

SERVICES & FACILITIES ANNUAL REPORT - FY April 2010 to March 2011

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|--|---------------------------------|------------------|---------------------------------------|-------------|
| SERVICE North East Amino Acid Racemization Laboratory (NEaar) | FUNDING Pay-As-You-Go | AGREEMENT | ESTABLISHED as S&F 2008 | TERM |
|--|---------------------------------|------------------|---------------------------------------|-------------|

TYPE OF SERVICE PROVIDED:

Amino acid dating, which depends on the predictable breakdown of proteins within fossil biominerals, has the potential to span the whole of the Quaternary time period. In order to use protein breakdown for geochronology, the integrity of the original organic fraction is of vital importance. In recent years significant advances have been made in analysing closed-system protein by identification of protein trapped within the biomineral crystals. Isolation of this 'intra-crystalline' protein fraction circumvents problems due to contamination, leaching and environmental effects. Recognition that calcitic biominerals provide a more robust repository for the closed system than the less geologically-stable aragonitic shells has resulted in the recovery of original amino acids from samples over 30 million years old. The chiral amino acid analysis possible in our facility allows age estimation in fossil samples through amino acid racemization (AAR) alongside other measures of protein breakdown.

The NERC "recognised facility" North East Amino Acid Racemization (hereafter NEaar) has three main scientific objectives:

- to continue actively pioneering analytical advances in amino acid research;
- to welcome visiting researchers and students, giving them the opportunity to learn the technique and analyse their own samples whilst supporting them in data interpretation;
- to provide a "Pay-As-You-Go" amino acid analysis service for the earth science and archaeological science community.

For each project, detailed data and / or reports are provided by NEaar, with assistance in the preparation of manuscripts for publication / proposals undertaken on a collaborative basis, ensuring scientific rigour in the data interpretation.

ANNUAL TARGETS AND PROGRESS TOWARDS THEM

There were no annual targets specified by NERC. In 2010 NEaar's work was included in 11 articles in ISI peer-reviewed journals and 2 book/monograph chapters, spanning both the development of innovative methodological techniques for amino acid analysis and their practical application to sites, addressing key questions in archaeology and Quaternary science. Our papers continue to be highly cited and in June 2010 Kirsty Penkman was awarded the Lyell Fund from the Geological Society of London. New projects have expanded the range of materials analysed and the research questions tackled. We have also hosted 3 international visiting researchers this financial year. KP co-organised a special session and a breakout workshop on AAR at the INQUA Congress in July 2011.

Our ongoing "Total Quality Management" system (TQM) seeks to identify possible areas of weakness in analyses and eliminate sources of error. In NEaar this includes regular monitoring of all potential sources of error and contamination, such as identification of the origin of all reagents, the use of specific reagent batches in preparations, regular calibration of pipettes, and methods for logging and storing samples and analytes. A new online system for sample submission and recording is under test. The TQM has undergone its annual review and update, and in addition the High Pressure Liquid Chromatography (HPLC) machines have undergone annual servicing and preventative maintenance. We have also instigated an inter-laboratory comparison study with several international AAR labs.

| SCORES AT LAST REVIEW (each out of 5) | | | Date of Last Review: | | N/A |
|---------------------------------------|------------|--------------------|-------------------------------|---------|-----|
| Need | Uniqueness | Quality of Service | Quality of Science & Training | Average | |

| CAPACITY of HOST ENTITY FUNDED by S&F | Staff & Status | Next Review (March) | Contract Ends (31 March) |
|---------------------------------------|---|---------------------|--------------------------|
| % | Dr. Kirsty Penkman: permanent academic staff Prof. Matthew Collins: permanent academic staff Mr. Richard Allen: laboratory technician | | |

| FINANCIAL DETAILS: CURRENT FY | | | | | | |
|--|--------------|---------|-----------|-------------------|-----------|-------------------|
| Total Resource Allocation £k | Unit Cost £k | | | Capital Expend £k | Income £k | Full Cash Cost £k |
| | Unit 1 | Unit 2 | Unit 3 | | | |
| FINANCIAL COMMITMENT (by year until end of current agreement) £k | | | | | | |
| 2010-11 | 2011-12 | 2012-13 | 2013-2014 | 2014-2015 | | |

| STEERING COMMITTEE | Independent Members | Meetings per annum | Other S&F Overseen |
|--------------------|---------------------|--------------------|--------------------|
|--------------------|---------------------|--------------------|--------------------|

| | | | | | | | | | |
|--|--|--|--|--|--|--|--|--|--|
| | | | | | | | | | |
|--|--|--|--|--|--|--|--|--|--|

APPLICATIONS: DISTRIBUTION OF GRADES (current FY — 2010/11)

| | α5 | α4 | α3 | α2 | α1 | β | R*/Pilot | Reject |
|----------------------|----|----|----|----|----|---|----------|--------|
| NERC Grant projects* | | | | | | | | |
| Other academic | | | | | | | | |
| Students | | | | | | | | |
| Pilot | | | | | | | | |
| TOTAL | | | | | | | | |

CASE Studentship awarded, starting Oct 2010, grading unknown

APPLICATIONS: DISTRIBUTION OF GRADES (per annum average previous 2 financial years —2008/2009 & 2009/2010)

| | α5 | α4 | α3 | α2 | α1 | β | R*/Pilot | Reject |
|----------------------|----|----|----|----|----|---|----------|--------|
| NERC Grant projects* | | 1 | | | | | | |
| Other Academic | | | | | | | | |
| Students | | | | | | | | |
| Pilot | | | | | | | | |
| TOTAL | | 2 | | | | | | |

PROJECTS COMPLETED (current FY – 2010/11)

| | α5 | α4 | α3 | α2 | α1/β | R*/Pilot | Not Graded |
|----------------------|----|----|----|----|------|----------|------------|
| NERC Grant projects* | | | | | | | |
| Other Academic | | | | | | | |
| Students | | | | | | | |
| Pilot | | | | | | | |

Project Funding Type (current FY – 2010/11) (select one category for each project)

| Grand Total | Infrastructure | | | | PAYG | | | | | |
|-------------|----------------------------|-------------------|-------|----------|-------|-------------|-------------------|-------|----------|-------|
| | Supplement to NERC Grant * | PhD Students NERC | Other | NERC C/S | Other | NERC Grant* | PhD Students NERC | Other | NERC C/S | Other |
| | | | | | | 2 | 2 | | | |

Project Funding Type (per annum average previous 3 financial years - 2008/2009 & 2009/2010)

| Grand Total | Infrastructure | | | | PAYG | | | | | |
|-------------|----------------------------|-------------------|-------|----------|-------|-------------|------------------|-------|----------|-------|
| | Supplement to NERC Grant * | PhD Students NERC | Other | NERC C/S | Other | NERC Grant* | PhD Student NERC | Other | NERC C/S | Other |
| | | | | | | 1 | 1 | | | |

User type (current FY – 2010/11) (include each person named on application form)

| Academic | NERC Centre/Survey | NERC Fellows | PhD Students | Commercial |
|----------|--------------------|--------------|--------------|------------|
| 39 | 0 | 1 | 15 | 6 |

User type (per annum average previous 2 financial years - 2008/2009 & 2009/2010)

| Academic | NERC Centre/Survey | NERC Fellows | PhD Students | Commercial |
|----------|--------------------|--------------|--------------|------------|
| 14.5 | 0 | 1 | 5.5 | 3.5 |

OUTPUT & PERFORMANCE MEASURES (current year)

| Publications (by science area & type) (calendar year 2010) | | | | | | | | | | |
|--|----|-----|----|-----|----|-------|-------------|----------|--------------------|------------|
| SBA | ES | MS | AS | TFS | EO | Polar | Grand Total | Refereed | Non-Ref/ Conf Proc | PhD Theses |
| 19.6 | 9 | 3.2 | 0 | 4.2 | 0 | 0 | 39 | 13 | 24 | 1 |

| Distribution of Projects (by science areas) (FY 2010/11) | | | | | | | |
|--|-------|-------|------|----|-----|----|-------|
| Grand Total | SBA | ES | MS | AS | TFS | EO | Polar |
| 45 | 19.25 | 13.87 | 5.37 | 0 | 7.5 | 0 | 0 |

OUTPUT & PERFORMANCE MEASURES (per annum average previous 3 years)

| Publications (by science area & type) (Calendar years 2007, 2008 & 2009) | | | | | | | | | | |
|--|-----|-----|----|-----|----|-------|-------------|----------|--------------------|------------|
| SBA | ES | MS | AS | TFS | EO | Polar | Grand Total | Refereed | Non-Ref/ Conf Proc | PhD Theses |
| 17.4 | 6.6 | 1.9 | 0 | 4.6 | 0 | 0 | 30.7 | 10 | 20 | 0.7 |

| Distribution of Projects (by science areas) (FY 2008/2009 & 2009/2010) | | | | | | | |
|--|-------|------|------|----|------|----|-------|
| Grand Total | SBA | ES | MS | AS | TFS | EO | Polar |
| 25 | 11.25 | 6.62 | 2.69 | 0 | 4.44 | 0 | 0 |

Distribution of Projects by NERC strategic priority (current FY 2010/11)

| Grand Total | Climate System | Biodiversity | Earth System Science | Sustainable Use of Natural Resources | Natural Hazards | Environment, Pollution & Human Health | Technologies |
|-------------|----------------|--------------|----------------------|--------------------------------------|-----------------|---------------------------------------|--------------|
| 46 | 20.25 | 10.5 | 11.75 | 0 | 0 | 0 | 3.5 |

*Combined Responsive Mode and Directed Programme grants

NOTE: All metrics should be presented as whole or part of whole number NOT as a %

OVERVIEW & ACTIVITIES IN FINANCIAL YEAR (2010/11):

The NEaer laboratory, judged to provide “world-leading research” in the RAE 2008 exercise, aims to:

- 1. provide excellent laboratory facilities, with rigorous quality control procedures
- 2. undertake fundamental research into the development and improvement of amino acid analysis and understanding of protein breakdown
- 3. apply these developments to the Quaternary fossil record in order to improve and refine the chronology and the implications for environmental and climate change, and human evolution and dispersal.
- 4. train both new and experienced researchers in routine analysis and the latest developments in amino acid geochronology
- 5. educate and inform the scientific community and the wider public of the pitfalls and potential of amino acid dating.

In this year, we have made great progress in each of these areas:

Aim 1: Excellent lab facilities: We now have two fully operational duplicate laboratories, one in the Chemistry department and one in Biology, allowing easy-access for the cross-discipline researchers using the technique. We continue to work on method development to update our HPLC method to “Ultra”-HPLC, a technique new to chiral amino acid analysis. On our new Rapid Resolution LC we have been able to achieve run times half that using the conventional HPLCs and have increased the number of amino acids which baseline elute. The number of researchers keen to learn the technique has enabled us to commit to additional projects. Our technician has been further developing the new data analysis software, significantly speeding up data processing. We were involved in a small-scale inter-laboratory comparison trial early in 2010, and have instigated a second wider trial which examined additional materials under robust statistically-significant conditions.

Aim 2: Novel research: Use of multiple amino acids from closed-system protein not only allows independent identification of compromised samples, but also improves resolution. Work is ongoing into the best use of this isochronic data and the evaluation of errors and the inter-laboratory trial results will help in gauging our measurement uncertainty. In 2010/11 we continued to explore new fossil materials and extend the intra-crystalline method to new geographical areas. A NERC grant has allowed us to pioneer a technique to track protein breakdown, linking chiral amino acid analysis with protein mass spectrometry for the first time. We have also been developing techniques and undertaking studies on diatomite and enamel.

Aim 3: Practical application: Over the last year we have worked on a number of different sites in the UK, Europe and Africa, to which the amino acid results have contributed significant insights, including 6 commercial projects. Analysis of archive material has enabled Middle Palaeolithic industries to be better constrained (e.g. Scott *et al.*, 2010). Wellcome-funded collaborations with European researchers have allowed us to extend the dating technique in calcitic opercula into continental Europe. Amino acid data from opercula have resolved a non-concordance between aminostratigraphy and biostratigraphy and helped date the Cromerian type-site (Penkman *et al.*, 2010). We have also undertaken fieldwork in the UK, Sicily and South Africa. Thanks to the EU-funded project mAARiTIME (Marine Amino Acid Racemisation Investigation of The Mediterranean; Demarchi & KP) we have started to develop a marine shell chronology in the Mediterranean. We were involved in a project with the National Oceanography Centre, analysing the freshwater material from marine cores in a bid to better understand the palaeo-landscape and sea-level change of the southern North Sea. A NERC CASE PhD studentship (based at Bristol and co-supervised at York) has been focusing on coral samples, showing a useful role for amino acids in coral dating, but also a potential indicator for coral-stress events. We were awarded a NERC CASE PhD studentship to study the organic preservation and degradation at the Mesolithic site of Star Carr, a site of worldwide importance but which appears to be undergoing rapid deterioration.

Aim 4: Training: We are extremely keen to support the growing field of AAR through collaborations, hosting researchers and providing training. We ran our fourth training course in December 2010 (an intensive 2-week course), which was attended by 2 visiting researchers, 3 York undergraduates and 2 York postgraduates. In 2010/11 3 international researchers undertook work in our labs. We participated in the Erasmus programme, hosting research students from Singapore and Italy. In addition to these visitors, two new CASE students began their PhDs (High on Star Carr, funded by NERC, & Stewart on eggshell, funded by AHRC). Our five other PhD students (Powell, Crisp, Williams, Tomiak and von Holstein) continue to pursue their studies successfully. We have hosted 3 MChem students in this financial year, undertaking research projects on carbonate, silicate and phosphate biominerals.

Aim 5: Dissemination: NEaer personnel contributed to 24 presentations at 18 national and international conferences during 2010. Public outreach has included lectures to school children and public lectures as part of a “Human Origins” series. KP was invited to write a review paper on amino acid geochronology for *Journal of Quaternary Science* (Penkman, 2010). We have peer-reviewed research for a wide range of journals and funding bodies and are on the editorial boards of *Quaternary Geochronology* (KP) and *Archaeological and Anthropological Sciences* (MC). KP is also heavily involved in the NSF-funded development of an AAR database, held by NOAA, to enable long-term data preservation.

SCIENCE HIGHLIGHTS:

A) Dating of the Blake Event at Neumark Nord 2

The sedimentary basin at Neumark Nord 2 in Germany yields a high-resolution pollen record alongside a magnetic excursion. AAR dating of opercula throughout the deposits helped confirm that the core represented a last interglacial sequence and that the excursion represented the Blake Event. The Neumark Nord sequence therefore enabled precise terrestrial-marine correlation for the Eemian stage in central Europe, and showed a remarkably large time lag of ~50000 years between the MIS 5e 'peak' in the marine record and the start of the last interglacial in this region. This means that the beginning of the Eemian as documented at Neumark Nord occurs not simply after the major ice sheets had melted, but considerably later, when sea levels had already begun to drop and substantial continental ice was once again accumulating. These findings have implications for the relationships between the marine record and the terrestrial realm, and for climate models (Sier *et al.*, 2011).

B) mAARiTIME (Marine Amino Acid Racemisation Investigation of The Mediterranean)

Bea Demarchi's PhD showed the utility of extending the new AAR methods to marine shells (Demarchi, 2009), leading to an EU grant to NEaar to expand the work to the Mediterranean rim. mAARiTIME is a highly interdisciplinary project, which brings together the fields of chemistry, archaeology, Quaternary sciences and biology and aims to constrain the timing of when early humans became "modern", and whether "modern" behaviour is isolated to our own species. By applying the closed-system method of AAR dating, over three years mAARiTIME will build chronological frameworks providing reliable dating control for the Mediterranean rim, an area previously seen as key to ideas about the development of behavioural modernity. This year has seen exhaustive tests undertaken on three common species of marine shells, all showing great potential for AAR.

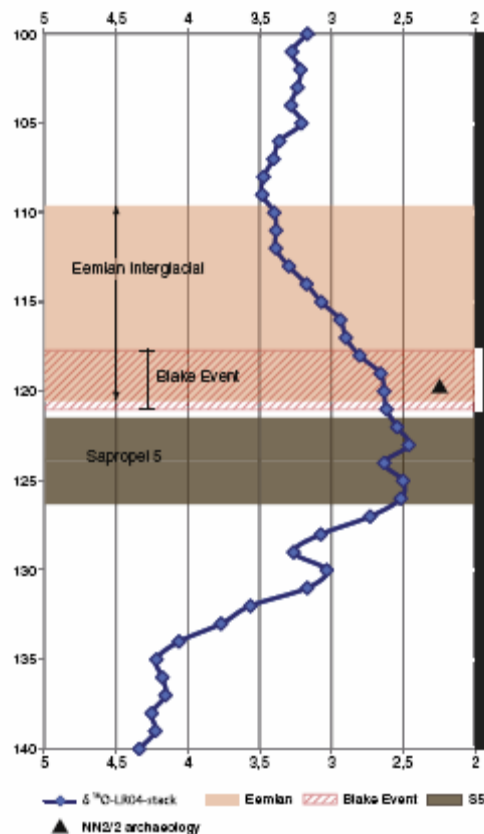
C) Building a Better Eggtimer



This year has seen the majority of the mechanistic studies undertaken for this NERC project, tracking the protein breakdown in ostrich eggshell peptides by chiral amino acid analysis and soft ionisation mass spectrometry. These experiments have thrown up some very interesting results, some confirming previous hypotheses on within-chain racemisation, along with data which will require a rethink into the mechanisms. Moving to the second stage of the project, in November 2010 a fieldtrip to South Africa was undertaken to visit the excavations at the Pinnacle Point sites and catalogue the eggshell coming from these deposits; these samples are currently being analysed.

References:

Demarchi, 2009, *Unpublished PhD thesis, University of York*; Penkman, 2010, *Journal of Quaternary Science*, **25**, 501-514; Penkman *et al.*, 2010, *Quaternary International*, **228**, 25-37; Sier *et al.*, 2011, *Quaternary Research*, **75**, 213-218; Scott *et al.*, 2010, *Journal of Quaternary Science*, **25**, 931-944.



FUTURE DEVELOPMENTS/STRATEGIC FORWARD LOOK

The new "UHPLC" method has been rigorously tested and we have encountered some secondary peaks for the acidic amino acids which we are investigating further by NMR and MS before submission for publication. The majority of the archaeological analyses for the Eggtimer grant will be undertaken in the next year, and these results will be integrated with the experimental results to ascertain the improvements in age determination through the use of these technical developments. The research on amino acids in enamel has yielded some promising results so this will be a continued focus. This year has been an exciting one for the international amino acid geochronology community, with the two inter-laboratory trials, the prospect of long-term data preservation through NOAA and the special session and breakout workshop at the INQUA conference in July 2011. Arising from this is a special issue of *Quaternary Geochronology* edited by KP and Darrell Kaufman (Northern Arizona University), a platform to present the state of the art of AAR geochronology in 2012.

