European Science Foundation Standing Committee for Life, Earth and Environmental Sciences (LESC)

REPORT ON AN ESF LESC EXPLORATORY WORKSHOP

Charcoal to Black carbon:

defining common issues of quantification and interpretation in archaeological, palaeoenvironmental and carbon cycle research



St Andrews, United Kingdom, 31 August - 2 September 2005

Convened by: Professor Michael Bird

University of St. Andrews (michael.bird@st-andrews.ac.uk)

Summary:

Pyrogenic carbon materials (the carbon-rich and O,H,N,S-poor products of incomplete combustion) are the focus of largely independent strands of research in archaeology, the global carbon cycle and palaeoenvironmental reconstruction. While many of the problems associated with the analysis of pyrogenic carbon are common across these disciplines, they have largely worked in isolation from each other. This workshop was convened to bring together leading researchers in these disparate fields to identify the crossdisciplinary synergies that exist in efforts to define, quantify and interpret pyrogenic carbon materials in the modern environment and the geological/archaeological record.

An ESF-funded workshop took place at the University of St. Andrews, Scotland, on September 1st and September 2nd 2005 and involved 16 established academic staff, 4 early career researchers and 4 post-graduate students from ten countries. Sessions were devoted to each of the three main strands where pyrogenic carbon research is actively being persued: (i) carbon cycle research, (ii) archaeology/radiocarbon dating and (iii) sedimentary records/palaeoenvironmental reconstruction. A final discussion session focused on defining commonalities in these three research themes, in terms of shared problems in quantifying/analyzing pyrogenic carbon and the potential for cross-fertilization of methodologies or insights between the themes.

What was most apparent from the workshop was the incredibly diverse range of research areas where the identification and/or quantification of pyrogenic carbon is of central importance and the wide range of techniques being applied to the imaging and analysis of pyrogenic carbon. Presentations covered pyrogenic carbon in the atmosphere (aerosols), modern soils from tropical to boreal, and ancient pyrogenic carbon preserved in the sedimentary and archaeological record. The size of material being studied ranged from macroscopic charcoal fragments and nanometer-scale domains within charcoal imaged at atomic level by transmission electron microscopy, to micron-sized aerosolic soot particles, to individual biomarkers produced during pyrolysis.

Individual studies relied on a wide range of chemical, imaging and instumental techniques including transmission electron microscopy (TEM), scaning electron microscopy (SEM), optical microscopy, nuclear magnetic resonance (NMR), x-ray tomography, raman spectroscopy, thermogravimetry, differential thermal analysis, electron spin resonance (ESR), conductivity, wet chemical oxidation, photoacoustic spectroscopy, aethalometry, chemothermal oxidation, stable-isotope mass spectrometry, accelerator mass spectrometry (AMS) and pyrolysis-gas chromatography mass spectrometry (py-GC-MS). The use of these techniques is 'compartmentalized' to varying degrees. Thus, while a limited number of techniques are routinely used across several reseach areas, many only applied in the specific field of research for which the technique was developed with the potential benefits to other fields not realized simply through lack of communication. This is most clearly the case across the broad 'divide' between researchers focused on pyrogenic carbon in the modern environment and those focused on pyrogenic carbon in the ancient environment. Hence, the potential of NMR and py-GC-MS which are routinely applied in studies of pyrogenic carbon in the modern environment has yet to be exploited in the context of improving radiocarbon dating techniques for archaeological charcoal, and new conductivity techniques developed by archaeologists have yet to be applied to studies of pyrogenic carbon in the modern environment. Thus the first major outcome of the workshop was to highlight the considerable potential for 'cross-fertilization' of technical expertise between researchers working on pyrogenic carbon in the context of very different research applications. The workshop itself has already catalysed this to some extent, with visits from workshop participants from both Oxford (Brock) and St. Andrews (Bird) to the Weissman Institute in Israel (Weiner) in 2006.

The issue of standardization of analytical techniques for quantifying pyrogenic carbon is being resolved through the international 'Black carbon ring trial' co-ordinated by Michael Schmidt (University of Zurich), but an additional major issue highlighted in several presentations at the workshop is large gap in knowledge concerning the reactivity and stability of pyrogenic carbon in the natural environment. Pyrogenic carbon has considerable capacity to sorb a range of organic and inorganic compounds including a range of pollutants and hence does chemically interact with its environment after formation.

Several presentations highlighted the fact that while conventional wisdom has it that pyrogenic carbon is 'inert' and, once formed, is very stable even on geological timescales of millions of years, evidence is accumulating that this is not the case. Pyrogenic carbon is now conceptualized as a range of products along a 'combustion continuum' from partly charred biomass (probably of low stability) to microcystalline graphite and individual molecules of pyrogenic origin (probably of high stability). Therefore it is likely that most pyrogenic materials contain a wide range of components of variable stability and longevity. This is of relevance studies of pyrogenic carbon in the modern environment as it is likely to be dynamically rather than passively involved in the global carbon cycle. In addition, as it seems likelty that nature of the pyrogenic carbon preserved in the sedimentary and archaeological record will change over time the reactivity and stability of pyrogenic carbon is also of central importance to radiocarbon dating and the interpretation of the sedimentary record of pyrogenic carbon accumulation.

The workshop participants would like to thank the ESF for providing the funding for this workshop which has already catalysed linkages to between researchers working in different disciplines on pyrogenic carbon who would not normally have come together and hence not have been made aware of new tools and insights that can be applied to their own research from other disciplines.

Assessment, outcomes and recommendations

The workshop highlighted three linked areas to facilitate future research into pyrogenic carbon in modern and ancient environments:

Quantification and method inter-comparability

Due to the increasing number of techniques being applied to quantify and chemically characterize pyrogenic carbon, the inter-comparability of measurements remains a significant issue, particularly where quantification of pyrogenic carbon is required. Considerable progress has been made in this area in the last few years through the 'Black carbon ring trial', and the results of this international collaborative research effort to develop analytical benchmarks will be published shortly. The good collaborative relationships developed over the course of this exercise means that a coherent international grouping has been developed that can continue to develop methodologies for ensuring intercomparability between methodologies and laboratories. A suite of standards have been developed and these can be used to incorporate and validate new methodologies as they emerge.

Recommendation: Efforts to ensure intercomparability should be continued and the circle of international researchers already collaborating effectively as part of the 'black carbon community' should be expanded as appropriate to include researchers from the archaeological and palaeoenvironmental communities.

Environmental stability and reactivity of pyrogenic carbon

The fate of pyrogenic carbon in the environment after its formation is poorly constrained. It is clear that some components pyrogenic origin are reactive and likely to undergo degration on a range of timescales, however the mechanisms by which this occurs are poorly understood and the implications for carbon cycle studies, palaeoenvironmental reconstruction and archaeology have yet to be explored at more than a cursory level.

Recommendation: Groupings of researchers with allied interests in pyrogenic carbon and appropriate technical expertise will develop collaborative research proposals to develop the environmental reactivity and stability of pyrogenic carbon as a research theme for future funding.

Disciplinary 'cross-fertilization'

The successful persuit of both the above can be best facilitated at this stage by local inter-laboratory visits between individual researchers and small focused workshops, with the aim of effectively introducing methodological expertise used in one discipline to other disciplines that could benefit from the application the expertise, and to assist in developing research proposals for funding.

Recommendation: The workshop group, expanded to include other allied researchers as appropriate will seek ESF a la Carte funding to facilitate inter-disciplinary cross-fertilization through laboratory visits and small targeted workshops.

Statistical information

The workshop brought together 24 conference participants from ten countries and also included four student helpers from St. Andrews. The delegates (excluding helpers) are broken up by country and career stage below:

By country:

United Kingdom - 7Germany - 6France - 1Spain - 2Portugal - 1Greece - 1Sweden - 2Ireland - 1Israel - 2 (one visiting UK) United States - 1

By career stage:

Established academic -16Early career academic -4PhD student -4Student helper -4

Workshop Programme

Thursday 1st September, 2005

08.15 – 08.30: Presentation of the European Science Foundation (ESF) – Fatima Abrantes (Standing Committee for Life, Earth and Environmental Sciences).

Session 1: Carbon Cycle Research

Chair: Örjan Gustafsson

- 08.30 09.00: *Keynote address*: **Claudia Czimczik** Why are there no black soils in the boreal region?
- 09.00 09.30: Michael Schmidt The Determination of Black Carbon in Soils.
- 09.30 10.00: Heike Knicker Humification and Stability of Charcoal in Soil.
- 10.00 10.30: Morning tea
- 10.30 11.00: Wulf Amelung Fate of black carbon in arable soil environment.
- 11.00 11.30: **Otmar Schmid** Biomass burning and black carbon production.
- 11.30 12.00: **Michael Bird** The stability of charcoal in natural environments.
- 12.00 12.30: **José Gonzalez-Perez** Pyrolysis GC/MS applications in black carbon research.
- 12.30 13.30: Lunch (including poster presentations by students).

Session 2: Archaeology and radiocarbon dating Chair: David Taylor

- 13.30 14.00: *Keynote address:* **Stephen Weiner** Modern and Fossil Charcoal: Aspects of Structure and Diagenesis.
- 14.00 14.30: **Yorgos Facorellis** Radiocarbon dating of charcoal at Theopetra Archaeological site.
- 14.30 15.00: Charlotte Bryant Radiocarbon dating of black carbon.
- 15.00 15.30: **Tom Higham** Problems with radiocarbon dating charcoal from archaeological sites.

15.30 – 16.00: Afternoon tea and discussion.

16.00 – 16.30: Jill Thompson - Archaeological perspectives on charcoal taphonomy: Tropical archaeobotany: an elusive search for charred plant macroremains.

- 16.30 17.00: **Neil Roberts** Mediterranean fire histories from micro-charcoal analysis: analytical methods and preliminary results for the LGIT.
- 17.00 17.30: Discussion from sessions 1 and 2.
- 19.30: Dinner at The Grill House, St. Andrews.

Friday September 2nd, 2005

Session 3: Sedimentary Records of charcoal / black carbon

Chair: Michael Schmidt

- 09.00 09.30: Örjan Gustafsson Further testing and application of the chemothermal oxidation approach to the study of BC in marine sediments.
- 09.30 10.00: **Kathy Willis** Analysis of microcharcoal for palaeoenvironmental reconstruction.
- 10.00 10.30: **Florian Thevenon** Biomass burning records from charcoal and black carbon in natural archives.
- 10.30 11.00: **David Taylor** The role of fire in seasonally-dry eastern Africa: evidence from sedimentary charcoal.

Session 4: Discussion, Consolidation and Recommendations

Chair: Michael Bird

- 11.00 14.00: *Morning tea* followed by general discussion, identification of common issues and formulation of research agenda for future funding proposals, closing remarks.
- 14.00: **Departure** for Edinburgh Airport and Leuchars train station.

List of workshop participants

/ · · ·	Departamento de Geológia Marinha,	fatima.abrantes@mail.ineti.pt
(academic - ESF)	Amadaro, Portugal	าสแกล.สมาสกเธรษากลแ.เกษแ.pt
Wulf Amelung (academic)	Institute of Soil Science, University of	
	Bonn, Nussallee 13, 53115 Bonn,	Wulf.Amelung@TU-Berlin.DE
	Germany	
	School of Geography &	
Michael Bird	Geosciences, University of St	michael.bird@st-andrews.ac.uk
(academic)	Andrews, St Andrews, Fife KY16	michael.bitu@st-anurews.ac.uk
	9AL, UK.	
	Oxford Radiocarbon Accelerator	
Fiona Brock	Unit, Research Laboratory for	
	Archaeology and the History of Art, 6	fiona.brock@rlaha.ox.ac.uk
(early career)	Keble Road, Oxford OX1 3QJ,	
	England.	
Cania Dradowski	Institute of Soil Science, University of	
Sonja Brodowski	Bonn, Nussallee 13, 53115 Bonn,	sonja.brodowski@uni-bonn.de
(early career)	Germany	
	NERC Radiocarbon Laboratory,	
Charlotte Bryant	Scottish Enterprise Technology Park,	c.bryant@nercrcl.gla.ac.uk
(academic)	Rankine Avenue, East Kilbride,	
	Glasgow G75 0QF	
	School of Geography &	
Alix Cage	Geosciences, University of St	agc10@st-andrews.ac.uk
(student helper)	Andrews, St Andrews, Fife KY16	
	9AL, UK.	
Illit Oak ar	Department of Structural Biology,	ilit@wicc.weizmann.ac.il
Illit Cohen	Weizmann Institute of Science,	
(student)	Rehovot 76100, Israel.	
	School of Geography &	
Matt Cox	Geosciences, University of St	mc34@st-andrews.ac.uk
(student helper)	Andrews, St Andrews, Fife KY16	
	9AL, UK.	
	Department of Earth System	
Claudia Czimczik	Science, 2103 Croul Hall, University	czimczik@uci.edu
(early career)	of California, Irvine, CA 92697-3100,	
	USA (replaced Carrie Masiello)	
José M ^a de la Rosa (student)	Instituto de Recursos Naturales y	
	Agrobiologia de Sevilla, IRNAS-	jmrosa@irnase.csic.es
	CSIC, jmrosa@irnase.csic.es	

Marie Elmquist (student)	Department of Applied Environmental Science and Department of Geology & Geochemistry, University, 10691 Stockholm, Sweden	marie.elmquist@itm.su.se
Yorgos Facorellis (academic)	Laboratory of Archaeology, Department of History-Archaeology- Social Anthropology, School of Human Sciences, University of Thessaly, Argonafton & Filellinon, 382 21 Volos, Greece	yfacorellis@yahoo.com
José A. González- Pérez (academic)	Instituto de Recursos Naturales y Agrobiología de Sevilla, IRNAS- CSIC, Avda. reina Mercedes 10 Seville 41012, Spain	jag@irnase.csic.es
Örjan Gustafsson (academic)	Stockholm University, Dept. of Applied Environmental Science (ITM), 10691 Stockholm, Sweden.	orjan.gustafsson@itm.su.se
Karen Hammes (student)	Department of Geography, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland	hammes@geo.unizh.ch
Tom Higham (academic)	Oxford Radiocarbon Accelerator Unit, Research Laboratory for Archaeology and the History of Art, 6 Keble Road, Oxford OX1 3QJ, England.	thomas.higham@archaeology- research.oxford.ac.uk
Heike Knicker (academic)	Lehrstuhl für Bodenkunde, TU München, 85350 Freising- Weihenstephan, Germany	knicker@wzw.tum.de
Stefan Morrocco (student helper)	School of Geography & Geosciences, University of St Andrews, St Andrews, Fife KY16 9AL, UK.	smm15@st-andrews.ac.uk
Neil Roberts (academic)	School of Geography, University of Plymouth, Drake Circus, Plymouth, PL4 8AA, UK	Neil.roberts@plymouth.ac.uk
Otmar Schmid (academic)	Institute of Inhalation Biology, GSF- National Research Center for Environment and Health, P.O. Box 1129, D-85764 Neuherberg/Munich, Germany	oschmid@mpch-mainz.mpg.de
Michael Schmidt (academic)	University of Zurich, Dept. of Geography, Zurich, Switzerland	mschmidt@geo.unizh.ch

David Taylor	Department of Geography, Trinity	taylord@tcd.ie
(academic)	College, Dublin, Ireland	
Florian Thevenon (early career)	37 Habsburgstrasse, 8037 Zurich, Switzerland (formerly CEREGE, France)	florian.thevenon@hispeed.ch
Jill Thompson (academic)	Department of Archaeological Sciences, University of Bradford, UK	J.B.Thompson@Bradford.ac.uk
Steve Weiner (academic)	Department of Structural Biology, Weizmann Institute of Science, Rehovot 76100, Israel.	Steve.Weiner@weizmann.ac.il
Kathy Willis (academic)	Oxford University Centre for the Environment, Dyson Perrins Building, South Parks Road, Oxford, OX1 3QY, UK	kathy.willis@geography.oxford.a c.uk
Jonathon Wynn (early career helper)	School of Geography & Geosciences, University of St Andrews, St Andrews, Fife KY16 9AL, UK.	jonathan.wynn@st- andrews.ac.uk