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## Combined $\delta^{13}\text{C}$ - $\delta\text{D}$ analysis of pentacyclic triterpenes and their derivatives

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Jérémy Jacob, Claude Le Milbeau, Nicolas Bossard, Jean-Robert Disnar, Yves Billaud. Combined  $\delta^{13}\text{C}$  -  $\delta\text{D}$  analysis of pentacyclic triterpenes and their derivatives. The 25th International Meeting on Organic Geochemistry, Sep 2011, Interlaken, Switzerland. 2p. insu-00842940

**HAL Id: insu-00842940**

**<https://insu.hal.science/insu-00842940>**

Submitted on 9 Jul 2013

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## *IMOG Abstract Template*

<b>Title only</b> (not Authors & Affiliations)	<b>Combined <math>\delta^{13}\text{C}</math> - <math>\delta\text{D}</math> analysis of pentacyclic triterpenes and their derivatives</b>

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Compound-specific carbon and hydrogen analyses have been proposed to quantify environmental variables because they afford a remarkable constrain on the biological source through the selection of specific biomarkers. Upon these biomarkers, higher plant pentacyclic triterpenes are reputed chemotaxonomical markers and can, in favourable cases, be related to a restricted number of taxa. Once they integrate geological systems, these compounds can undergo several structural modifications that potentially affect their original  $\delta\text{D}$  and  $\delta^{13}\text{C}$ . Previous work showed that the aromatisation of pentacyclic triterpenes has little effect on the  $\delta^{13}\text{C}$  (Freeman et al., 1994). Reversely, there is presently no estimate on the impacts of pentacyclic triterpene diagenesis on  $\delta\text{D}$ .

Here we report on the  $\delta\text{D}$  and  $\delta^{13}\text{C}$  of pentacyclic triterpenes and their diagenetic derivatives recovered from Bronze Age settlement layers preserved in sub-aqueous conditions (3 m depth) at the Châtillon station of Lake le Bourget (Chindrieux, France). This site was selected because preserved organic matter is constituted by restricted sources of C4 plant material (*Panicum miliaceum* and *Setaria italica*) that produce original compounds such as  $\alpha$ - and  $\beta$ -amyrins, miliacin, germanicol and glutinol (Tulloch, 1982).

Lipids were extracted and separated into neutrals and acidic compounds. The neutral compounds were further separated into aliphatics, aromatics, ethers and ketones before identification and quantitation by gas chromatography-mass spectrometry.

Pentacyclic triterpenes and their diagenetic derivatives are the dominant compounds in the lipid extract. The aliphatic fraction comprises a set of des-A-triterpenes with various structures. Aromatic derivatives of intact or ring A-degraded pentacyclic triterpenes are found in the aromatic fraction. Miliacin was found at high concentrations in the ether fraction. The ketone fraction contains several triterpenoids ketones such as friedelin, taraxerone, lupanone, lupenone, and isomultiflorenone. The variability in triterpene imprints probably reflects variable sources of organic material in archaeological levels and differential physico-chemical conditions in the medium.

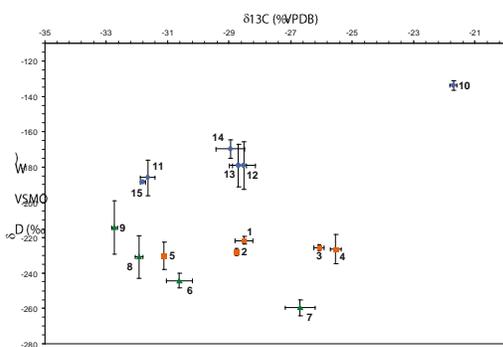


Figure 1:  $\delta\text{D}$  and  $\delta^{13}\text{C}$  of pentacyclic triterpenes and their diagenetic derivatives extracted from archaeological layers. 1: des-A-olean-13(18)-ene; 2: des-A-olean-12-ene; 3: des-A-olean-18-ene; 4: des-A-urs-12-ene; 5: des-A-lupane; 6: 24,25-dinorolean-1,3,5(10)-triene; 7: 24,25-dinorolean-1,3,5(10),12-tetraene; 8: 24,25,26,27-tetranorolean(ursan)-1,3,5(10),6,8,11,13-heptaene; 9: 24,25,26,27-tetranorlupan-1,3,5(10),6,8,11,13-heptaene; 10: miliacin; 11: taraxerone; 12: isomultiflorenone; 13: lupenone; 14: lupanone; 15: friedelin.

Miliacin  $\delta^{13}\text{C}$  is in agreement with its C4 origin. Taraxerone and friedelin are characterized by low  $\delta^{13}\text{C}$  that attest to a quasi-exclusive C3 origin. Lupanone, lupenone and isomultiflorenone could originate from mixed sources. Miliacin is enriched in deuterium when compared to other pentacyclic triterpenes of C3 origin (-140 and -180 ‰, respectively). Des-A-triterpenes 1, 2, 3, 4, 5 and aromatic des-A-triterpenes 9 and 8 are depleted in D by ca. 30 ‰ when compared to pentacyclic triterpenes of C3 origin. Pentacyclic aromatic derivatives 6 and 7 are the most D-depleted compounds found in our extracts.

These results indicate the diagenesis of pentacyclic triterpenes can lead to  $\delta\text{D}$  shifts as large as 100 ‰. The analysis of triterpene alcohols and minor diagenetic derivatives in the same sample is expected to give additional information on genetic relationships between original compounds and their diagenetic derivatives and to provide more quantitative data on the isotopic effects associated with these transformations.

## References

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