

Middle Devonian palynomorphs and Carbon isotope stratigraphy of borehole cores in the Dounreay area, Caithness

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Middle Devonian palynomorphs and Carbon isotope stratigraphy of borehole cores in the Dounreay area, Caithness

M H Stephenson

Isotope analysis carried out by Dr M J Leng

Front cover

Part of Cycle 21 in the core of UKAEA borehole SHIP2 (BGS Photograph No. P546867, Photographed by Clive Auton, 2003).

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Summary

This preliminary report describes progress in the use of fossil palynomorph assemblages and $\delta^{13}C_{org}$ stratigraphy in correlating cores of Devonian strata from the Dounreay Site area. A total of 134 samples from Nirex BH 2, SHIP-2, SHIP-8, SHIP-9, SWB-6, SWB-8 and SWB-9. boreholes have been analysed for palynology, while a further 94 samples from Nirex BH 2 and SHIP-2 boreholes were analysed for bulk $\delta^{13}C_{org}$. A list of samples and sampling intervals is given in Section 13. The objectives of the study were to:

- 1. determine the age of spore assemblages in the cores, using standard Devonian biozonation schemes;
- 2. test the presently accepted lithological and geophysical correlations between the boreholes, using standard palynostratigraphical methods;
- 3. characterise cycles 21 and 26 within the Nirex BH 2 and SHIP-2 boreholes using palynology and $\delta^{13}C_{org}$;
- 4. correlate the most complete cored reference sequences in the Nirex BH 2 and SHIP-2 boreholes using characterised cycles, and thus test traditional correlation based on the lithological character of cycles and cycle position.

Overall, the organic yield of the samples is high. The organic residue is dominated by yellow brown amorphous organic material (AOM), and palynomorphs (land plant spores, fungal spores and ?spores of unknown affinity) are usually rare. A small number of samples, notably within cycles 21 and 26 (Nirex BH 2 and SHIP-2) contain significant quantities of land-derived phytoclasts (resistant particles of plant material) and very poorly preserved spores of vascular plant origin.

Spore colour indicates that thermal maturity is low (TAI value 2 to 2+) and comparable to that recorded in other studies from the Dounreay area (Stephenson 2003, Auton 2004). Spores-pergramme yields vary between 0 and approximately 1200. The detailed trends of palynofacies, palynology and yields-per-gramme of spores within the boreholes are shown in Figures 1-7.

The scarcity of age-diagnostic palynomorphs makes age determination of these sequences difficult. However, most of the sections contain spores similar to *Rhabdosporites langii* and zonate spores similar to *Grandispora velata*, and none contain the distinctive spore *Geminospora lemurata*. This indicates a probable early Eifelian to earliest Givetian age for the sampled sections (Stephenson 2003, Richardson & McGregor 1986, Marshall 2000).

Conventional palynostratigraphic correlation between the boreholes using the ranges of palynomorph taxa is difficult to apply because the assemblages are dominated by long ranging taxa, which are commonly poorly preserved. In addition, the sparse nature of assemblages prevents reliable correlation, because presence or absence of significant palynomorphs is probably as much a matter of chance as evolution and phylogeny.

In order to improve the precision of correlation between the cores and to improve knowledge of Dounreay Middle Devonian palaeoecology and palaeoenvironment, a new correlation method has been employed. This involves determining the palynological, palynofacies and $\delta^{13}C_{org}$ characteristics of certain groups of strata in order to 'fingerprint' them. Using this approach it has been possible to fingerprint lacustrine cycles 21 and 26 in Nirex BH 2, and match these to fingerprints of corresponding cycles previously identified by lithological logging in SHIP-2 (Figures 9 and 10). Thus, the presently accepted correlations (JacobsGIBB 2002) based on down-hole geophysical logs (notably natural gamma) and lithological correlations based on 'cycle-counting' between Nirex BH 2 and SHIP-2 are now also supported by palynological,

palynofacies and $\delta^{13}C_{org}$ evidence. This is crucial independent evidence required for the development of an accurate 3D model of the geology of the Dounreay site area and should provide firm constraints on the estimates of the cumulative throw of faults between the 2 borehole sites, c. 1 km apart.

The presence of abundant AOM, which has been shown throughout the Orcadian Basin to be of lacustrine algal origin, indicates that the sediments in the Dounreay site area were deposited in a lake that was occupied by algae. The scarcity of terrestrially-sourced phytoclasts, as well as the low spores-per-gramme values throughout the sections, even in facies indicating a relatively proximal depositional position, could indicate a relatively sparse flora occupied the hinterland of the Dounreay during the mid-Devonian. This may have been due to aridity or to plant assemblages reflecting only early stages of colonisation. The low ratio of phytoclasts to spores, which is unlike that seen in younger sediments (for example of the Carboniferous or Permian), probably indicates the lack of supportive plant tissues in the hinterland plants, which were likely to have been small and herbaceous in character.

This joint palynological, palynofacies and $\delta^{13}C_{org}$ analysis has the potential to provide a better broad correlation between the cored sequences than palynology alone can achieve and may allow better correlation between units mapped at the surface and those recognised in the cores. Consequently, the next phase of work, which mainly consists of collection and analysis of surface samples from across the area will use a similar methodology to that developed here. The aim of this new work will be to link the surface exposures in the Site Area to the cores, put the Dounreay sequence in its regional context, and also allow (in conjunction with petrological studies) correlation of the Baligill and Achanarras fish bed maker horizons across the district. An understanding will also be gained of how the Dounreay sequence differs from younger Orcadian successions farther east.

1 Introduction

This preliminary report outlines the palynology and palynofacies characteristics of 134 samples collected from 7 borehole cores in the Dounreay Site area. Samples were collected from Nirex BH 2, and UKAEA boreholes SHIP-2, SHIP-8, SHIP-9, SWB-6, SWB-8 and SWB-9. In addition, a further 94 samples from Nirex BH 2 and SHIP-2 boreholes were analysed for bulk $\delta^{13}C_{\text{ org.}}$ A list of samples and sampling intervals is given in Section 13. The sampling of the Nirex BH 2 core, was undertaken at BGS Keyworth, by M H Stephenson and U Michie, between September and December 2003. Sampling of the cores from the remaining boreholes was undertaken at the UKAEA core-store at Norfrost, Castletown, Caithness in November 2003 by U Michie and C A Auton. The palynological data described from Nirex BH 2 also incorporate the results of a previous study (Stephenson 2003).

The Middle Devonian sequence in the Dounreay area has well developed cyclicity, expressed in the form of repeating lithologies. These 'Donovan cycles' (Donovan 1980) ideally comprise 4 distinct lithologies (units A-D): laminated limestone (Unit A), and carbonate mudstone and siltstone (Unit B) represent sediments deposited in a permanent lake. Siltstone and mudstone with subaqueous shrinkage cracks (Unit C) and laminated sandstone with desiccation cracks (Unit D), both comprise sediments of an ephemeral lake (playa) complex. These cycles have been numbered upwards from 1 to 40 in the Nirex BH 2 borehole core. Lithologically similar cycles, which have been recognised during logging of the UKAEA cores, have been assigned the same numbers as their equivalent in Nirex BH 2. This has allowed detailed local lithological correlation between the cores (JacobsGIBB 2002), which is tested by this palynological investigation. The cyclicity is also clearly displayed in natural gamma logs of each borehole, which have been used to calibrate and support the lithological correlations. A selection of natural gamma peaks that equate with A or B units in the cores of Nirex BH2 and UKAEA borehole SHIP-2 are shown in Figures 2 and 8.

The objectives of this study are to:

- 1. determine the age of the palynomorph assemblages using standard Devonian biozonation schemes;
- 2. correlate all the boreholes, as far as possible, using standard palynostratigraphical methods;
- 3. characterise cycles 21 and 26 within the Nirex BH 2 and SHIP-2 boreholes using palynology and carbon isotopes;
- 4. correlate Nirex BH 2 and SHIP-2 boreholes using characterised cycles, and thus test previous correlation based on the lithological character of cycles and cycle position.

2 Bulk $\delta^{13}C_{org}$ stratigraphic studies

The use of bulk $\delta^{13}C_{org}$ from sedimentary organic matter (SOM) is becoming established as a stratigraphic correlation technique (e.g. Heimhofer et al. 2003, Stephenson *et al.* in press). The technique uses the ability of plant tissues in the SOM of sequences to reflect gross palaeo-atmospheric ratios of ¹³C and ¹²C. As well as reflecting palaeo-atmosphere, the stratigraphic $\delta^{13}C_{org}$ signature is affected by factors such as the proportions of different plant degradation compounds in SOM, plant type input to SOM, and the presence of formation oil and bitumen (Stephenson *et al.* in press). Ninety-four of the samples taken for palynology for this study were

split and submitted for bulk δ^{13} C _{org} analysis, following bitumen removal. The results of this analysis are discussed in Sections 7 and 8.

3 Materials and methods

The preparation of strew mounts for palynological analysis involved well established procedures of crushing and hydrochloric and hydrofluoric acid treatments (Wood *et al.* 1996). Post-hydrofluoric acid organic residues were oxidised with Schultze's Solution and dilute nitric acid. Counts of a minimum of 150 specimens per slide were made initially (where possible) and slides were then scanned for accessory taxa.

The method for removing hydrocarbon prior to isotope ratio and C/N concentration ratio analysis was as follows. Rock fragments were crushed using a ball mill and the soluble organic matter from all rock samples extracted using a soxhlet apparatus. The samples were refluxed for 24 h in an azeotropic mixture of dichloromethane and methanol (93:7, v:v). All materials (cellulose soxhlet thimbles, silica wool, vials) were cleaned with analytical grade organic solvents prior to use. Any remaining solvent was then removed by evaporation and the dried sediments transferred to vials.

Samples for isotope ratio and C/N concentration ratio analysis were ground to a fine powder, washed in 5% HCl for 12 hours (to remove carbonate), and rinsed with deionised water. ${}^{13}C/{}^{12}C$ analyses were performed by combustion in a Carlo Erba 1500 on-line to a VG TripleTrap and Optima dual-inlet mass spectrometer, with δ ${}^{13}C$ values calculated to the VPDB scale using a within-run laboratory standard (cellulose, Sigma Chemical prod. no. C-6413) calibrated against NBS-19 and NBS-22. Replicate analysis of well-mixed samples indicated a precision of \pm <0.1‰ (1 SD). C/N ratios are analysed on a Carlo Erba 1500 elemental analyser, the ratios are calibrated through an acetanilide standard with a certified composition. Replicate analysis of well-mixed samples indicated a precision of \pm <0.1 (1 SD).

4 Description of palynofacies and palynomorph assemblages

4.1 NIREX BOREHOLE 2

Overall, the organic yield of the samples is high, though palynological assemblages recovered are very sparse, and the majority of samples are barren of palynomorphs. The organic residue of the rocks is dominated by yellow brown amorphous organic material (AOM), though a small number of samples, notably within cycles 21 (210.04-212.98m depth in the core) and 26 (121.51-126.63m depth) contain significant quantities of phytoclasts and very poorly preserved spores of vascular plant origin. Spores are otherwise rare; many show the effects of pyrite growth. Spore colour indicates that thermal maturity is low (TAI value 2 to 2+). Spores pergramme yields vary between 0 and approximately 1200. The detailed trends of palynofacies, palynology, yields-per-gramme of spores, $\delta^{13}C_{org}$, C/N ratio and natural gamma in the borehole core are shown in Figure 1.

The following palynomorph taxa were recorded:

?*Apiculiretusispora* spp. ?Dyad

?Emphanisporites spp. ?Fungal spore ?Lunbladispora spp. ?Retusotriletes sp. ?Rhabdosporites sp. ?Spinose acritarch ?Tetraporina spp. ?Verrucosisporites spp. 'Tubes' of probable vascular plant origin Ancyrospora ?grandispinosa Ancyrospora ancyrea Ancyrospora ancyrea cf. var. brevispinosa Ancyrospora ancyrea var. brevispinosa Ancyrospora cf. longispinosa Ancyrospora longispinosa Ancyrospora/Hystricosporites Auroraspora cf. macromanifestus Calamospora spp. Cristatisporites cf. mediconus Cristatisporites spp. Dibolisporites spp. *Emphanisporites* spp. Punctatisporites spp. *Retusotriletes* sp. Spores indet Verrucosisporites sp. A Verrucosisporites spp. Zonate spore indet Zonate spore sp. A

4.2 SHIP-2 BOREHOLE

The overall organic, palynological and palynofacies yield of the samples is closely similar to that of Nirex BH 2. A small number of samples notably within cycles 21 (123.88-125.69m depth) and 26 (39.59-45.33m depth) contain significant quantities of phytoclasts and spores of vascular plant origin. Spores-per-gramme yields vary between 0 and approximately 600. Palynofacies, palynology, yields-per-gramme of spores, $\delta^{13}C_{org}$, C/N ratio and natural gamma in the borehole core are shown in Figure 2.

The following palynomorph taxa were recorded

?Dyad
?Fungal spore
?Lunbladispora spp.
?Retusotriletes sp.
?Rhabdosporites sp.
Ancyrospora ancyrea
Ancyrospora ancyrea var. brevispinosa
Ancyrospora longispinosa
Ancyrospora/Hystricosporites
Auroraspora cf. macromanifestus
Calamospora spp.
Cristatisporites cf. mediconus
Cristatisporites spp.

Emphanisporites spp. *Retusotriletes* sp. Spores indet Tubes *Verrucosisporites* spp. Zonate spore indet

4.3 SHIP-8 BOREHOLE

The overall organic, palynological and palynofacies yield of the samples is closely similar to that of Nirex BH 2. The palynofacies are dominated by yellow brown amorphous organic material (AOM), though the sample from 24.60 - 24.64m depth contains significant quantities of phytoclasts and spores of vascular plant origin. Spores-per-gramme yields vary between 0 and approximately 300. The detailed trends of palynofacies, palynology, yields-per-gramme of spores and natural gamma within the borehole are shown in Figure 3.

The following palynomorph taxa were recorded:

?Ancistrospora sp.
?Apiculiretusispora sp.
?Rhabdosporites sp.
?Tetraporina sp.
Ancyrospora ancyrea
Ancyrospora ancyrea var. brevispinosa
Ancyrospora cf. longispinosa
Ancyrospora/Hystricosporites
Cristatisporites cf. mediconus
Dibolisporites sp.
Retusotriletes sp.
Spores indet
Zonate spore indet

4.4 SHIP-9 BOREHOLE

The overall organic, palynological and palynofacies yield of the samples is closely similar to that of Nirex BH 2. Spores-per-gramme yields vary between 0 and approximately 500. The detailed trends of palynofacies, palynology, yields-per-gramme of spores and natural gamma within the borehole are shown in Figure 4.

The following palynomorph taxa were recorded:

?Apiculiretusispora sp.
?Punctatisporites sp.
?Retusotriletes sp.
?Rhabdosporites sp.
Ancyrospora ancyrea
Ancyrospora ancyrea var. brevispinosa
Ancyrospora cf. longispinosa
Ancyrospora/Hystricosporites
Cristatisporites cf. mediconus
Rhabdosporites sp.
Spores indet
Zonate spore indet

4.5 SWB-6 BOREHOLE

The overall organic, palynological and palynofacies yield of the samples is closely similar to that of Nirex BH 2. Spores-per-gramme yields vary between 0 and approximately 400. The detailed trends of palynofacies, palynology, yields-per-gramme of spores and natural gamma within the borehole are shown in Figure 5.

The following palynomorph taxa were recorded:

?Apiculiretusispora sp. ?Retusotriletes sp. Ancyrospora/Hystricosporites Spores indet

4.6 SWB-8 BOREHOLE

The overall organic, palynological and palynofacies yield of the samples is closely similar to that of Nirex BH 2. The palynofacies are dominated by yellow brown amorphous organic material (AOM), though the sample from 60.15 - 60.20m depth is relatively rich in terrestrially sourced phytoclasts and spores. Spores-per-gramme yields vary between 0 and approximately 650. The detailed trends of palynofacies, palynology, yields-per-gramme of spores and natural gamma within the borehole are shown in Figure 6.

The following palynomorph taxa were recorded:

?Fungal spore
?Rhabdosporites sp.
Ancyrospora ancyrea
Ancyrospora ancyrea var. brevispinosa
Ancyrospora/Hystricosporites
Emphanisporites spp.
Grandispora cf. velata
Spores indet
Zonate spore indet

4.7 SWB-9 BOREHOLE

The overall organic, palynological and palynofacies yield of the samples is closely similar to that of Nirex BH 2. Spores-per-gramme yields vary between 0 and approximately 250. The detailed trends of palynofacies, palynology, yields-per-gramme of spores and natural gamma within the borehole are shown in Figure 7.

The following palynomorph taxa were recorded:

?*Rhabdosporites* sp. *Ancyrospora/Hystricosporites* Spores indet

5 Age determination based on present and previous studies

The scarcity of age-diagnostic palynomorphs makes age determination of these sequences difficult. However, most of the sections contain spores similar to *Rhabdosporites langii* and zonate spores similar to *Grandispora velata*, and none contain the distinctive spore *Geminospora lemurata*. This indicates a probable early Eifelian to earliest Givetian age for the sections (Stephenson 2003, Richardson & McGregor 1986, Marshall 2000). *Densosporites devonicus*

(mid-Eifelian to Frasnian) was recorded from Nirex BH 1 by Bolt & Cole (1992, above 260.25m depth). On the basis of the lithological correlation given by NIREX (1994; figure 2.2) this level would correlate to approximately 335m depth in Nirex BH 2, hence the age of the sequence above this depth in Nirex BH 2 may more precisely be given as mid- late Eiflian to earliest Givetian, rather than early Eifelian to earliest Givetian.

6 Correlation of boreholes using conventional biostratigraphic techniques

A considerable palynostratigraphic dataset is now available for Nirex BH 2 by combining the present data with that of previous work (Stephenson 2003). This combined stratigraphic dataset is shown in Figure 8. Despite the difficulties of correlation using conventional biostratigraphic techniques outlined below (see Section 8) a broad correlation between a few of the boreholes is possible using these techniques.

The first appearances of most significance are those of:

Cristatisporites mediconus Ancyrospora ancyrea var. brevispinosa Ancyrospora longispinosa Emphanisporites spp.

This is because these taxa are easily recognisable and distinct, even when poorly preserved.

6.1 CORRELATION OF NIREX BH 2 WITH OTHER BOREHOLES

Overall, the palynological assemblages are similar in Nirex BH 2 and SHIP-2 boreholes, indicating the broadly similar ages of the Devonian sequences encountered in each. More precise correlation of specific levels within the two boreholes is difficult, however. *Ancyrospora ancyrea* var. *brevispinosa* occurs in both boreholes, and its first occurrence suggests that level 123.88m in SHIP-2 correlates with level 241.84m in Nirex BH 2 (Figure 8), and this seems broadly consistent with the position of cycles correlated on lithological grounds (see Section 8). Similarly, the distribution of *Emphanisporites* spp. in the two boreholes seems consistent with lithological correlations. The first occurrence of *Cristatisporites* cf. *mediconus* is too high in the SHIP-2 core to be consistent with previous correlations suggested by *Ancyrospora ancyrea* var. *brevispinosa* and *Emphanisporites* spp., and by present lithological correlations.

Correlations of Nirex BH 2 with other boreholes are more difficult due to poorer sample coverage and palynological yield in the latter. Only four samples were collected from SHIP-8 spanning the interval between 10.75 and 24.64m depth, and these yielded sparse assemblages. The presence of *Ancyrospora ancyrea* var. *brevispinosa* and *Cristatisporites* cf. *mediconus* allows only a broad correlation with the upper part of the studied section in Nirex BH 2. Similarly, only 6 samples were collected from SHIP-9, spanning 2.76 and 16.27m depth. The presence of *Ancyrospora ancyrea* var. *brevispinosa* and *Cristatisporites* cf. *mediconus* again suggests a very broad correlation of the sampled interval in SHIP-9 with the upper part of the studied section in Nirex BH 2. Sampling from SWB-8 spans 3.50 to 60.20m depth and yielded *Ancyrospora ancyrea* var. *brevispinosa* and *G*. cf. *velata*. This suggests a broad correlation with the upper part of the studied section in Nirex BH 2. The samples collected from SWB-6 and -9 contain no palynomorphs that allow correlation.

7 Bulk $\delta^{13}C_{org}$ stratigraphic signature

 $\delta^{13}C_{org}$ and Carbon/Nitrogen ratios for Nirex BH 2 and SHIP-2 boreholes are shown in Figures 1 and 2 respectively. Detailed $\delta^{13}C_{org}$ and Carbon/Nitrogen ratios for cycles 21 and 26 in Nirex BH 2 and SHIP-2 are shown in Figures 9 and 10. Overall the $\delta^{13}C_{org}$ ratio for Nirex BH 2 and SHIP-2 boreholes varies between -30 and -35%, and this low ratio is consistent with a dominantly algal source for organic matter. There are no marked large scale stratigraphic changes in $\delta^{13}C_{org}$ through Nirex BH 2 and SHIP-2.

8 Preliminary correlation using cycle 'fingerprinting'

Conventional palynostratigraphic correlation uses the ranges of palynomorph taxa. The present borehole sections contain closely similar palynological assemblages, which are dominated by taxa that range throughout, thus preventing significant first or last appearance datums to be identified. In addition, the sparse nature of assemblages prevents reliable detailed palynological correlation between the boreholes, because presence or absence of significant palynomorphs is probably as much a matter of chance, as evolution and phylogeny. Similarly, poor palynomorph preservation prevents many reliable determinations to species or even genus level. The standard palynostratigraphic schemes used in the Devonian (Richardson & McGregor 1986, Streel *et al.* 1987) offer insufficient resolution to be of value in local Caithness stratigraphy and correlation, despite being able to allow broad correlation to the standard Devonian stages.

In order to improve the precision of correlation and to improve knowledge of the Middle Devonian palaeoecology and palaeoenvironment of the Dounreay Site area, a new correlation strategy is employed here. This involves determining the palynological and palynofacies characteristics of certain 'Donovan cycles', in order to 'fingerprint' them. Similar approaches are common in hydrocarbon production biostratigraphy where, for example, narrow baffles to hydrocarbon fluid flow are correlated on the basis of their unique palynological or micropalaeontological character (see for example Stephenson & Osterloff 2002, Payne *et al.* 1999). To further improve the precision of the method, the samples analysed for palynology and palynofacies were also analysed for $\delta^{13}C_{org}$. Essentially, the stratigraphic trend of $\delta^{13}C_{org}$ is controlled by palaeoclimate and by relative proportions of types of SOM (sedimentary organic material). Theoretically such patterns are very unlikely to be the same in any two cycles, and hence may be used to identify them.

For this project, cycles 21 and 26 in Nirex BH 2 were selected; these were also tentatively identified in SHIP-2 on the basis of lithological and natural gamma log correlation. The cycles in both boreholes were sampled at relatively high resolution for palynology, palynofacies and $\delta^{13}C_{org}$. The palynological samples were also processed so as to allow the palynomorph numbersper-gramme to be calculated. Cycles 21 and 26 in Nirex BH 2 occur from 210.04-212.98m depth and 121.51-126.63m depth respectively; detailed palynological and facies characteristics of Cycle 26 in Nirex BH 2 are shown in Figure 9. The palynological characteristics of Nirex BH 2 Cycle 21 and SHIP-2 cycles 26 and 21 are shown in Figure 10.

8.1 CYCLE 26

In Nirex BH 2 this cycle contains a broadly symmetrical set of facies either side of a carbonate laminite facies (Unit A), which forms the 'centre' of the cycle (Figure 9), and probably represents deposition at the lake maximum. The highest yields of spores and highest spore diversity occur in units B and C. C units, which contain synaeresis (subaqueous shrinkage) cracks, might represent shallowing of the lake, since salinity changes would be consequent on lake water evaporation. Thus, high terrestrial spore content may be related to proximity to the

lakeshore. However, B units probably represent relatively deep lake water, hence high palynomorph yields are the opposite of what might be expected. The high yields may be related to high plant productivity in the hinterland, and therefore to increased plant debris input, even to the deeper parts of the lake. Alternatively, they may be due to transport within small sandy turbidity flows to the deep lake. The cycle contains a relatively diverse palynological assemblage that includes *A. ancyrea, Verrucosisporites* sp., *A. ?grandispinosa, Dibolisporites* sp., common *Ancyrospora/Hystricosporites* and *?Rhabdosporites* spp, as well as spores similar to *Emphanisporites* spp.

The interval in SHIP-2 (39.59-45.33m depth, Figure 10c), identified as Cycle 26, is closely similar in palynological and palynofacies terms to Cycle 26 in Nirex BH 2. In particular, the presence of relatively common *Emphanisporites* spp. (or spores similar to that taxon) suggests a palynological affinity between the two intervals. Thus, if such a correlation of these intervals is valid, the presence of relatively common *Emphanisporites* spp might serve to characterise this cycle in Dounreay boreholes.

 $\delta^{13}C_{org}$ ratios for the intervals in Nirex BH 2 and SHIP-2 are closely similar, varying between – 30 and -34‰. In broad terms the stratigraphic pattern is also similar with the lowest values around -34‰ occurring around the lithological middle of the cycle in both boreholes. Toward the top of the cycle, in lithofacies C and D, an increasing trend is noted in both boreholes. The overall congruity of the $\delta^{13}C_{org}$ pattern in the two intervals supports the correlation as suggested by palynology.

8.2 CYCLE 21

Cycle 21 in Nirex BH 2, and the interval in SHIP-2 identified on lithological grounds as Cycle 21 (123.88-125.69m depth) are shown in Figures 10a and b respectively. In palynological and palynofacies terms, they are closely similar. Taxa that occur in common include *A. ancyrea* and *A. longispinosa*. In addition, a taxon informally termed '?Fungal spore' (see plates) not previously recorded from the Dounreay Middle Devonian, occurs only in these intervals. This indicates likely correlation of the two intervals. If such a correlation is valid, the presence of '?Fungal spore' might serve to characterise this cycle in Dounreay boreholes.

 $\delta^{13}C_{org}$ ratios and stratigraphic patterns for the intervals in Nirex BH 2 and SHIP-2 are also closely similar. Again the lowest values of about -34‰ occur around the lithological middle of the cycle in both boreholes and similar increases in $\delta^{13}C_{org}$ ratio occur in corresponding parts of the upper and lower parts of the cycle in both boreholes. Again the overall congruity of the $\delta^{13}C_{org}$ and C/N ratio patterns in the two boreholes supports the correlation of the interval in the two boreholes as suggested by palynology. The distinct difference in $\delta^{13}C_{org}$ and C/N ratio stratigraphic patterns for cycles 21 and 26 supports the use of these geochemical attributes in fingerprinting and correlating lithological horizons.

9 Preliminary interpretation of palaeoecology and environment

The abundance of AOM, which has been shown elsewhere to be of lacustrine algal origin (see Marshall *et al.* 1985) - as well as various facies evidence - indicates that the sediments were deposited in lakes that were occupied by algae, though no obvious algal structures such as filaments or algal spores are present. The scarcity of terrestrially sourced phytoclasts, as well as the low spores-per-gramme values throughout the sections (even in facies indicating a relatively proximal depositional position) could indicate a sparse hinterland flora, perhaps due to arid conditions. It may also reflect the general scarcity of vegetation cover during the Devonian,

which, in turn, reflects the fact that terrestrial vascular plants had only recently evolved. The low ratio of phytoclasts to spores, which is unlike that seen in younger Carboniferous or Permian sediments, probably indicates the lack of supportive plant tissues in the hinterland plants, which are likely to have been small and herbaceous in character.

10 Ongoing work

The next planned phase of work will focus on collection and analysis of surface samples from across the area and will use similar palynological and isotopic methods to those reported here. The aim will be to link the surface exposures in the Site Area to the cores, put the sequences from the Dounreay cores into a regional context, and allow (in conjunction with petrological studies) correlation of the Baligill and Achanarras fish bed maker horizons across the district.

11 References

Auton, C A. 2004. The Quaternary and Devonian geology of Sheet 115E (Reay). British Geological Survey Commissioned Report, CR/04/055

Bolt, B. & Cole, D. C. 1992. Devonian palynology of Caithness and Orkney. Unpublished MSc thesis, University of Southampton.

Donovan, R N. 1980. Lacustrine cycles, fish ecology and stratigraphical zonation in the Middle Devonian of Caithness. *Scottish Journal of Geology*, **16**, 35-50.

NIREX 1994. Dounreay Geological Investigations: Dounreay Site/District Geology. Report No. 658.

JacobsGIBB 2002. Phase 2 Revision to the development of the Gamma stratigraphy and lithostratigraphy of the Dounreay site. Report Number J20419/20, Issue 2.

Heimhofer, U., Hochuli, P. A., Burla, S., Anderson, N. & Weissert, H. 2003. Terrestrial carbonisotope records from coastal deposits (Algarve, Portugal): a tool for chemostratigraphic correlation on an intrabasinal and global scale. *Terra Nova*, **15**, 8-13.

Marshall, J. A. E. 2000. Devonian (Givetian) miospores from the Walls Group, Shetland. In: Friend, P. F. & Williams, B. P. J. (eds.) *New perspectives on the Old Red Sandstone*. Geological Society, London, Special Publications, 180, 473-483.

Marshall, J. A. E., Brown, J. F. & Hindmarsh, S. 1985. Hydrocarbon source rock potential of the Devonian rocks of the Orcadian Basin. *Scottish Journal of Geology*, **21**, 301-320.

Payne S. N. J. Ewen, D. F. Bowman, M. J. 1999. The role and value of high impact biostratigraphy in reservoir appraisal and development. In: Jones, R. W. & Simmons, M. D. (eds). *Biostratigraphy in production and development geology*. Geological Society, London, Special Publications, 152, 5-22.

Richardson, J. B. & McGregor, D. C. 1986. Silurian and Devonian spore zones of the Old Red Sandstone continent and adjacent regions. *Bulletin of the Geological. Survey of Canada*, **364**, 1-79.

Stephenson, M. H. 2003. Devonian palynology of samples from Caithness. *BGS Internal Report* **IR/02/035**

Stephenson, M. H. & Osterloff, P. L. 2002, Palynology of the deglaciation sequence represented by the Lower Permian Rahab and Lower Gharif members, Oman. *AASP Contribution Series* No. **40**. 1-41.

Stephenson, M. H. Leng, M. J., Vane, C. H., Osterloff, P.L. & Arrowsmith, C. (in press) Investigating Permian climate change from deglacial argillaceous sediments in Oman. Geological Society Special Publications 'Wrestling with Mud'.

Streel, M., Higgs, K., Loboziak, S. Riegel, W., Steemans, P. 1987. Spore stratigraphy and correlation with faunas and floras in the type marine Devonian of the Ardenne-Rhenish regions. *Review of Palaeobotany and Palynology*, **50**, 211-229.

Wood, G. D., Gabriel, A. M. and Lawson, J. C. 1996. Palynological techniques – processing and microscopy. In Jansonius, J. and McGregor, D. C. (eds.) *Palynology: Principles and Applications*. American Association of Stratigraphical Palynologists Foundation vol. **1**, 29-50.

12 Glossary

Palynology. The study of spores and pollen.

Palynomorph. A general term for all microscopic plants or animals, or parts thereof, present in palynological preparations.

Palynofacies. The organic debris in palynological preparations. Consists commonly of amorphous organic matter, phytoclasts, spores, pollen.

Phytoclast. A general term for plant-derived, relatively resistant, particles in sediments. Usually consist of cuticle, tracheids and sheet cellular material.

13 Sample lists

Palynology and palynofacies					
Borehole SHIP 2	Palaeontology				
Depths (m)	registered				
	MPA no				
15.58-15.63	52762				
16.45-16.50	52763				
21.66-21.79	52764				
32.38-32.41	52765				
33.30-32.33	52766				
39.59-39.62	52767				
41.09-41.13	52768				
42.55-42.59	52769				
43.35-43.39	52770				
43.87-43.92	52771				
44.69-44.72	52772				
45.30-45.33	52773				
46.00-46.03	52774				
65.21-65.25	52775				
66.07-66.13	52776				
70.18-70.23	52777				
83.16-83.20	52778				
84.39-84.44	52779				
91.85-91.90	52780				
92.64-92.68	52781				
112.90-112.95	52782				
118.92-118.95	52783				
120.01-120.04	52784				
123.88-123.93	52785				
124.13-124.17	52786				
124.58-124.63	52787				
125.10-125.14	52788				
125.32-125.35	52789				
125.64-125.69	52790				
130.40-130.44	52791				
131.24-131.28	52792				
134.19-134.23	52793				
143.44-143.48	52794				
143.98-144.02	52795				
151.21-151.26	52796				
152.53-152.58	52797				
L					

157.17-157.21	52798
Borehole SHIP 2	Palaeontology
Depths (m) (cont)	registered
	MPA no (cont)
152 02 152 00	50000
173.83-173.88	52800
181.17-181.21	52801
188.57-188.62	52802
200.33-200.37	52803
204.39-204.44	52804
219.85-219.90	52805
Borehole SWB8	Registered
Depths (m)	MPA no
3.50-3.54	52806
8.33-8.38	52807
8.60-8.65	52808
9.19-9.24	52809
12.66-12.71	52810
13.05-13.10	52811
21.96-22.00	52812
29.60-29.64	52813
30.43-30.47	52814
36.68-36.72	52815
42.00-42.04	52816
45.35-45.39	52817
47.96-48.00	52818
56.75-56.80	52819
60.15-60.20	52820
Borehole SWB9	Registered
Depths (m)	MPA no
14.24-14.28	52821
15.26-15.30	52822
18.90-18.95	52823
19.69-19.73	52823
Borehole SWB6	Registered MPA no
Depths (m) 4.45-4.50	52825
5.86-5.90	52826
12.02-12.06	52827
13.40-13.44	52828

17.62-17.66	52829
30.21-30.25	52830
Borehole SHIP 8	Registered
Depths (m)	MPA no
10.75-10.79	52831
17.14-17.18	52832
17.66-17.70	52833
24.60-24.64	52834
Borehole SHIP 9	Registered
Depths (m)	MPA no
2.76-2.83	52835
3.54-3.59	52836
9.70-9.74	52837
10.57-10.61	52838
15.46-15.50	52839
16.23-16.27	52840
Borehole Nirex BH 2	Registered
Depths (m)	MPA no
8.49-8.56	52735
9.39-9.45	52736
16.8-16.85	52737
22.13-22.18	52738
25.48-25.53	52739
34.5-34.55	52740
56.49-56.54	52741
62.45-62.5	52742
67.35-67.4	52743
76.9-76.95	52744
85.62-85.68	52745
92.5-92.55	52746
98.45-98.5	52747
98.5-98.55	52748
121.51	52728
121.73	52727
121.83	52726
122.7	52721
123.03	52724
123.25	52719
123.55	52729
124.1	52725
Borehole Nirex BH 2	Registered
Depths (m) (cont)	MPA no (cont)
124.6	52717
L	•

124.84	52716
125.02	52723
125.17	52718
125.37	52730
125.47	52720
125.65	52734
125.84	52733
126	52731
126.3	52722
126.63	52732
210.04	52712
210.48	52710
210.73	52714
211.13	52711
211.45	52713
211.61	52715
211.86	52708
212.05	52709
212.5	52707
212.98	52706
300.57-300.63	52749
301.38-301.43	52750
306.97-307.02	52751
338.18-338.22	52752
339.87-339.92	52753
343.48-343.53	52754
344.57-344.62	52755
349.65-349.70	52756
351.13-351.18	52757
387.05-387.10	52758
399.92-399.98	52759
402.62-402.68	52760
408.45-408.51	52761

	d13C and C/N ratio						
<u>MPA</u>	<u>d13C</u>	%C	<u>%N</u>	<u>C/N</u>			
52762	-33.5	1.3	0.0	29.7			
52763	-33.2	3.1	0.1	32.9			
52764	-32.7	2.3	0.1	33.4			
52765	-32.8	1.4	0.0	28.1			
52767	-32.1	0.2	0.0	18.2			
52768	-32.7	0.4	0.0	14.8			
52769	-33.8	0.6	0.0	20.4			

CR/04/055

Commercial-in Confidence

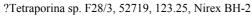
52770			0.0	24.8
52771	-33.2	2.6	0.1	30.8
52772	-33.4	0.9	0.0	27.3
52774	-32.5	0.1	0.0	13.9
52775	-33.1	0.9	0.0	29.3
52776	-33.6	2.1	0.1	32.3
52777	-33.1	1.3	0.0	27.3
52778	-33.4	2.0	0.1	28.4
52779	-33.4	1.7	0.1	30.3
52780	-33.3	4.8	0.1	40.3
52782	-34.0	2.8	0.1	40.3
52783	-34.1	1.2	0.0	36.1
52784	-33.7	2.5	0.1	34.0
52786	-32.8	0.2	0.0	11.6
52787	-33.7	2.7	0.1	32.2
52788	-33.8	3.9	0.1	37.3
52789	-33.5	1.1	0.0	28.0
52791	-33.1	2.4	0.1	34.7
52792	-32.1	0.4	0.0	21.5
52793	-32.4	0.3	0.0	15.3
52794	-34.0	3.7	0.1	39.6
52795	-32.9	0.5	0.0	22.0
52796	-33.6	0.9	0.0	20.5
52797	-33.3	1.1	0.0	24.8
52798	-33.7	1.3	0.0	27.2
52799	-33.4	1.8	0.1	29.4
52800	-33.0	1.2	0.0	31.4
52801	-33.7	0.4	0.0	20.0
52802	-33.8	1.6	0.0	33.3
52803	-32.6	1.5	0.1	29.3
52804	-33.6	1.9	0.1	28.8
52805	-33.9	1.6	0.1	31.7
52708	-33.4	2.5	0.1	29.6
52709	-31.9	0.2	0.0	10.8
52710	-29.6	0.1	0.0	4.3
52711	-33.2	5.2	0.1	34.8
52713	-33.4	2.1	0.1	25.1
52714	-31.6	0.2	0.0	7.0
52715	-32.8	2.1	0.1	23.2
52716	-33.0	0.4	0.0	14.0
52717	-32.7	0.2	0.0	9.3
	L	I	L	

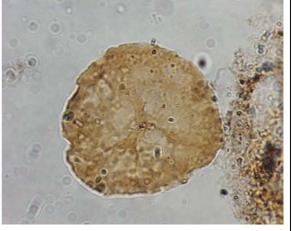
52719 -33.3	0.2	0.0	15.3
52720 -31.2	7.1	0.6	12.4
52721 -32.6	0.3	0.0	13.6
52722 -32.9	2.6	0.1	28.0
52723 -32.9	0.3	0.0	14.2
52724 -32.9	0.5	0.0	15.6
52725 -33.2	0.3	0.0	13.6
52726 -31.9	0.2	0.0	11.9
52727 -31.3	0.3	0.0	13.1
52729 -32.7	0.6	0.0	18.5
52730 -33.3	0.6	0.0	22.3
52731 -32.9	1.4	0.1	18.5
52732 -33.1	0.8	0.0	26.6
52733 -32.9	1.3	0.1	17.9
52734 -33.0	1.7	0.1	27.8
52735 -32.9	1.4	0.1	22.0
52736 -32.9	1.2	0.0	24.1
52737 -33.2	1.4	0.1	25.7
52738 -33.8	0.9	0.0	21.4
52739 -33.5	1.5	0.1	23.4
52740 -33.5	0.8	0.0	28.1
52741 -33.0	1.4	0.0	30.8
52742 -31.5	0.1	0.0	9.1
52743 -33.0	2.8	0.1	21.8
52744 -32.7	1.8	0.1	31.2
52745 -33.1	0.5	0.0	18.1
52746 -33.0	1.1	0.0	27.7
52747 -33.1	3.3	0.1	37.2
52748 -32.9	1.6	0.0	33.2
52749 -33.3	1.3	0.1	25.4
52750 -33.6	1.5	0.0	34.4
52751 -32.3	0.7	0.0	27.4
52752 -33.5	0.8	0.0	23.0
52754 -33.5	0.5	0.0	20.8
52755 -33.2	0.9	0.0	27.2
52756 -33.1	0.6	0.0	24.3
52757 -33.6	1.1	0.0	28.2
<u>. </u>		. <u> </u>	

14 Plates

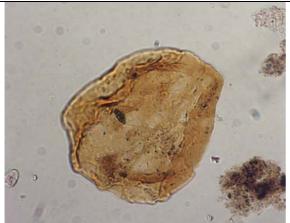
Taxon name is followed by England Finder code, slide code, depth and borehole.

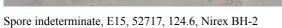






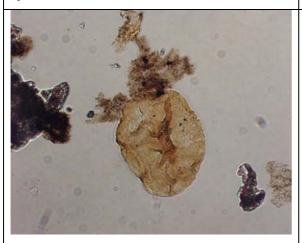
?Emphanisporites spp. N16, 52729, 123.55, Nirex BH-2



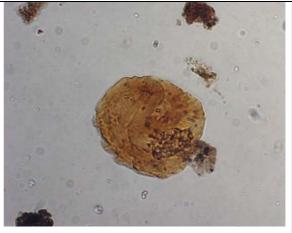




Spore indeterminate, F34, 52717, 124.6, Nirex BH-2



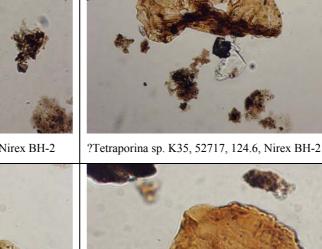
Spore indeterminate, K20, 52717, 124.6, Nirex BH-2

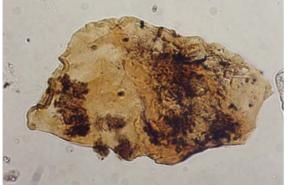


Spore indeterminate, K18, 52717, 124.6, Nirex BH-2

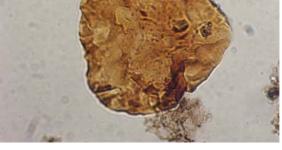


Spore indeterminate, T27/3, 52717, 124.6, Nirex BH-2

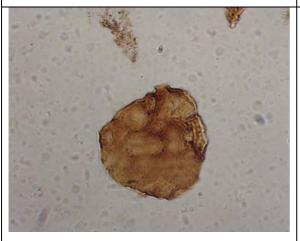




?Tetraporina sp. L20, 52717, 124.6, Nirex BH-2



Spore indeterminate, C20, 52716, 124.84, Nirex BH-2



Spore indeterminate, D34, 52716, 124.84, Nirex BH-2



Zonate spore sp. A, X26/2, 52716, 124.84, Nirex BH-2



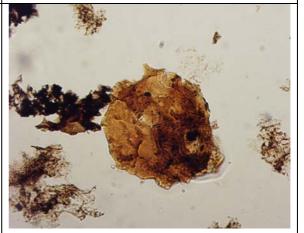
Verrucosisporites sp. A, Z20, 52723, 125.02, Nirex BH-2



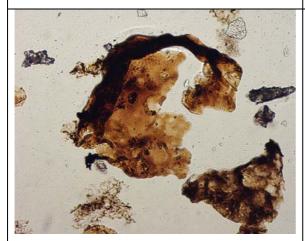
?G. douglastownense, X45/2, 52720, 125.47, Nirex BH-2



?G. douglastownense, X45/2, 52720, 125.47, Nirex BH-2



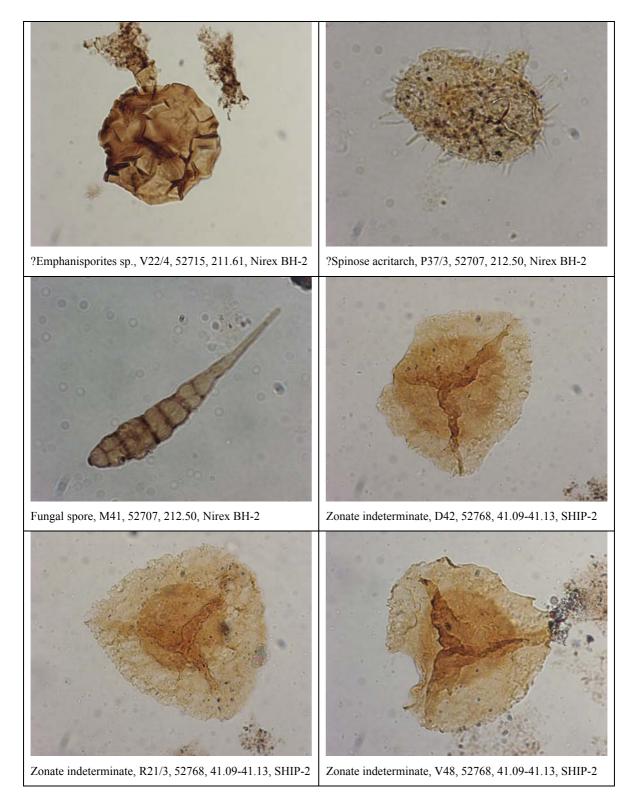
Transition *Ancyrospora* to 'non haptotypic spore', T45/2, 52720, 125.47, Nirex BH-2

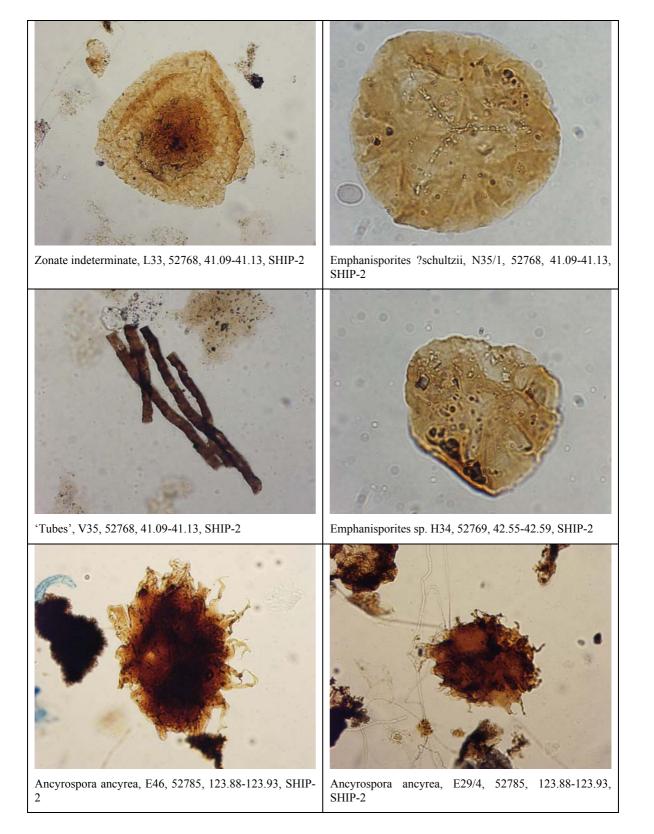


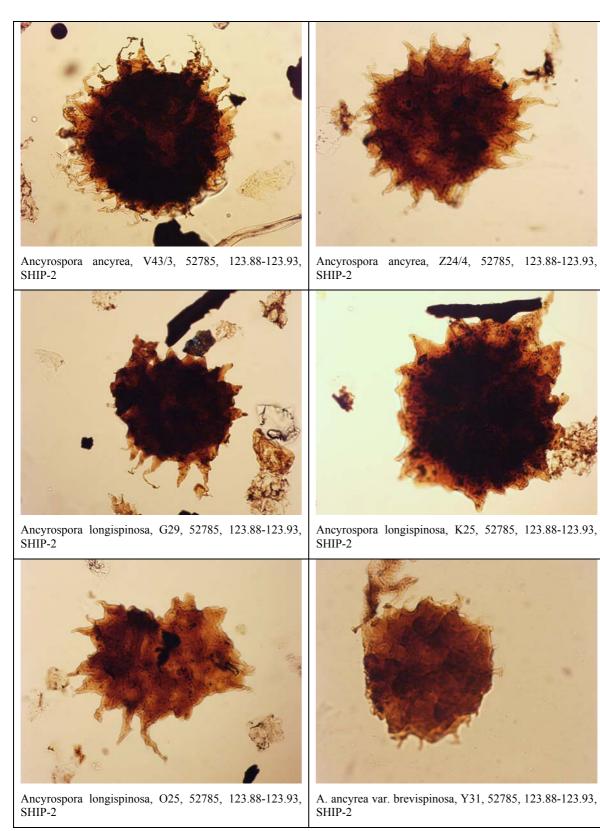
?Tetraporina sp. F33/4, 52710, 210.48, Nirex BH-2



A. cf. longispinosa, Q49, 52710, 210.48, Nirex BH-2





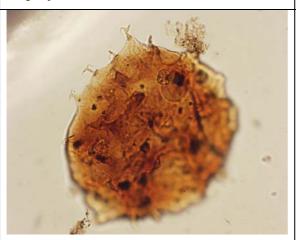




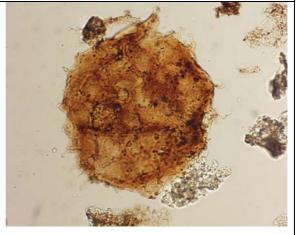
Fungal spore, S30/4, 52785, 123.88-123.93, SHIP-2



?Rhabdosporites sp. F27, 52832, 17.14-17.18, SHIP-8

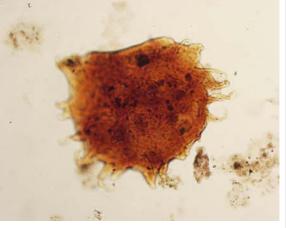


A. ancyrea var. brevispinosa, E46, 52832, 17.14-17.18, SHIP-8

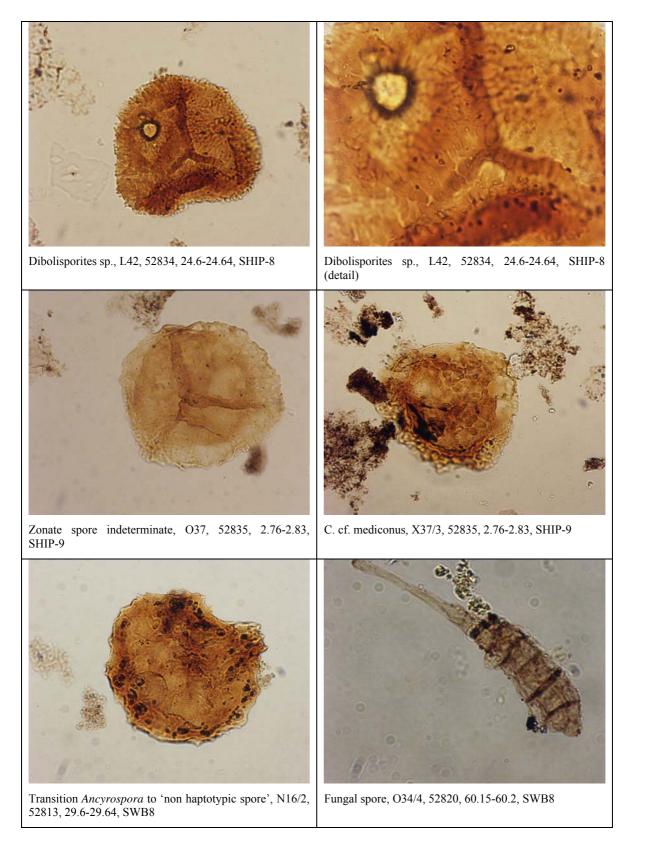


A. ancyrea cf. var. brevispinosa, O35, 52832, 17.14-17.18, SHIP-8





A. ancyrea, N15, 52834, 24.6-24.64, SHIP-8



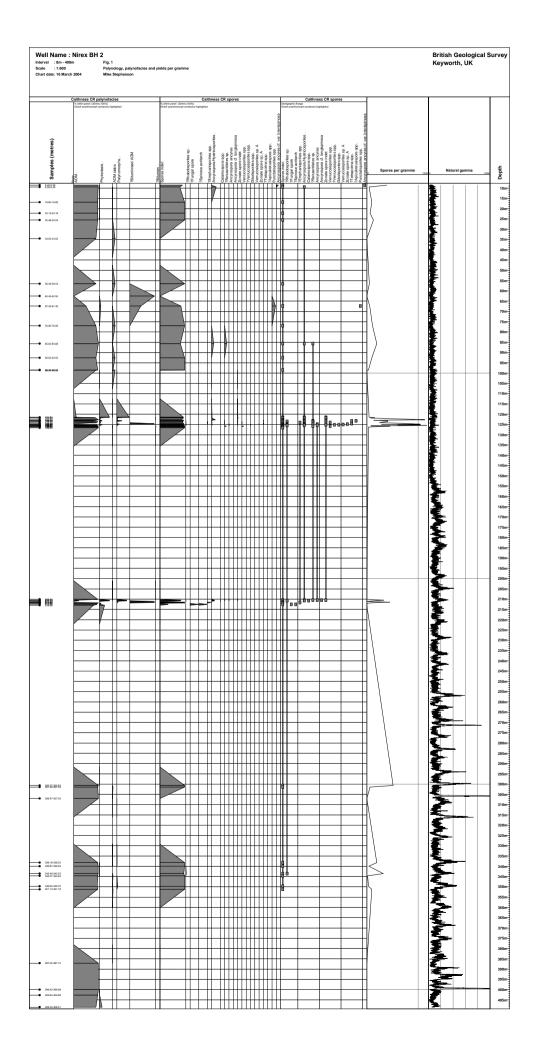


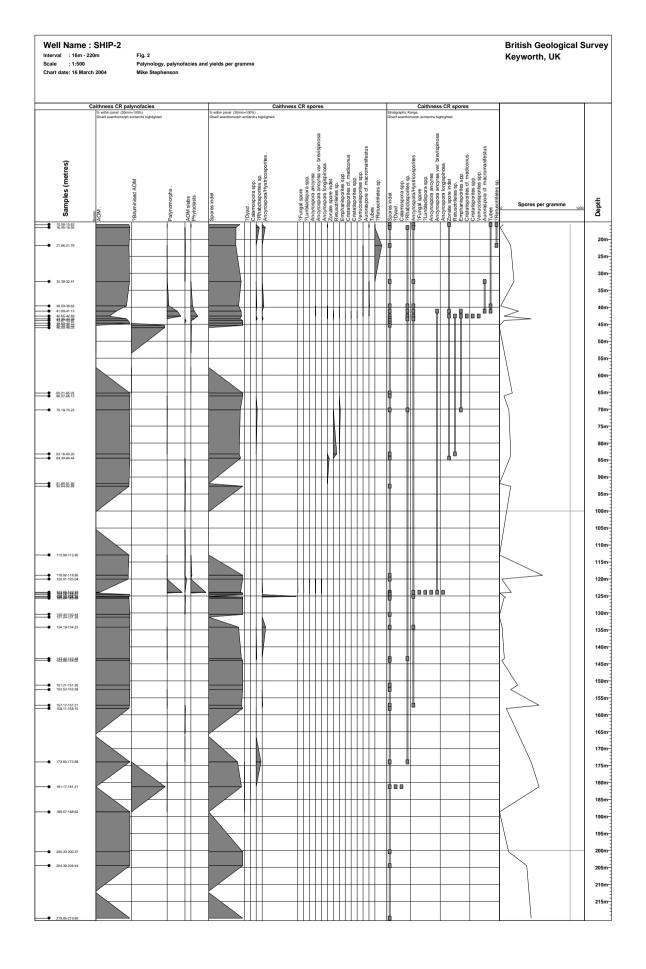
Wood fragments, L22/3, 52820, 60.15-60.2, SWB8

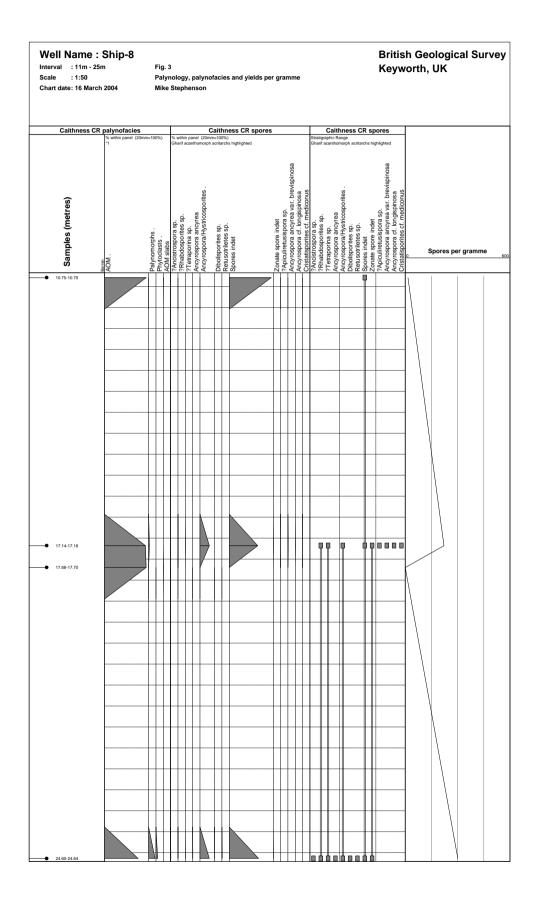


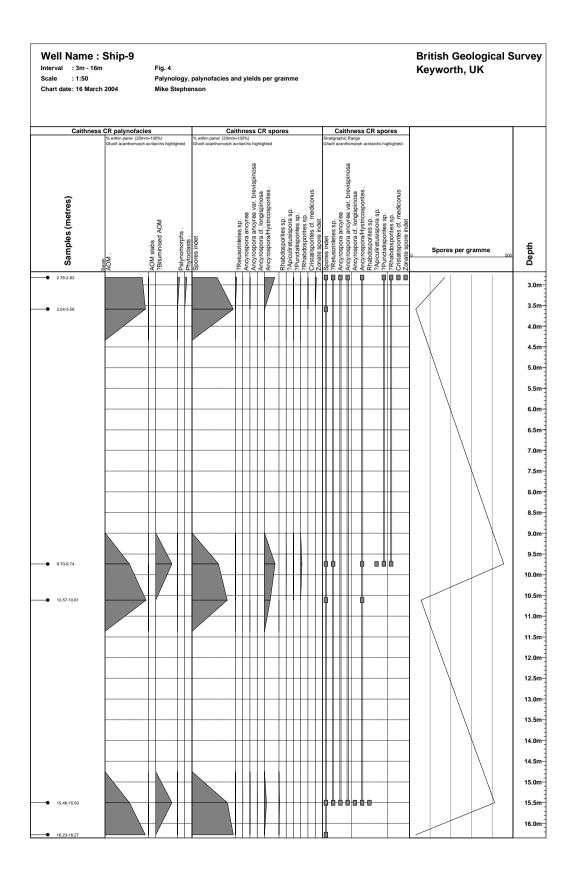
Wood fragments, 52820, 60.15-60.2, SWB8

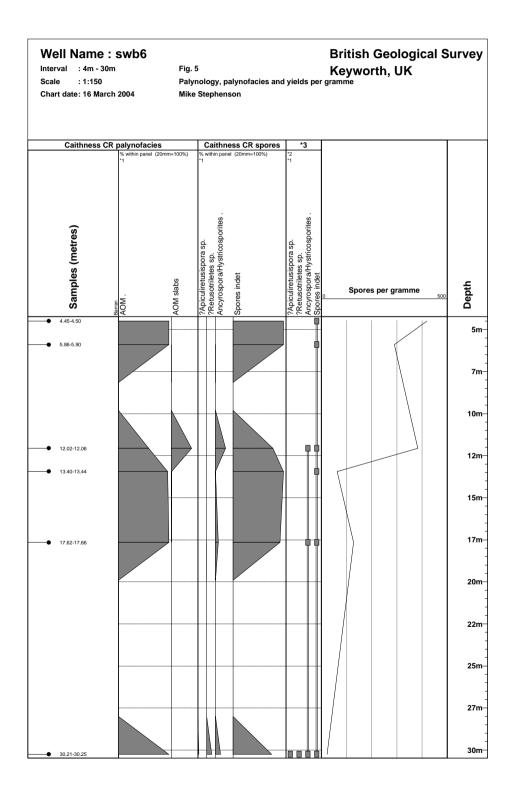
15 Stratigraphic charts; Figs 1-10

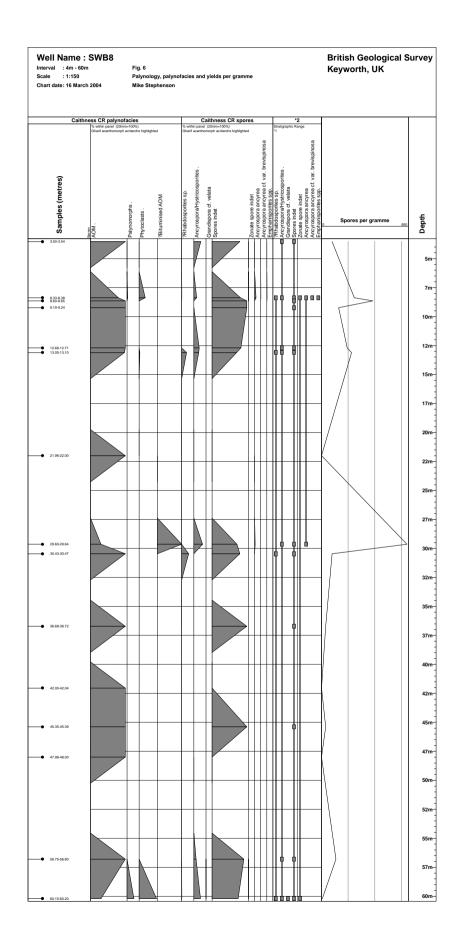


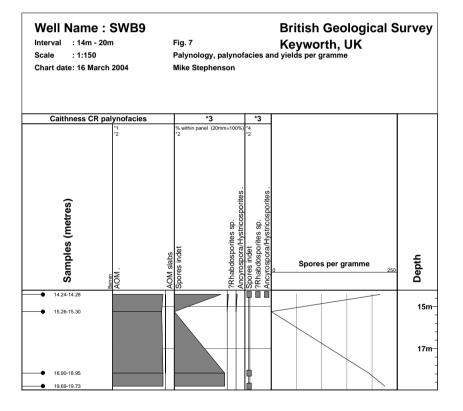












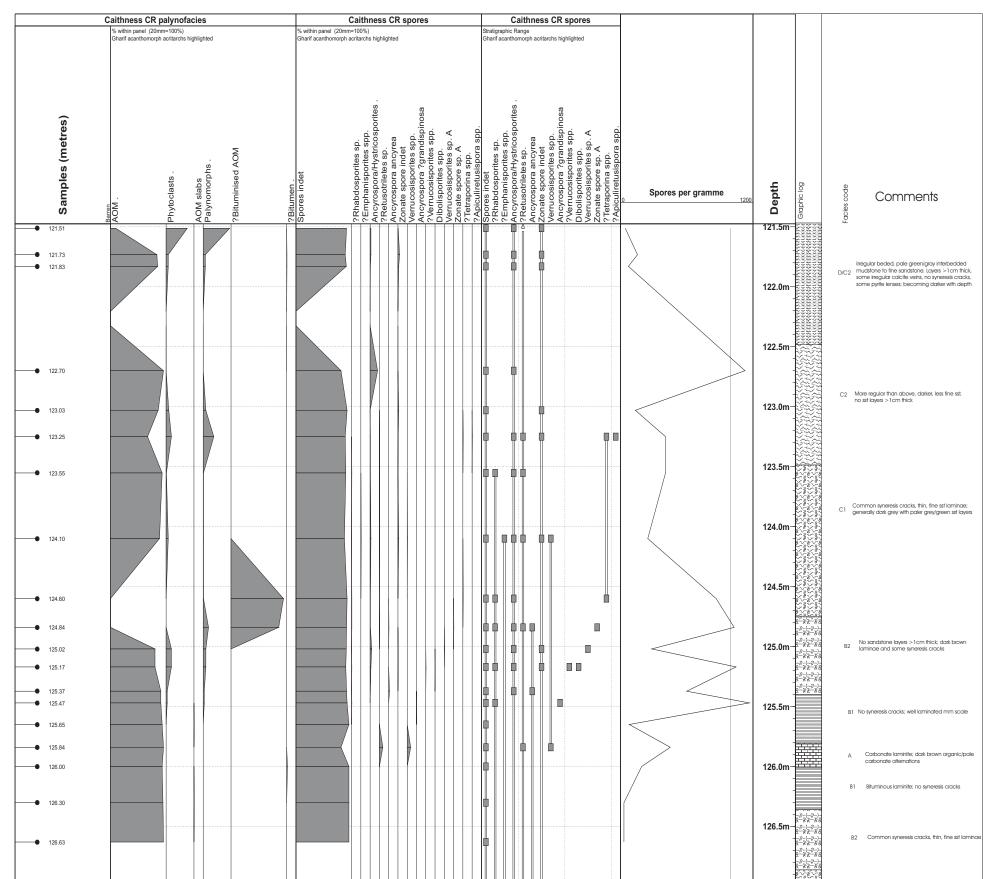
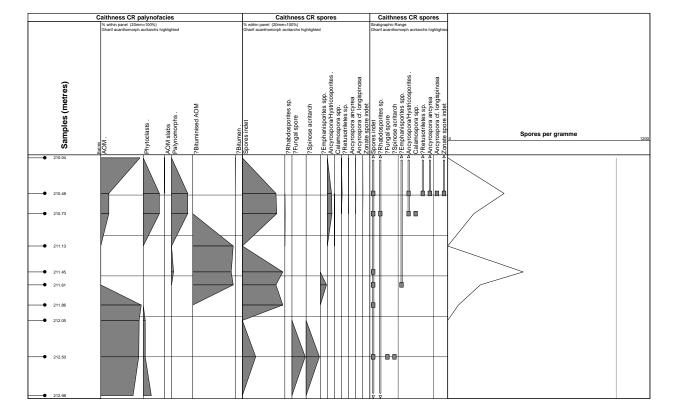


Fig. 8 Palynological and palynofacies characteristics of Cycle 26, Nirex-2

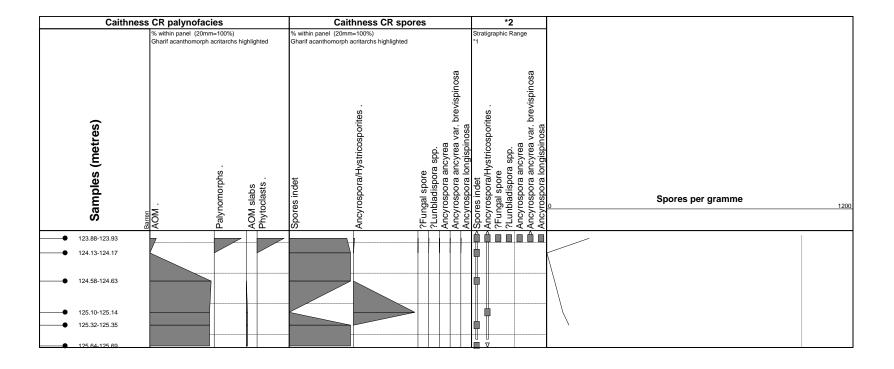
	127.0m	C1
	127.5m	C2
	128.0m	D More massive fine sst; mid grey, irregular bedding

Fig. 9 Palynological and palynofacies characteristics of cycles 21 and 26, Nirex-2



Nirex-2, Cycle 21

Ship-2 Cycle 21



Ship-2 Cycle 26

