Geophysical Research Abstracts
Vol. 17, EGU2015-10953-1, 2015
EGU General Assembly 2015

An estimation of Central Iberian Peninsula atmospheric δ13C and water δD 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 oligiostomata are studied in bulk (C, H, O, N IRMS) and in specific compounds released by pyrolysis (C, H, Py-CSIA).
Well preserved F. oligiostomata 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 (δ13C, δD, δ18O, δ15N 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 (δ13C, δD): 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$\pm$0.02 ‰ was in accordance with previous studies [2, 7–9]. This heavy isotopic δ13C signature indicates a depleted stomatal conductance and paleoenvironmental growth conditions of water and salt stress. This is in line with the morphological and depositional characteristics [3] confirming that F. oligostomata was adapted to highly xeric and saline habitats being a component of salt-marsh vegetation. The values obtained for δD (-101.9$\pm$2.2 ‰, δ15N (10.7$\pm$0.2 ‰ and δ18O (20.9$\pm$0.39 ‰ lay within those previously reported for fossil floras [10] growing in warm environment and probably with very high evaporation rates.
δ13C Py-CSIA was recorded for biogenic compound; polysaccharides, lipid series, lignin and degraded lignin compounds (alkyl benzenes and alkyl phenols) and for a S containing compounds probably with a diagenetic origin. In general δ13C Py-CSIA values were more depleted that the bulk ones and can be considered a better approach to the real plant δ13C value (c. -22 ‰. Considering that plant-air C fractionation in degraded lignin compounds for a C4 photosystem plant is c. Δ13C$\approx$ 20.0 ‰ [11] and a an extra fractionation (Δ13C≈ -3.0 ‰ due to the plant depleted stomatal conductance growing in extreme warm, saline and dry conditions, we estimate atmospheric δ13C value in the area during the Upper Cretaceous in c. δ13C = -5.3 ± 0.2 ‰Ṫhis indicates that our F.oligostomata probably grew on a 13C enriched atmosphere, more enriched than preindustrial one (δ13C ≈ -6.5 ‰ [12]).$Thiscouldbecausedbyacombinationofreasonsi.e.emissionsofheavy13Cisotopetotheatmospherebyanincreaseinc$
$Valuesfor\delta$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 δD 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 δD for long chain alkane/alkene series in the range C24–C29 (δD = $^{-1}$24.44$\pm$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 δDpalaeowarter= δDC24–C29 n-alkanes + 100 giving a value for plaeowater δD = -24.44 ± 5.2‰Ṫhis indicates that 75 Mya our plant probably uptake deuterium enriched rain water that again points to warm growing environmental conditions.

(1) Gómez, B.; Martín-Closas C.; Brale G.; Solé de Porta N.; Thévenard F.; Guignard G. Paleontology 2002 45, 997–1036.
(2) Nguyen Tu, T.T.; Kvaček, J.; Uličny, D.; Bocherens, H.; Mariotti, A.; Broutin, J. Palaeogeogr. Palaeoclimatol.

Palaeoecol. 2002 183, 43–70.
(3) Almendros, G.; Álvarez-Ramis, C.; Polo, A. Revista de la Real Academia de Ciencias Exactas, Físicas y Naturales 1982 76, 285–302.
(4) Dabin, B. Chah. ORSTOM Ser. Pedol. 1976 4, 287–297.
(5) Schnitzer, M.; Khan, S.U. Humic Substances in the Environment. Marcel Dekker Inc. 1972, New York, N.Y.
(6) Dorado, E.; Polo. A. An. Edafol. Agrobiol. 1976 55, 723–732.
(7) Bocherens, H.; Friis, E.M.; Mariotti, A.; Pedersen, K.R. Lethaia 1993 26, 347–358.
(8) Nguyen Tu, T.T.; Bocherens, H.; Mariotti, A.; Baudin, F.; Pons, D.; Broutin, J.; Derenne, S.; Largeau C. Palaeogeogr. Palaeoclimatol. Palaeoecol. 1999 145, 79–93.
(9) Aucour, A-.M.; Gomez, B.; Sheppard, S.M.F., Thévenard, F. Palaeogeogr. Palaeoclimatol. Palaeoecol. 2008 257, 462–473.
(10) Michener, N.; Lajtha K. (Eds). Stable Isotopes in Ecology and Environmental Science (2nd Ed) 2007 Blackwell Publishing.
(11) Poole, I., van Bergen, P.F.; Kool, K.; Schouten , S.; Cantrill, D. J. Org. Geochem. 2004 35, 1261–1274.
(12) Gerber, S.; Joos, F.; Brügger, P.; Stocker, T.F.; Mann, M.E.; Sitch, S.; Scholze, M. Clim. Dyn. 2003 20, 281–299, 2003
(13) Pedentchouk, N.; Freeman, K.H.; Harris, N.B. Geochim. Cosmochim. Acta 2006 70, 2063–2072.
(14) Radke, J.; Bechtel, A.; Gaupp, R.; Püttmann, W.; Schwark, L.; Sachse D.; Gleixner, G. Geochim. Cosmochim. Acta 2005 69, 5517–5530.

Acknowledgements
Projects CGL2012-38655-C04-01 and CGL2008-04296 and fellowship BES-2013-062573 given by the Spanish Ministry for Economy and Competitiveness to N.T.J.M. Dr. J.M. R. is the recipient of a fellowship from the JAE-Doc subprogram financed by the CSIC and the European Social Fund.