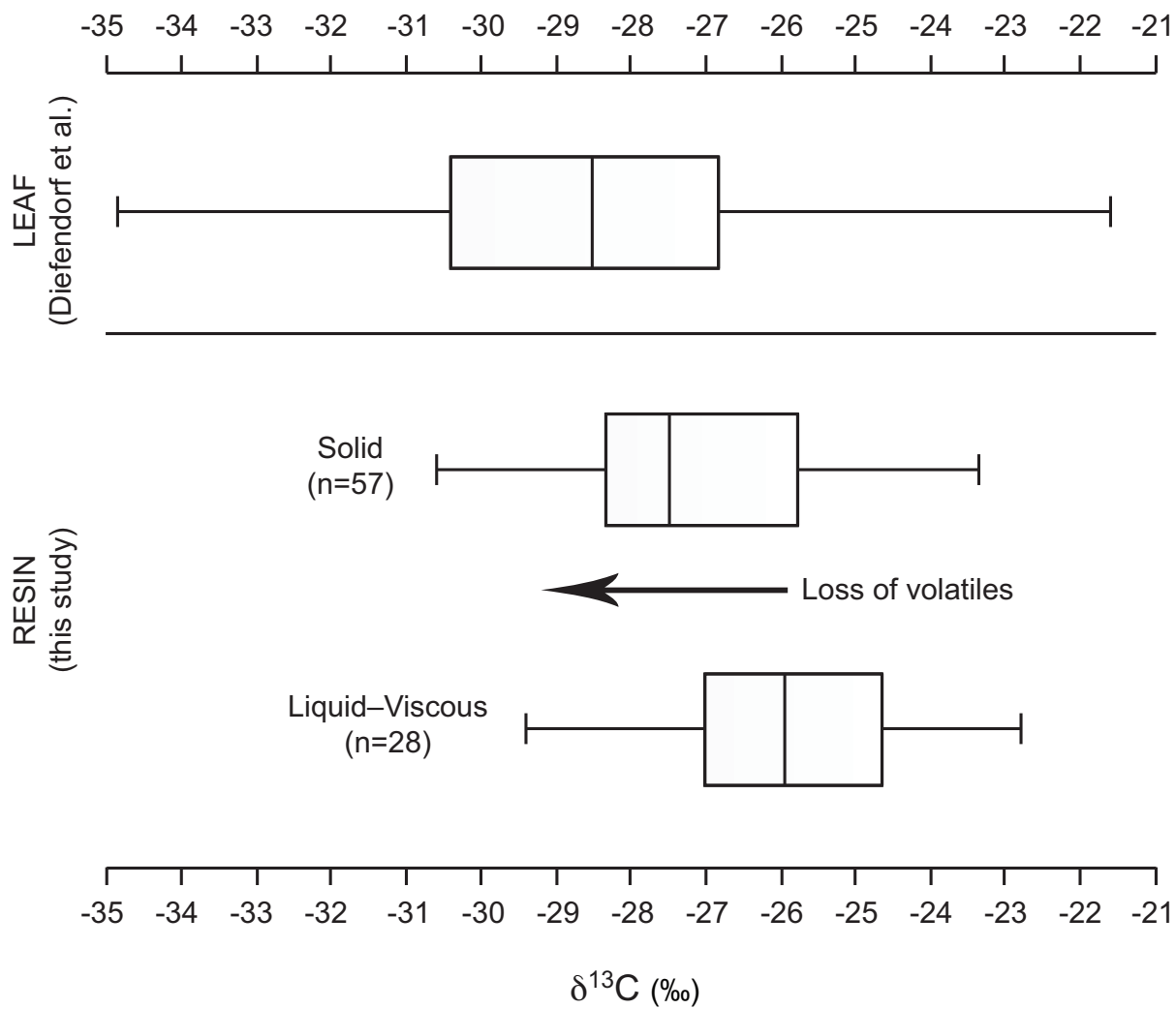
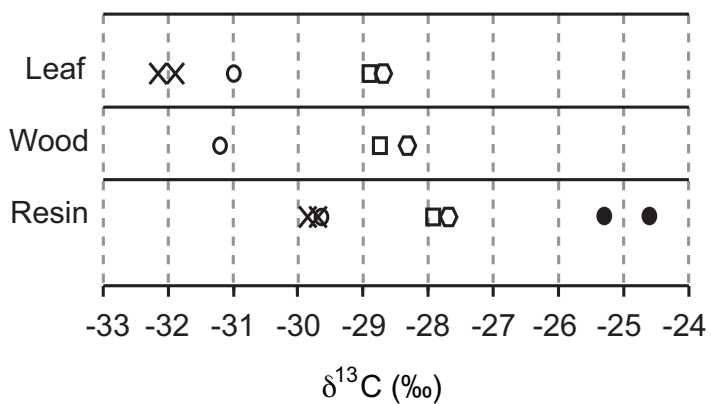


Figure 3  
A

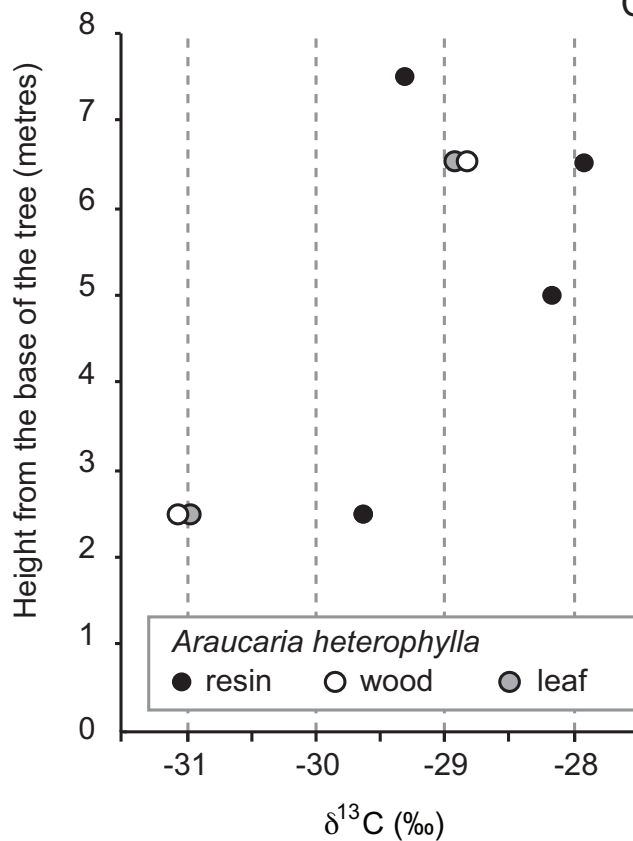


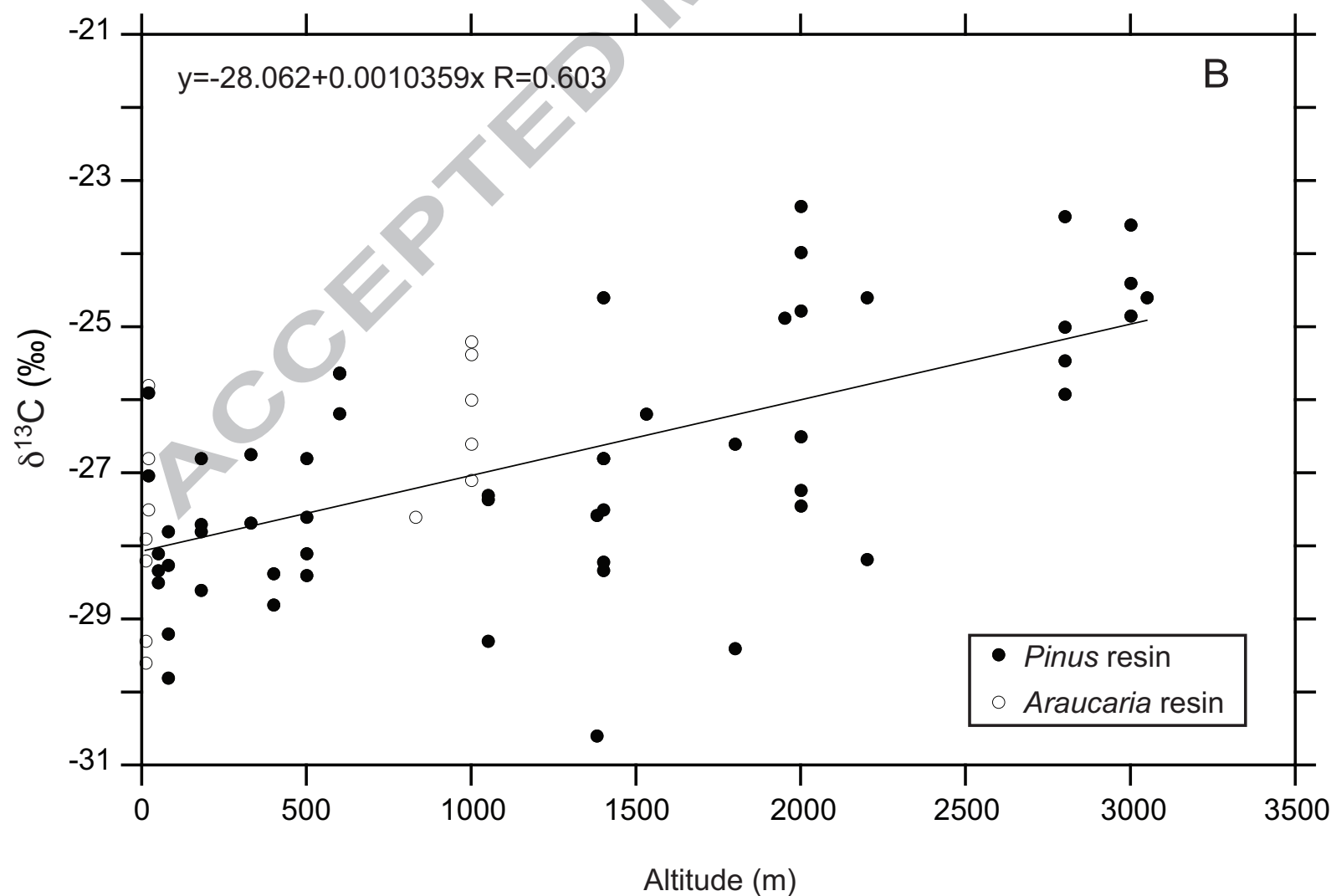
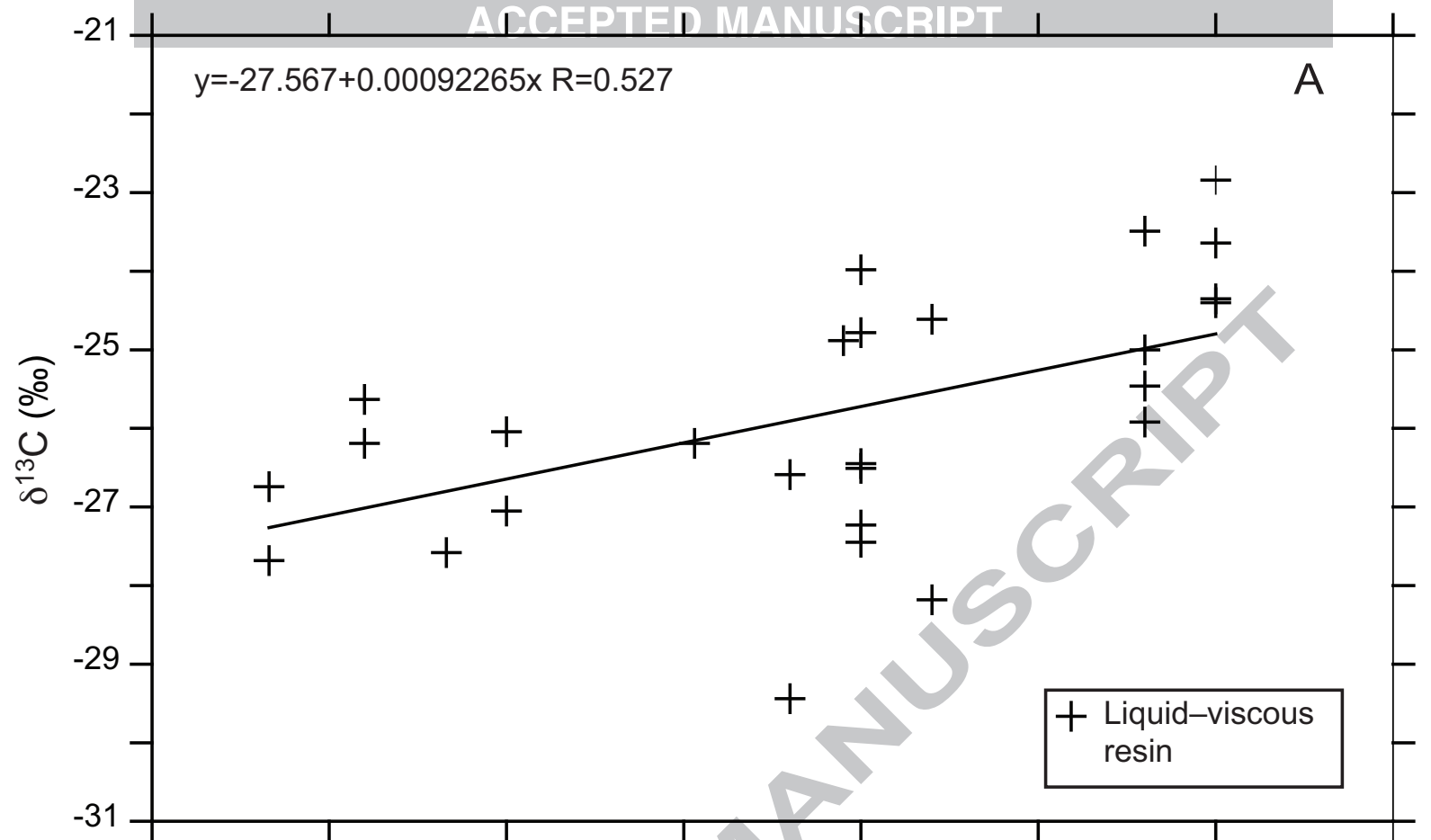
B



○ *Araucaria heterophylla*    ◇ *Picea abies*  
 □ *A. heterophylla*    × *Cupressus arizonica*  
 ● *Cedrus deodara*

C





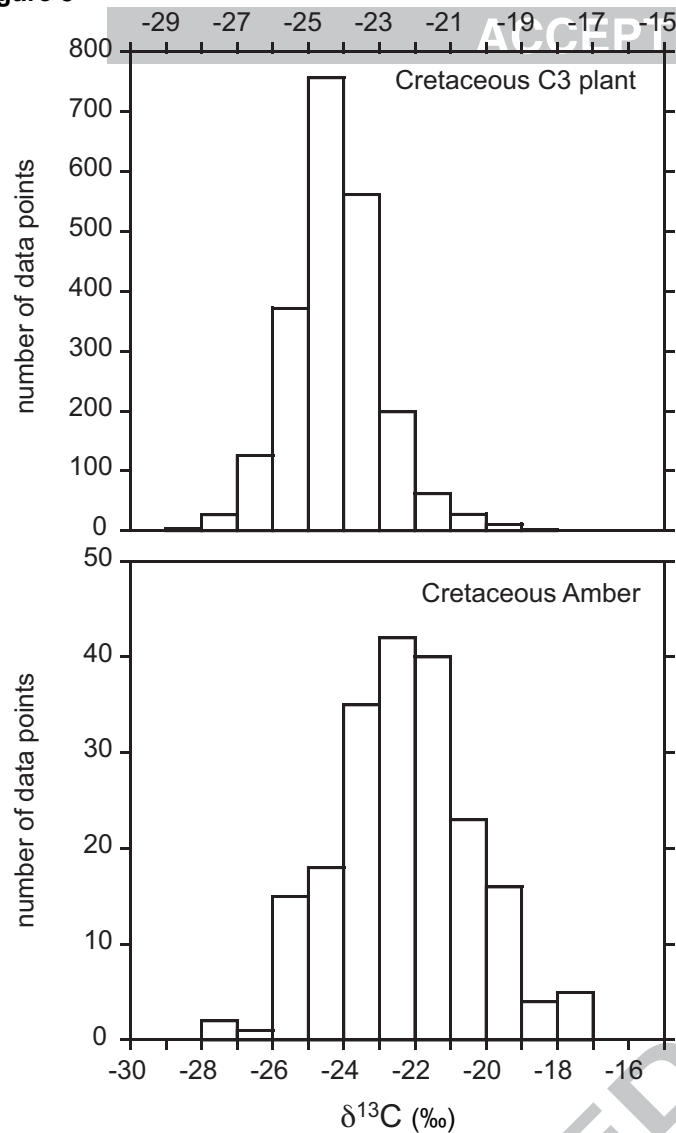
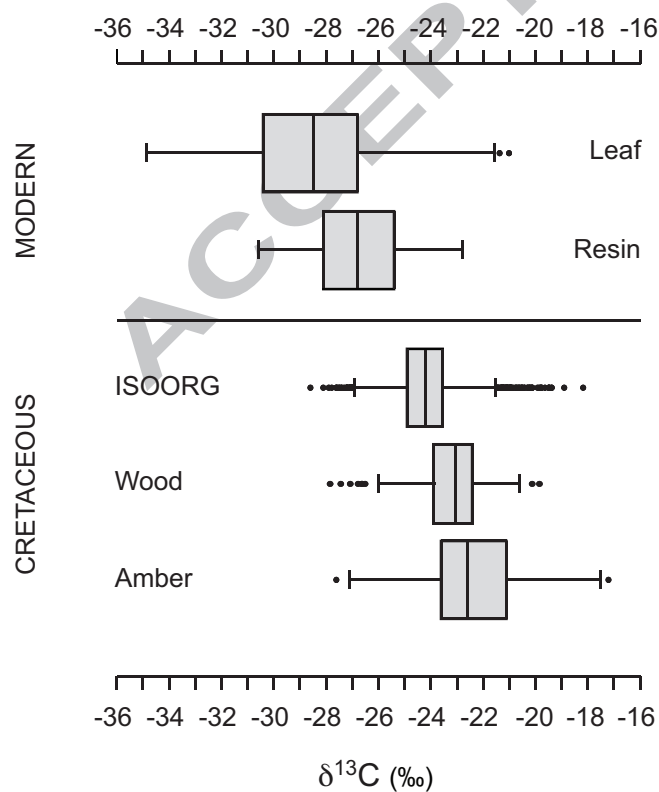
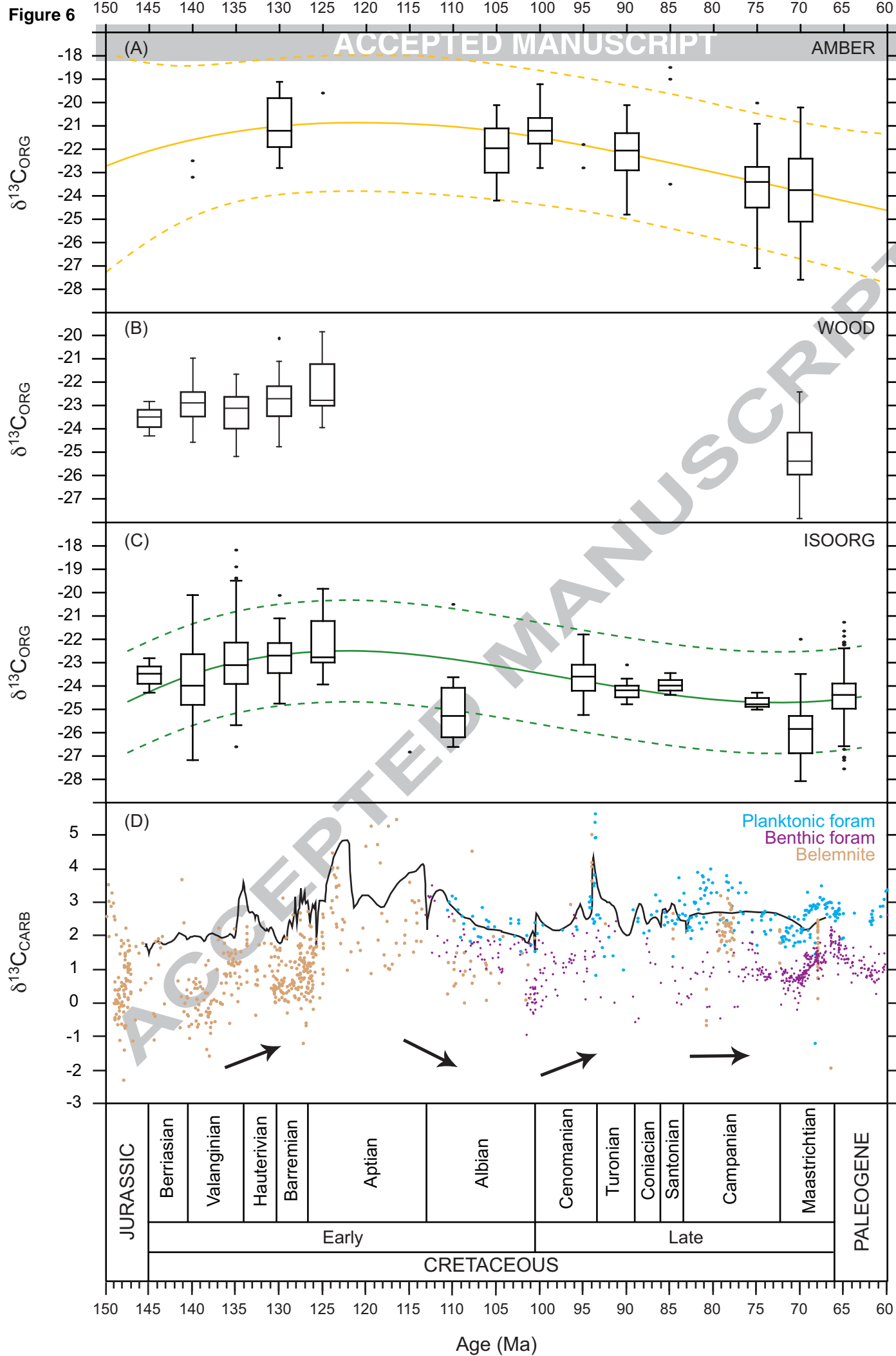
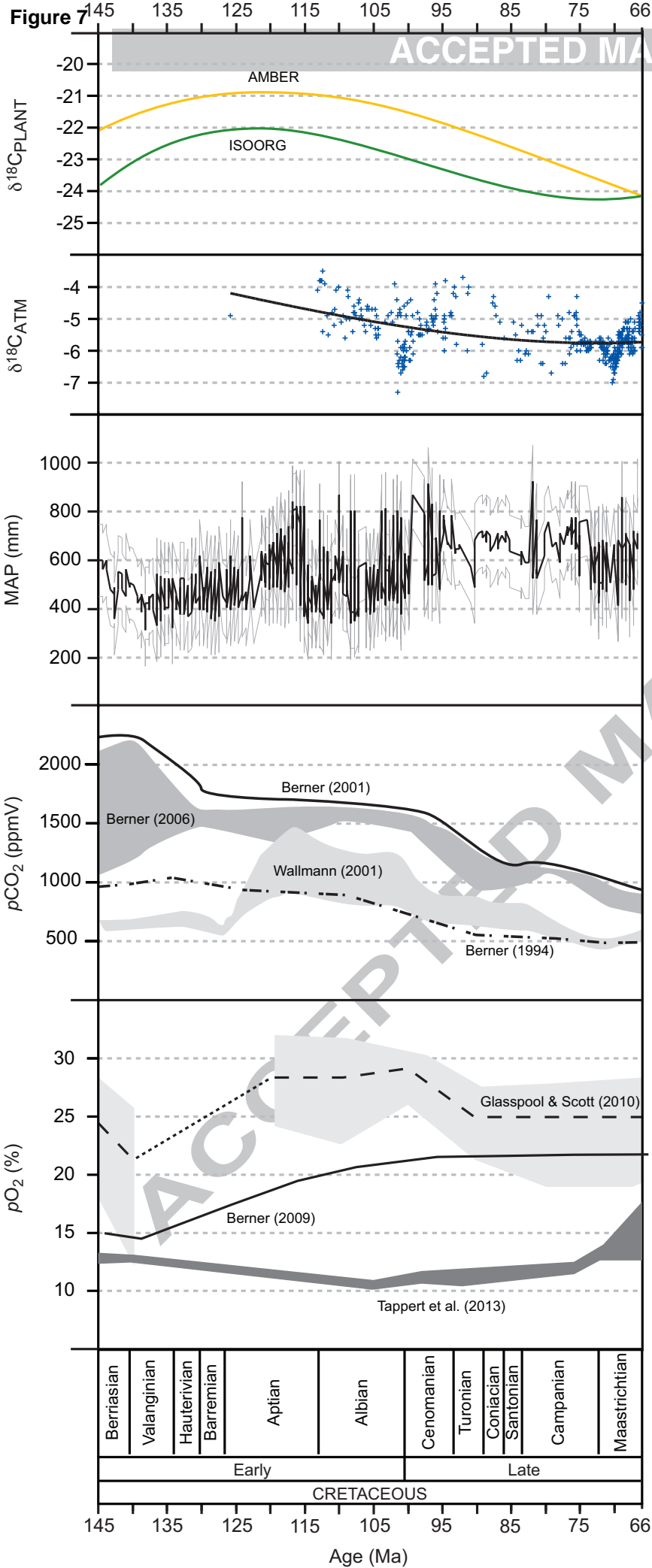
**Figure 5****B**



Figure 6





**Table 1.** Plant species, from which resin was collected, resin mean carbon-isotope values for each species (mean  $\pm$  standard deviation (SD) and sample size.

Species	$\delta^{13}\text{C} \pm \text{SD} (\text{‰})$	n.
<i>Abies concolor</i>	-23.7	1
<i>Abies magnifica</i>	-23.6 $\pm$ 1.1	2
<i>Agathis lanceolata</i>	-24.5 $\pm$ 0.2	2
<i>Agathis moorei</i>	-25.9 $\pm$ 0.4	2
<i>Agathis ovata</i>	-25.7	1
<i>Araucaria</i> (all species listed below)	-27.1 $\pm$ 1.4	13
<i>Araucaria columnaris</i>	-26.3 $\pm$ 1.3	4
<i>Araucaria excelsa</i>	-28.8 $\pm$ 0.8	4
<i>Araucaria humboldtensis</i>	-26.3 $\pm$ 0.7	4
<i>Araucaria rulei</i>	-27.6	1
<i>Cedrus deodara</i>	-24.9 $\pm$ 0.5	2
<i>Cupressus arizonica</i>	-29.8 $\pm$ 0.1	2
<i>Falcatifolium taxoides</i>	-24.4	1
<i>Juniperus occidentalis</i>	-27.4	1
<i>Picea abies</i>	-27.7	1
<i>Pinus</i> (all species listed below)	-26.9 $\pm$ 1.7	55
<i>Pinus balfouriana</i>	-24.3 $\pm$ 0.6	2
<i>Pinus coulteri</i>	-25.8 $\pm$ 0.32	3
<i>Pinus edulis</i>	-24 $\pm$ 0.7	3
<i>Pinus elliotii</i>	-28.3 $\pm$ 0.2	3
<i>Pinus jeffreyi</i>	-28.2 $\pm$ 1.1	10
<i>Pinus lambertiana</i>	-26.5 $\pm$ 1	5
<i>Pinus longaeva</i>	-24.6	1
<i>Pinus monophylla</i>	-24.9 $\pm$ 0.9	5
<i>Pinus monticola</i>	-28 $\pm$ 2	2
<i>Pinus muricata</i>	-28.2 $\pm$ 0.9	8
<i>Pinus ponderosa</i>	-27.2 $\pm$ 1.3	9
<i>Pinus radiata</i>	-26.5 $\pm$ 0.8	2
<i>Pinus sabiniana</i>	-27.2 $\pm$ 0.7	2

**Table 2.** Standard deviation (SD), interquartile range (IQR) and sample size (n.) of  $\delta^{13}\text{C}$  data of modern resin and leaf, and Cretaceous amber, wood and other mixed C3 plant material (from ISOORG; TOM = bulk terrestrial organic matter). For the Cretaceous, SD and IQR have been also calculated per each 5Myrs age bin from 65Ma to 145Ma (see text and Nordt *et al.*, 2016 for explanations). Bins not listed in the table contain no data. ISOORG and wood data are taken from Nordt *et al.* (2016) and Salazar-Jaramillo *et al.* (2016).

AGE	Type	Mean (‰)	SD (‰)	IQR (‰)	n.
Modern	Resin	-26.7	1.77	2.7	85
	Leaf	-28.4	2.52	3.6	513
Cretaceous	Amber	-22.3	1.95	2.5	201
	C3 Plant	-24.2	1.31	1.4	1384
	Charcoal	-22.9	1.55	2	192
	Coal	-24.2	1.43	1.23	95
	Leaf and cuticle	-24.7	1.72	2.14	16
	TOM	-24.4	0.98	1.1	874
	Wood	-23.1	1.31	1.47	207
AGE bin	Type		SD (‰)	IQR (‰)	n.
65Ma	C3 Plant (TOM, leaf, coal)	-24.5	0.88	1.08	677
70Ma	Amber	-23.7	1.79	2.60	40
	C3 Plant (TOM, leaf, coal)	-25.9	1.17	1.60	43
	Wood	-25.2	1.32	1.80	27
75Ma	Amber	-23.5	1.39	1.75	51
	C3 Plant (TOM)	-24.7	0.30	0.38	5
85Ma	C3 Plant (TOM)	-24	0.31	0.42	14
90Ma	Amber	-22.1	1.10	1.60	36
	C3 Plant (TOM)	-24.1	0.51	0.50	9
95Ma	C3 Plant (TOM)	-23.6	0.73	1.12	167
100Ma	Amber	-21.1	0.98	1.33	11
105Ma	Amber	-22	1.33	1.85	14
110Ma	C3 Plant (leaf)	-24.8	2.03	1.88	8
125Ma	Wood	-22.2	1.15	1.78	19
130Ma	Amber	-20.8	1.20	2.10	25
	Wood	-22.8	0.93	1.29	89
135Ma	C3 Plant (coal, charcoal)	-22.9	1.49	1.78	231
	Wood	-23.3	1.04	1.36	35
140Ma	C3 Plant (coal, wood)	-23.6	1.56	2.18	87
	Wood	-22.9	0.87	1.05	37
145Ma	Wood	-23.6	0.45	0.69	12