Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

$\delta^{13}C$ in α-cellulose from oak latewood 1631-1765 AD

Małgorzata Szczepanek[1], Mariusz Fogtman[1], Sylwia Korput[1], Anna Pazdur[1], Stanisław Hałas[2], Marek Krąpiec[3]

[1]Department of Radioisotopes, Institute of Physics, Silesian University of Technology, Krzywoustego 2, 44-100 Gliwice, e-mail: m.szczepanek@carbon14.pl

[2] Mass Spectrometry Laboratory, Institute of Physics, UMCS, 20-031 Lublin,

[3] Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Cracow

This work presents $\delta^{13}C$ measurement using α-cellulose from oak latewood of annual growth rings (*Quercus robur L.*) 1631-1765 AD.

In Gliwice (Pawełczyk *et al.*, 2004) we used a modified technique based upon the sodium chlorite oxidation method of Green (1963) utilities an ultrasonic bath. This technique yields a material with sufficient homogeneity as required for isotopic composition measurements. The diagram of α-cellulose extraction from wood samples can be briefly presented as follows (Robertson and Waterhouse, 1998):

$$\text{wood} \xrightarrow[CH_3COOH]{NaClO_2} \text{holocellulose} \xrightarrow{NaOH} \alpha\text{-cellulose}$$

To receive holocellulose a sample was put into a beaker filled with distilled water, sodium chlorite and acetic acid, in amounts as below.

Reagent	*Amount*
Wood shavings	1 g
Distilled water	175 ml
Sodium chlorite	2.5 g (per addition)
Acetic acid [80%]	1.7 ml (per addition)
10% sodium hydroxide	75 ml
17% sodium hydroxide	67 ml

The beaker was covered with glass and placed in an ultrasonic bath (70^{o}C). Five times, one an hour, acetic acid and sodium chloride were added. The beakers were taken out and the solution was removed. Holocelullose was rinsed, first with hot distilled water and then with cold distilled water. Its colour was checked – holocellulose should be quite white. In case of tinge the cleaning was repeated. Holocellulose was dried in 70^{o}C.

To holocellulose 10% solution of NaOH was added and beaker was placed in an ultrasonic bath for 45 min (about 70^{o}C). After that sample was rinsed with cold distilled water. The samples were put into beaker with 17% solution of NaOH and they were subjected to ultrasonic for 45 min in the room temperature. α-cellulose was rinsed, first with 17% solution of NaOH, next with big amount of distilled water, then with 1% solution of hydrochloric acid and finally with big amount of cold distilled water (until the solution was neutral). α-cellulose was dried in 70^{o}C.

For $\delta^{13}C$ measurements with mass spectrometer CO_2 was prepared from the dried α-cellulose. The cellulose sample was placed into individual pyrex tubes with copper oxide. The tube, in which 10 mg of cellulose, 1300 mg of preheated CuO and 150 mg silver wool are placed, was sealed under vacuum. Next, it was put into a metal thimble and heated in muffle furnace for 18 hours in the temperature of 450°C. The resulting gases were separated cryogenically and the CO_2 was collected.

In $\delta^{13}C$ α-cellulose time record the cooling between *ca* 1650-1700 AD is clearly visible. Comparison of this record with $\Delta^{14}C$, width tree rings, sunspot numbers and $\delta^{13}C$ in nitrate cellulose indicate on correlation or anti-correlation of these records according to predictions. Results of $\delta^{13}C$ measurements in nitrate cellulose from the paper Krąpiec et al., 1998) were taken.

Acknowledgments

This work was supported by EU grants No. EVK2-2001-237 (ISONET) and by State Committee for Scientific Research grant SPB-12/RMF-1/2003.

References

Green, J.W., 1963. Methods of Carbohydrate Chemistry, III (Ed. R.L. Whistler). Academic Press, New York, NY, 9-21.

Epstein, S., Yapp, C.J. , Hall J. H., 1976. The determination of the D/H ratios of non-exchangeable hydrogen in cellulose extracted from aquatic and land plants. Earth and Planetary Sciences Letters 30, 241-251.

Robertson, I. Waterhouse, J. S., 1998. Tree of knowledge. Chem. Br., 27-30.

Pawełczyk, S., Pazdur, A., Hałas, S., 2004. Stable carbon isotopic composition of tree rings from a pine tree from Augustów Wilderness, Poland, as a temperature and local environment conditions indicator. Isotopes Environ. Health Stud. 40(2), 145-154.

Krąpiec, M., Jędrysek, M.O., Skrzypek, G., Kałużny, A., 1998. Carbon and hydrogen isotope ratios in cellulose from oak tree-rings as a record of palaeoclimatic conditions in Southern Poland during the last millenium. Folia Quaternaria 69,135-150.