Hydropyrolysis as a method for radiocarbon pre-treatment, and the quantification of black carbon

W. MEREDITH[1]*, P.L. ASCOUGH[2], C.E. SNAPE[1], D.J. LARGE[1], M.I. BIRD[3], F. BROCK[4], T.F.G. HIGHAM[4], R.E. WOOD[4] AND C.H. VANE[5]

[1]Department of Chemical and Environmental Engineering, University of Nottingham, Nottingham NG7 2RD, UK (*correspondence: william.meredith@nottingham.ac.uk)
[2]SUERC, Glasgow G75 0QF (p.ascough@suerc.gla.ac.uk)
[3]James Cook University, Cairns 4870, Australia
[4]University of Oxford, Oxford OX1 3QY, UK
[5]British Geological Survey, Nottingham NG12 5GG, UK

Within the pyrolysis continuum, black carbon (BC) is defined as having both high aromaticity and high resistance to oxidative degradation, although as yet there is currently no accepted standard methodology for its determination [1]. Hydropyrolysis (hypy) has been recently reported as a new method for BC quantifiaction [2], which is also of great interest in radiocarbon measurement. Here, we test hypy as a method of BC isolation for both quantification and dating purposes, using a selection of standard soil samples and ancient charcoals, including some previously tested by a variety of methods as part of the recent BC ring trail [1]. Fig. 1 shows a trend of decreasing TOC for soil hypy residues up to 550°C This corresponds to the reductive removal of carbon from the labile (i.e. non-BC) organic matter in the soil (A), and is followed by a plateau in TOC representing the BC content (B), and a further decrease due to hydrogasification (C). For a sample of contaminated charcoal the removal of lignocellulosic carbon is apparent from the NMR data shown.

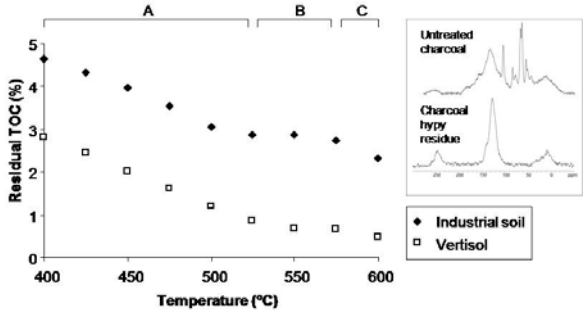

Figure 1: Residual soil TOC vs. hypy temperature (from [2]). Inset - ^{13}C-CP-SSNMR traces from hypy of charcoal.

[1] Hammes, K., *et al*. (2007) *Global Biogeochem. Cycles* 21, GB3016, doi: 10.1029/2006GB002914. [2] Ascough, P.L., *et al.* (2009) *Quatern. Geochronol*. **4**, 140-147.

Paleomagnetic rates of *terra rossa* formation vs. rates calculated by dynamic modeling of clay-for-limestone replacement

ENRIQUE MERINO[1] AND AMLAN BANERJEE[2]

[1]Geological Sciences, Indiana University, Bloomington, IN 47401, USA (merino@indiana.edu)
[2]Earth & Environmental Sci., New Mexico Inst. Mining & Technology, Socorro, NM 87801 (amlan@nmt.edu)

New field and petrographic evidence at Bloomington, Indiana, indicates that *terra rossa* is forming at 2 m of depth, where it replaces the underlying Salem Limestone at a narrow moving reaction front. The front consists of a replacement zone 6 cm wide and a leaching zone 3 cm wide. In the replacement zone kaolinite replaces limestone according to:

$$0.45CaCO_{3(calc)} + 1/3\ Al^{+3} + 1/3SiO_2 + 0.83H_2O = [Al_2Si_2O_5(OH)_4]_{1/6(kaol)} + 0.45Ca^{+2} + 0.45HCO_3^- + 0.55H^+,$$

where the 0.45 coefficient reflects the fact that the replacement is isovolumetric. The aqueous Al and SiO_2 are provided to the front from above. It is the H^+s released by that replacement that leach an additional slice of limestone according to $CaCO_3 + H^+ = Ca^{+2} + HCO_3^-$, forming the observed leaching zone. When today's replacement zone becomes completely replaced, the replacement will continue in what is today the leaching zone, and the H^+s released there will start leaching limestone that is still fresh today. This is how the front moves, consuming limestone at its front end and leaving behind a trail of clay (+ iron oxide). [1,2].

We have modeled that chemical dynamics in the framework of the differential equation of mass-conservation, incorporating infiltration, diffusion, appropriate mass-action rate laws for kaolinite and calcite, and a mechanism of replacement [3] that always preserves bulk volume [4] *via* induced-stress-driven pressure solution of host by guest mineral. (The traditional "dissolution-precipitation" cannot ensure that solid volume is preserved.)

All variables in the model are scaled such that reaction and transport terms in the continuity equation are *of the same order of magnitude*, as suggested by the fact that the reaction front is *narrow*. Numerical solutions of the scaled system of equations do produce two adjacent zones and a porosity wave, as observed. Predicted front velocity values bracket an independent paleomagnetic rate of > 2.5 m/ m.yrs. [5]. The predicted front thickness of a few centimeters also agrees with observed values.

[1] Merino & Banerjee, *J Geol* 08. [2] Banerjee & Merino *Chem Geol* 2009. [3] Maliva & Siever, *Geology* 1988. [4] Nahon & Merino 1997 [5] Meert *et al, J. Geology* 2009.