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ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · MAY 1999

Impact Factor: 5.33 · DOI: 10.1021/es981091r

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Sediment Microfabric of Oil Rig Drill Spoil Heaps: Preliminary Observations Using Low-Temperature Scanning Electron Microscopy

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Low-temperature scanning electron microscopy is a specialized technique shown to be appropriate for the high-resolution examination of unconsolidated sea floor sediments. Newly developed cryogenic sediment sampling techniques combined with low-temperature scanning electron microscopy (LTSEM) protocols developed for the analysis of biological materials now permits the sampling of fully hydrated bottom sediments while preserving the structural integrity of the sampled material. This enables the direct observation of the sediment fabric as it exists at the seabed and the examination of delicate biological structures that are normally obliterated or distorted by the removal of water required for standard SEM preparation. This paper demonstrates the value of LTSEM and shows variation in microfabric structure between a station located on a spoil heap below an oil rig and a more remote (400 m distant) station. Energy-dispersive X-ray analysis (EDXA) was also conducted on the frozen samples and provided support for the qualitative differences found between the two sites. The results suggest that an organic film was more pervasive on the drill spoil heap and that biological activity in the form of foraminifera was much more extensive on the remote site. Insufficient data has yet been collected to allow statistical analysis of the results, but the paper provides the first microfabric analyses of submerged spoil sediments using LTSEM and confirms the potential of this technique in terms of environmental assessment and analysis of the nature of the sediment fabric of oily, drill spoil heaps from a location in the North Sea.

Introduction

Commercial drilling operations for oil on continental shelf sea areas give rise to the accumulation of cutting spoil heaps and oily residues underneath platforms. The drill cuttings comprise pulverized rock fragments and sands brought to the surface during drilling combined with oil-based muds, which are frequently used as the drilling fluid. Although the cuttings are washed to remove hydrocarbons before disposal, a significant amount of drilling mud and its associated components, including oils, remain associated with the cuttings. Studies have shown that cuttings are usually 5−10% drilling mud. Drilling operations in the central and northern U.K. continental shelf, where tidal currents and wave activity are insufficient to disperse piles, are estimated to yield around 1 470 000 ton of static cuttings and 68 000 ton of entrained oil (*1*).

The drill cuttings and the residues of drilling muds affect the benthic environment and seabed habitat in the immediate vicinity of the rig (*2, 3*). The cuttings pile may blanket the seabed to a thickness of 20 m in some instances, and an entirely new benthic habitat with unique physical, biological, and biogeochemical properties is created underneath and nearby drilling rigs. This paper addresses techniques for the analysis of the physical and biological nature of the cuttings pile on a scale appropriate to flux measurements and microbial activity. Most cuttings mounds are soft, moderately watery (water content typically varies between 20 and 60%) agglomerations of poorly sorted particulate matter and greasy oil. The sediment structure, in particular the microfabric, exerts a fundamental control on the porosity and permeability characteristics of the pile−seawater interface and has implications for seabed erosion (*4, 5*), biogeochemical exchanges (*6*), and organic mineralization.

This study reports some preliminary investigations into the nature of the microfabric and microbial composition of drill cuttings from the Amoco U.K. NW Hutton platform in the northern North Sea. Low-temperature scanning electron microscopy (LTSEM) was employed in order to preserve the structure of seabed samples as much as possible. A new cryogenic sampling method, whereby sediments are preserved by LN_2 vapor-freezing, was applied (*12*). The freezing of sediment samples preserves water as a structural element and allows the storage of the material and later examination, while still frozen, on the specially adapted stage of an SEM. The use of LSTEM has proved valuable in placing biogeochemical studies within a qualitative framework (*4, 7*) and for understanding the erosional processes, microstructure, and cohesive properties of fine-grained marine sediments (*8−10*).

Materials and Methods

Field Study Area. Seabed samples were retrieved from the cuttings pile underneath a drilling platform and from a location 400 m from the pile associated with the Amoco NW Hutton oil field, east of the Shetland Islands, U.K. (Figure 1).

Seabed Sampling. Sampling of the cuttings pile was undertaken from the ROV support vessel *Kommandant SubSea 2000* during October 29−November 3, 1997. A large volume 'mega-corer' (courtesy of Southampton Oceanography Centre) was used to obtain undisturbed samples of surficial sediment. Eight 10 cm diameter core tubes were deployed simultaneously. Two stations were occupied: station 1 adjacent (within 30−40 m) to the rig structure located on the drill spoil field (confirmed by video observation); a second area, station 2, ca. 400 m from the platform.

Sample Freezing. The sampling of unconsolidated sediments without compaction or distortion of the fabric and with an accurate submillimeter resolution is problematic. Even when sampling with large corers (diameters upward of 10 cm), a certain amount of compaction of the sediment fabric is caused (*11*), although where properties of interest are at scales greater than a centimeter this distortion can be seen as negligible. This is not the case when dealing with the vertical distribution of physical properties or materials on a micrometer to millimeter scale (*7*), and subsampling of larger

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10.1021/es981091r CCC: $18.00
Published on Web 05/06/1999

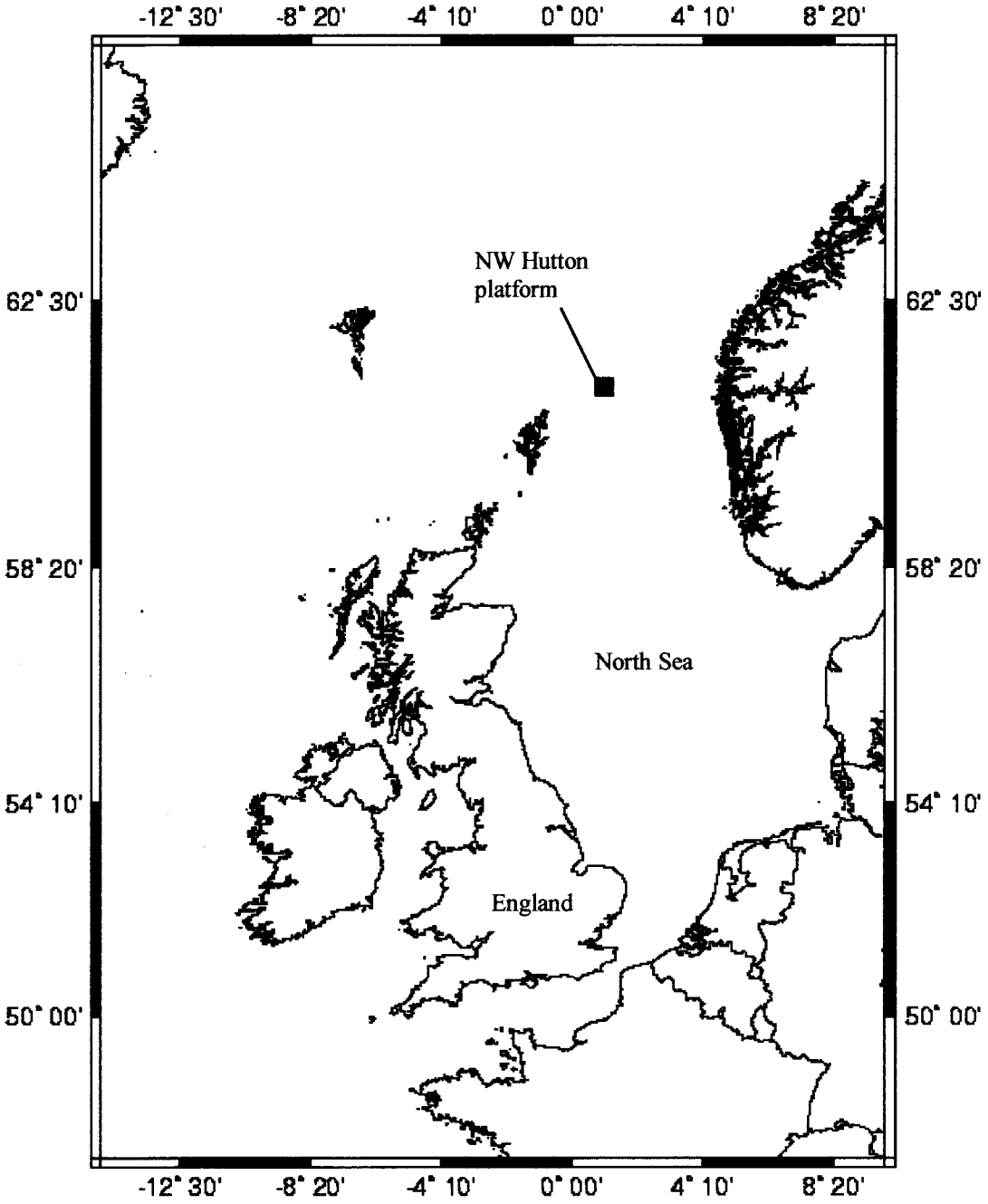

FIGURE 1. Field study area, Amoco NW Hutton drilling platform, North Sea, U.K.

cores leads to further fabric disruption. The problem is compounded when working on comparatively deep-water shelf sediments. Once the mega-cores had been retrieved, most of the overlying water was siphoned off. The sediment was carefully extruded until nearly flush with the top of the mega-core tube, and the thin layer of overlying seawater was removed using a pipet. The sediment surface was sampled using the Cryolander technique (Figure 2) of Wiltshire et al. (*12*). This technique is an improvement on the direct freezing of cores since the sediment is not constrained within the walls of a chamber. When frozen, water expands by approximately 9%, and this leads to the distortion of samples contained within a defined area. The usual expression of this is the formation of a dome in the center of the core as the outer areas freeze before the central region that leads to a buildup of pressure tending to extrude the center of the samples (*12*). However, the Cryolander method uses the gradual freezing of the natural surface delimited, but not penetrated, by a brass cylinder (Figure 2, wall thickness 1 mm, i.d. 50 mm, 80 mm in height). Liquid nitrogen is at first dribbled onto the absorbent cotton surface. The resulting vapor diffuses through the cotton, passing through the nylon mesh underneath and thence into the lower compartment of the chamber. The nitrogen vapor collects in the cylinder and freezes a surface film. Excess nitrogen vapor escapes through a small outlet in the side wall of the chamber. Once the surface is frozen, and therefore protected, further liquid nitrogen is slowly added to the cylinder, and the depth of the frozen zone can be varied by the time of exposure to liquid nitrogen. The expansion that takes place may influence sediment beyond the freezing zone, but the surface is well-preserved (*12*). A frozen disk of sediment (1−2 cm thick, area = 20.41 cm^2) is produced that can then be wrapped in metal foil and stored under liquid nitrogen for further analysis.

Low-Temperature Scanning Electron Microscopy. The frozen disks of sediment were unwrapped while submerged

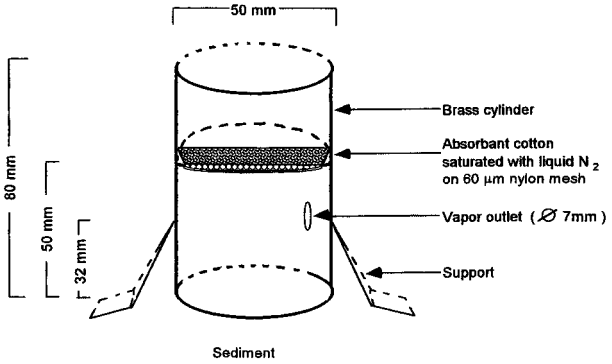

FIGURE 2. Schematic representation of the Cryolander. The central cylinder is placed onto the sediment but not pressed into the surface. The cotton membrane, which completely covers the nylon mesh, permits gaseous nitrogen only to contact the sediment surface during the initial freezing (Reprinted with permission from Wiltshire, K. H.; Blackburn, J.; Paterson, D. M. *J. Sediment. Res.* 1997, *67* (5), 980−984. Copyright 1997 SEPM (Society for Sedimentary Geology). (*12*)).

in a liquid nitrogen bath. The disks are too large to be placed on the stage of the microscope, so they are fractured under nitrogen to produce smaller subsamples or cut while still frozen by a lapidary saw (*12*). The pieces are mounted on a mechanical stub that clamps the frozen sediment in place for transfer into the electron microscope (model JEOL 35CF with EDAX model Oxford AN10000). The specimen is examined under vacuum at approximately −180 °C, and any surface water is removed by "heat etching". The temperature of the microscope stage is raised to −90 °C, at which point ice sublimes directly from the solid phase to the gas phase without passing through a liquid phase. Water on the surface of the specimen exists in two forms: as frozen "free water", which can be sublimed off, or as frozen "bound water" in which the molecules form part of a higher molecular structure such as a membrane, polymer, or other hydrated material (*13*). Bound water does not sublimate off and is retained on the sample. This provides one of the major advantages of LTSEM in that the structure of hydrated material is retained. The etching process can be observed under the SEM at a low accelerating voltage (cf. 4 kV) until the desired amount of etching has taken place. The samples are then coated with gold while being maintained at low temperature (<180 °C) and reexamined. The advantages of LTSEM in the study of hydrated sediment has been outlined by several authors (*8, 14, 9*).

Results and Analyses

Preliminary findings on the nature of the microfabric and microflora associated with organic-rich drill spoil heaps are presented. Although there is some limited work from an earlier study (*5*), to our knowledge this is the first time detailed microfabric information has been gathered on these sediments. Microstructural analysis of cutting pile material is not without complications, which arise principally due to the high hydrocarbon levels (loss on ignition typically 20%) associated with grain surfaces and occupying the interstices between grains. In some instances, the oil−seawater matrix blankets the sediments, and the appearance under the microscope is a smooth, continuous surface. Visualization of the various mineral and biological components of the pile under these circumstances is virtually impossible. Nonetheless, fracture face analysis has the potential to reveal the depth of the layering and the nature of the underlying sediment.

General Microstructure of the Surface. The three-dimensional microfabric of the shelf bed was examined by LTSEM visualization of the surface and freeze-fracture preparations through the surficial layers (Figures 3−5). EDXA microanalysis was also performed to examine, in qualitative terms, the elemental composition of selected samples. The surface of the sediments obtained from beneath the oil rig was surprisingly consistent in terms of composition. The surface was composed of a matrix comprised of organic material, the remains of biogenic structures, polymeric secretions, and remnant hydrocarbon contamination. At low magnification (Figure 3A), the bed appeared most uniform with scattered particles amid a relatively confluent layer of organic material punctuated by occasional pore spaces. At this low magnification, it was difficult to distinguish between particles and the organic film. The particles themselves varied from relatively clean sand-like grains to those covered with a matrix of smaller particles and organic material (Figure 3B). Black et al. (*5*) described these sediments as clayey silts with a percentage sand:silt:clay content typically of 10:80:10. Some smooth bodies that did not appear mineral or of recognizable biological form were also found within the matrix (Figure 3C) and may be of anthropogenic origin. At higher magnification, differences between areas of the sediment bed became more apparent. The organic film was patchy in distribution, appearing fibrilar in some cases, and when present tended to disguise the outlines of the primary particles. The matrix produced a more hydrodynamically smooth bed (Figure 3C). Where the organic film was less pervasive, particles were more easily distinguished and the areas between the grains were clearly void spaces (Figure 3D). At higher magnification, the nature of the particles and the adjoining fibers became more discernible. The particles are generally of a composite nature comprising quartzitic particles and clay minerals, biogenic fragments, and organic material. Few clean particles were present (Figure 3E,F).

Organic Film. The discontinuous nature of the surface organic film is only clear at relatively high magnification. At lower magnification, it is impossible to distinguish between the organic matrix and the presence of frozen water between the particles. Both materials have a similar gray scale appearance under LTSEM and provide the illusion of a similar confluent layer. Regions of the polymer sheet appear as a network of fibrils suspended between the particles (Figure 4A−D). The matrix appears relatively thin, and void spaces can be seen underlying the matrix elements (Figure 4A−C). Oblique visualization of the edge of discontinuous areas confirms that the layer was relatively thin varying from 0.5 to 3 μm (Figure 4D). The nature of the fibrillar material also varied. In some areas the fibers were relatively thick and appeared to have smooth, even sides often graduating to a fine end similar to stretched elastic (Figure 4B,C). On closer examination, some regions of the filament appeared to be composed of a series of smaller blebs arrange in a linear sequence (Figure 4E). This material had a more biological appearance similar to bacterial or fungal filaments, although this could not be confirmed.

In much of the material examined, the surface matrix had the appearance of stretched and decaying rubber sheet (Figure 4F). Many instances were found where sheets of this nature obscured the underlying sediment, precluding identification of the sediment constituents. These sheets appeared to have an eroded quality with pores edged by a folded membrane giving a tattered appearance to the film (Figure 4E). Thus the organic layer is present in a variety of forms:

a confluent sheet (Figure 4A),
a network of fibrils (Figure 4B,C)
an eroded sheet (Figure 4F)

Comparison between Sites. The sediments of the site underlying the oil rig (Figures 3 and 4) contained relatively few signs of biological activity. There were no signs of bioturbation (e.g., the presence of fecal pellets or macrofauna shell debris), and the calcareous shells of foraminifera were

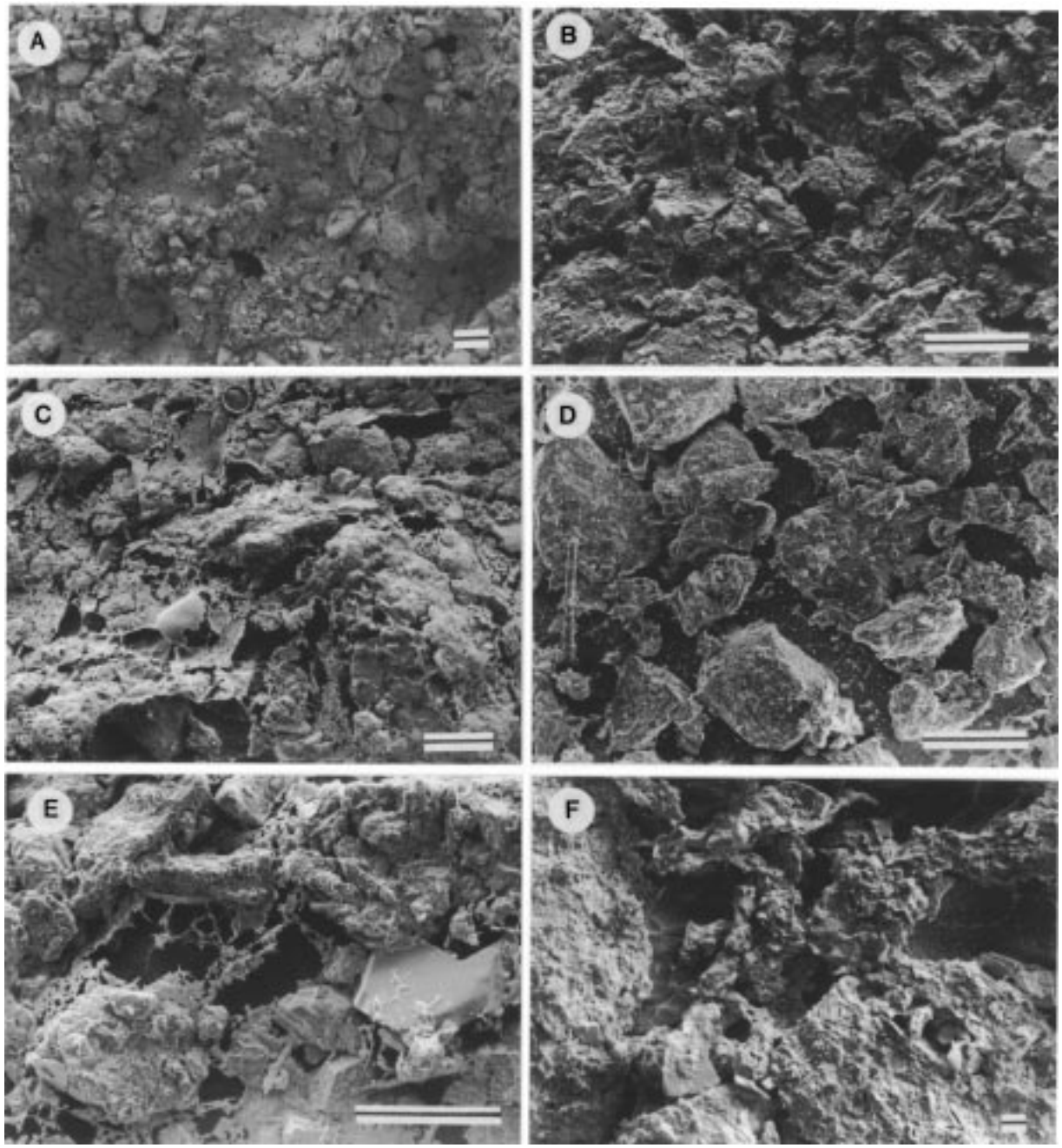

FIGURE 3. Low-temperature scanning electron micrographs of shelf sediments obtained from station 1 beneath an oil rig. (Panel A) Low magnification surface view of sediment bed comprised of a matrix of particles and organic material. (Panels B−E) Increasing detail of the sediment surface. Even at low magnification (panels A and B) there is little evidence of microbial life. Some organic material is apparent at higher magnification (panels C−E), but the coverage of organic material is patchy with some areas showing little evidence of an organic film (panels D and F). Bar markers for panels A−E = 100 μm and for panel F = 10 μm.

either rare or absent. At the second station, located at a distance of 400 m from the platform, signs of biological activity were much more frequent within the sediments. The tests of foraminifera were abundant (Figure 5A) while the organic fibrils pervasive under the rig were less apparent (Figure 5A,B). Higher magnification of the surface revealed foraminifera and particles among coarser sediment, and the density of foraminifera was sufficient that several were fractured in the preparation process (Figure 5C).

EDXA (Double Analysis). EDXA (double analysis) of sediments provides broadly quantitative information on the elemental composition of the sediments. Figure 6 shows EDXA spectra after gold sputtering of samples from each of the sites. EDXA (double analysis) was performed in two modes: general spectra were generated from areas covering approximately 100 μm^2 (Figure 6A,C), while focused spectra were taken from areas of specific interest (ca. 10 μm^2). The relative proportions of aluminum and silicon, indicative of the dominant siliciclastic nature of the sediment, was very similar between the two sampling stations (Figure 6A,C). The iron and chromium content were also very similar between the stations. Slight barium contamination of the cuttings pile material was evident at station 1 (Figure 6A). Barium is a common constituent of cuttings piles because it is used during the drilling process. Black et al. (*5*), for instance, reported barium concentrations of ca. 7.34% from samples underneath the rig, which represents an enormous increase over expected background levels.

The spectra reported by Black et al. (*5*) from underneath the rig platform and included here for comparison (Figure

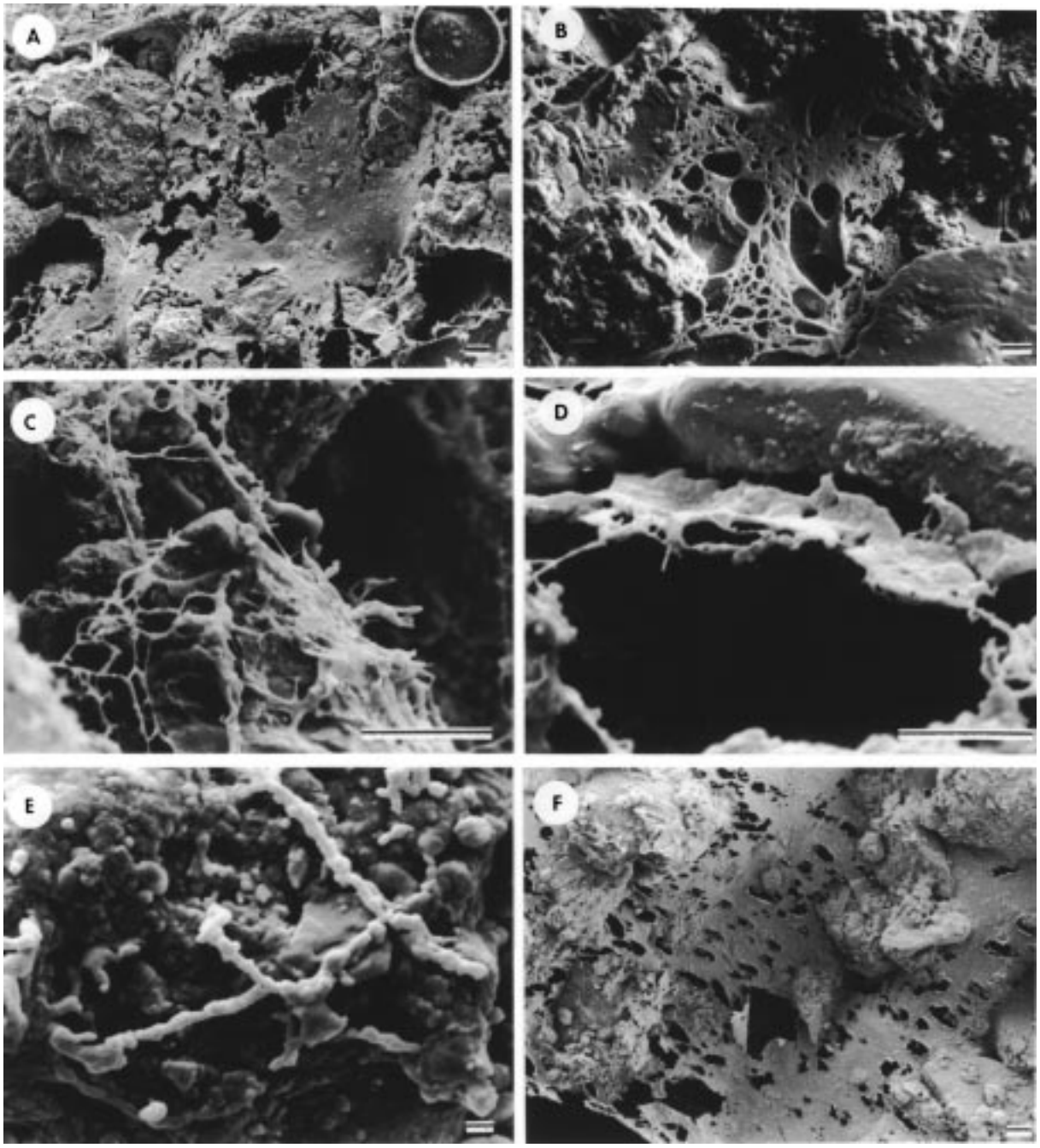

FIGURE 4. Low-temperature scanning electron micrographs of shelf sediments obtained from station 1 beneath an oil rig. Detail of organic matrix. (Panel A) A confluent matrix was present between some particles, which become more easily recognized at higher magnification (see Figure 3C). (Panel B) The matrix was variable appearing sometimes as a network or web of fibrils. (Panels C and E) The fibrils often appeared as blebs of material arranged in a linear fashion. (Panel D) Examination of oblique views show the organic matrix to be relatively thin, often less than 2 μm in thickness. (Panel F) In some areas the film took on the appearance of a thin tattered or eroded organic sheet. All bar markers = 10 μm except panel E, which is 1 μm.

6B) was dominated by a large sulfur peak. This is attributable to sulfur bacteria attached to the surface of mineral grains. Black et al. acknowledge that the EDXA probe was aimed directly at a bacteria-like assemblage some 2−3 μm^2 in diameter and that the coverage of bacteria was not pervasive (*5*). Quantitative X-ray fluorescence (XRF) analysis of the elemental composition of these sediments indicate a sulfur content of 3.24−3.75 wt % (*5*). Samples collected from both sites during this study (Figure 6A,C) reveal only a small sulfur peak. It was not possible from the data to establish clear differences in the biomass of sulfur bacteria between the two sites.

Station 2 was characterized by a greater calcium content, and there was no evidence of barium contamination (Figure 6C). Calcium reflects the presence of general calcareous microfauna such as foraminifera. The difference in calcium content verified the qualitative observation of foraminifera abundance suggested by LTSEM analysis.

Discussion

The use of LTSEM has been more commonly applied to the analysis of biological samples and plant material (*13*). The technique has been especially used to examine biological material because of the requirement to stabilize the water that forms an important structural role in turgid cells.

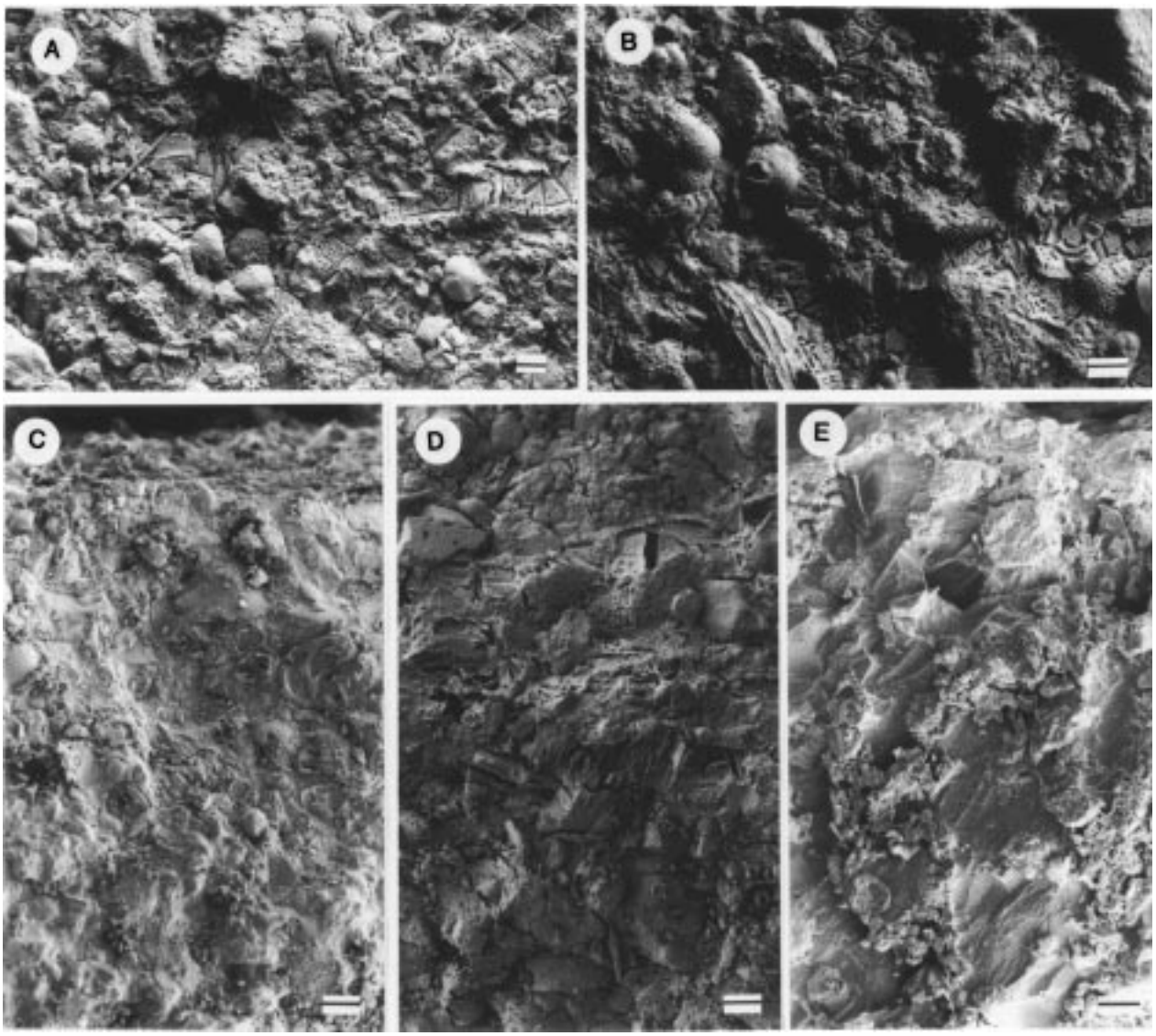

FIGURE 5. Low-temperature scanning electron micrographs of shelf sediments from stations 1 and 2. (Panels A−C) Material obtained from station 2, 400 m from the platform. (Panels D and E) Material obtained from station 1 beneath the rig. (Panel A) Surface view of the sediment. Many foraminifera tests are visible within the surface matrix, and there is no obvious organic film. (Panel B) Detail of the surface area depicting a variety of foram tests. (Panel C) Oblique fracture face of sediment−water interface obtained from station 2. The sediment has a flocculant appearance. (Panels D and E) Fracture faces through the surface of material from station 1 beneath an oil rig. The sediment surface has notably less evidence of biological activity. Some foraminifera tests are visible within the matrix. Particulate debris is smothered in a partially torn thin film (panel D). (Panel E) Vertical fracture face showing a high porosity section through the sediment−water interface. 'Blocky' appearance is due to ice-filled void spaces. All bar markers = 100 μm.

Removal of the water from biological or sedimentological samples can lead to disastrous distortion of the fabric matrix and the misinterpretation of the natural structure (*15*). This is especially true of saturated sediment systems, particularly those that are fine-grained and cohesive. The fragility of hydrated cohesive sediments may even exceed that of many cellular structures, which are at least bound by cell membranes. The pore water of a natural sediment is free to move in response to minute pressure changes or gradients (*16*). The alternative procedure of environmental scanning electron microscopy (ESEM) is also useful in determining the "actual" structure of hydrated material (*17*). However, in the current work, samples must be taken and preserved on board ship as they are retrieved from the mega-core and stored for analysis. Thus, unless ESEM is immediately available, LTSEM is the technique of choice. In addition, some problems of beam damage and resolution can occur where ESEM is used in conjunction with EDXA (*17*). Future work in the comparison of ESEM and LTSEM would however be valuable.

The requirement to analyze the microfabric of sediment is a relatively recent consideration (*10*). Two critical processes are governed by events at the very surface of the sediment matrix. First, erosion takes place at the interface with the suspension of flocs and particles, and second the flux of nutrients and other dissolved materials across the seabed−seawater interface is mediated by the nature of the surface and the presence of organic films. The microstructure of the surface layer therefore has profound effects on these processes and governs the nature of the surface region, and the steep physical and chemical gradients established within the surface region are an area of increasing interest (*18*).

Advances in the use of microsensor systems (*6*) has begun to unravel the physicochemical nature of the upper millimeters of the sediment bed, but fewer attempts have been made to place physical measurements on the same scale. Recent work by Taylor and Paterson (*7*) has shown that the freezing and subsequent analysis of sediment material can provide hitherto unknown information regarding the physical

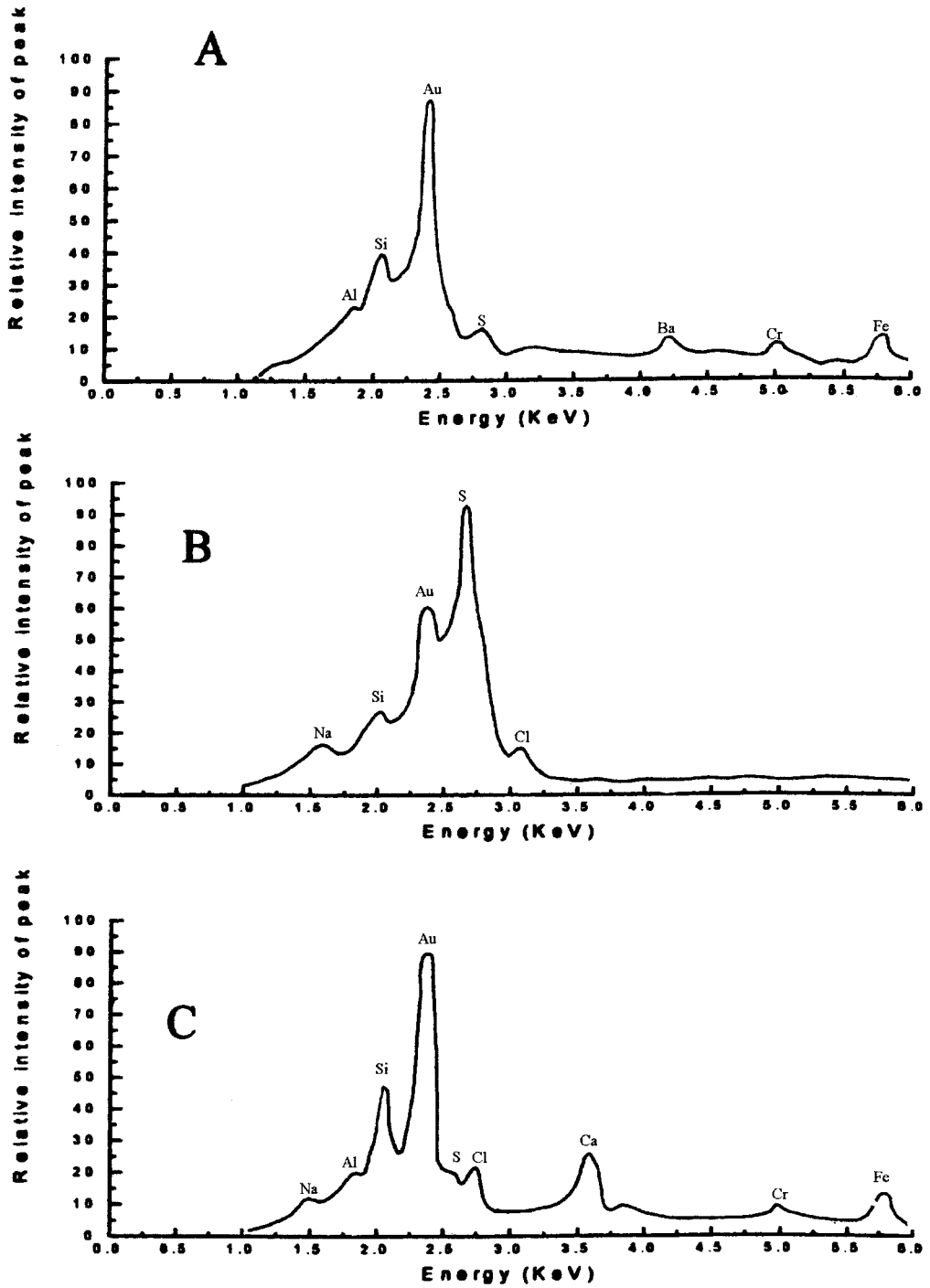

FIGURE 6. EDXA spectra from frozen samples maintained under SEM. (Panel A) General spectrum from the surface of station 1. The major gold peak represents the preparatory sputtering of the sample with gold for SEM analysis. The other major peaks represent aluminum, silicon, barium, chromium and iron. (Panel B) Defined area of sediment featuring a bacterial consortium (from Black et al. (*5*)). The sulfur peak is greatly enhanced and no barium was detected. This spectrum represents a scanned area of ca. 100 μm^2. (Panel C) General spectrum from station 2. The difference between station 2 and station 1 spectra is a peak of calcium and no evidence of a barium peak. KEY: Al, aluminum; Ba, barium; Si, silicon; Au, gold; S, sulfur; Cl, chlorine; Ca, calcium; Cr, chromium; Fe, iron; Na, sodium.

properties of the surface layer over a scale of tens of microns. Analogous information has yet to be obtained from shelf or deep ocean material. Although lander systems are now capable of placing microsensors on the seabed (e.g., ref *19*), the retrieval of material for structural analysis is still a problem, and the use of coring followed by freezing on onboard ship is one approach to the problem. This technique has been applied successfully in intertidal and subtidal mat systems (*20, 4, 8, 21*), and we have shown that this technique can be used to provide qualitative information about the structure and variability of subtidal oily drill spoil sediments, which are inherently more difficult to work with. It is clear that the high organic content (ca. 20%; *5*) and the seawater–oil–clay mineral admixture causes substantial methodological and analytical difficulties in comparison to uncontaminated sediments. The pervasive coverage of oily organic sheets on sediments in particular makes the visualization of microfabric and the identification of indigenous microorganisms troublesome. Further work in the laboratory, on combinations of spoil/clean sediment, should help to

overcome many of the problems encountered in the field study and will aid in the assessment of microfabric and of microbial composition of these unique sediments. In addition, complementary studies, involving measurement of physical (bulk density, porosity, mineralogy) and biological (organic content, extracellular organic substances, pigment, lipids, etc.) properties on a similar scale, should be conducted in tandem with microstructural analyses.

This paper describes, for the first time to our knowledge, an analysis of the microstructure of oil rig drill spoil heaps and provides evidence that the next steps can be achieved. The utility of LTSEM in delimiting varying degrees of contamination in these cutting piles may be of use to future disposal options, such as bioremediation, leaving the piles undisturbed or capping with sand. It may also prove a valuable tool in the assessment of secondary pollution associated with other options such as recovery and reinjection back into the well or recovery and discharge following cleaning treatment.

Acknowledgments

The authors acknowledge the support of the EC through funding to Project EV5V-CT94-0411 for the development of the Cryolander system and refinement in LTSEM protocols. Assistance during field collection of sediments provided by the crew of the *Kommandant SubSea 2000* and Dr. John Hartley is also gratefully acknowledged.

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Received for review October 22, 1998. Revised manuscript received February 25, 1999. Accepted March 16, 1999.

ES981091R