An estimation of Central Iberian Peninsula atmospheric δ\(^13\text{C}\) and water δ\(^2\text{H}\) in the Upper Cretaceous using pyrolysis compound specific isotopic analysis (Py-CSIA) of a fossil conifer.

José A González-Pérez (1), Nicasio T Jiménez-Morillo (1), José M De la Rosa (1), Gonzalo Almendros (2), and Francisco J González-Vila (1)

(1) IRNAS-CSIC, Seville, Spain, (2) MNCN-CSIC, Madrid, Spain.

Frenelopsis is a frequently found genus of the Cretaceous floras adapted to dry, saline and in general to environmental conditions marked by severe water stress [1]. Stable isotope analysis of fossil organic materials can be used to infer palaeoenvironmental variables helpful to reconstruct plant paleohabitats [2]. In this study stable isotope analysis of organic fossil remains (FR) and humic fractions (FA, HA and humin) of Frenelopsis oligostomata are studied in bulk (C, H, O, N IRMS) and in specific compounds released by pyrolysis (C, H, Py-CSIA).

Well preserved F. oligostomata fossils were handpicked from a limestone included in compacted marls from Upper Cretaceous (Senonian c. 72 Mya) in Guadalix de la Sierra (Madrid, Spain) [3]. The fossils were decarbonated with 6M HCl. Humic substances were extracted from finely ground fossil remains (FR) by successive treatments with 0.1M Na4P2O7 + NaOH [4]. The extract was acidified resulting into insoluble HA and soluble FA fractions. The HA and FA were purified as in [5] and [6] respectively. Bulk stable isotopic analysis (δ\(^13\text{C}\), δ\(^2\text{H}\), δ\(^18\text{O}\), δ\(^15\text{N}\) IRMS) was done in an elemental micro-analyser coupled to a continuous flow Delta V Advantage isotope ratio mass spectrometer (IRMS). Pyrolysis compound specific isotopic analysis Py-CSIA (δ\(^13\text{C}\), δ\(^2\text{H}\)): was done by coupling a double-shot pyrolyzer to a chromatograph connected to an IRMS. Structural features of specific peaks were inferred by comparing/matching mass spectra from conventional Py-GC/MS (data not shown) with Py-GC/IRMS chromatograms obtained using the same chromatographic conditions.

Bulk C isotopic signature found for FR (-20.5±0.02 %) was in accordance with previous studies [2, 7–9]. This heavy isotopic δ\(^13\text{C}\) signature indicates a depleted stomatal conductance and palaeoenvironmental growth conditions of water and salt stress. This is in line with the morphological and depositional characteristics [3] confirming that F. oligostomata was adapted to highly xeric and saline habitats being a component of salt-marsh vegetation. The values obtained for δ\(^2\text{H}\) (-101.9±2.2 %), δ\(^15\text{N}\) (10.7±0.2 %) and δ\(^18\text{O}\) (20.9±0.39 %) lay within those previously reported for fossil floras [10] growing in warm environment and probably with very high evaporation rates.

δ\(^13\text{C}\) Py-CSIA was recorded for biogenic compound; polysaccharides, lipid series, lignin and degraded lignin compounds (alkyl benzenes and alkyl phenols) and for a S containing compounds probably with a diagenetic origin. In general δ\(^13\text{C}\) Py-CSIA values were more depleted that the bulk ones and can be considered a better approach to the real plant δ\(^13\text{C}\) value (c. -22 %). Considering that plant-air C fractionation in degraded lignin compounds for a C4 photosystem plant is c. Δ\(^13\text{C}\)≈ 20.0 % [11] and a an extra fractionation (Δ\(^13\text{C}\)≈ − 3.0 %) due to the plant depleted stomatal conductance growing in extreme warm, saline and dry conditions, we estimate atmospheric δ\(^13\text{C}\) value in the area during the Upper Cretaceous in c. δ\(^13\text{C}\) = −5.3±0.2 % This indicates that our F. oligostomata probably grew on a 13C enriched atmosphere, more enriched than preindustrial one (δ\(^13\text{C}\) ≈ −6.5 %) [12]. This could be caused by a combination of reasons i.e. emissions of heavy 13C isotopotated atmosphere by an increase in terrestrial CO2 values.

Values for δ\(^2\text{D}\) CSIA of lipid compounds such as n-alkanes with C chain lengths, C23–C31 are believed to derive exclusively from leaf waxes of higher plants. Plant δ\(^2\text{H}\) carries isotope information of environmental water that is particularly preserved during the geological record in n-alkyl structures, whereas other structures i.e. isoprenoids, are most prone to hydrogen exchange [13–14]. We were able to measure δ\(^2\text{H}\) for long chain alkane/alkene series in the range C24–C29 (δ\(^2\text{D}\) = −124.44±5.2 %). This was taken as a proxy to infer the original H isotopic signal of water in the area in the Upper Cretaceous. Poole et al. (2004) proposed that δ\(^2\text{D}\)palaeowatereq = δ\(^2\text{D}\)C24–C29 n-alkanes + 100 giving a value for placeowater δ\(^2\text{D}\) = −24.44±5.2 %. This indicates that 75 Mya our plant probably uptake deuterium enriched rain water that again points to warm growing environmental conditions.

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