2. EXPLANATORY NOTES¹

Shipboard Scientific Party²

INTRODUCTION

In this chapter, we have assembled information that will help the reader understand the observations on which our preliminary conclusions are based and provide guidance to investigators who wish to select samples for further analysis. This information concerns only shipboard operations and analyses described in the site reports in the *Initial Reports* volume of the Leg 164 *Proceedings of the Ocean Drilling Program.* Methods used by various investigators for shorebased analyses of Leg 164 data will be described in the individual scientific contributions to be published in the *Scientific Results* volume.

AUTHORSHIP OF SITE CHAPTERS

The separate sections of the site chapters were written by the following shipboard scientists (authors are listed in alphabetical order, with no seniority implied):

Principal Results: Matsumoto, Paull Background and Objectives: Matsumoto, Paull Operations: Pollard, Wallace Lithostratigraphy: Black, Damuth, Hesse, Nähr, Pierre, Watanabe Gas Hydrate: Matsumoto, Paull, Watanabe Biostratigraphy: Okada Paleomagnetism: Hiroki, Musgrave Microbiology ("Explanatory Notes" chapter): Goodman Downhole Tools and Sampling: Borowski, Dickens, Egeberg, Stahl, Wehner Organic Geochemistry: Lorenson, Thiery, Wehner Inorganic Geochemistry: Borowski, Dickens, Egeberg Physical Properties: Lodolo, Ruppel, Satoh, Winters Geophysics: Holbrook, Hoskins, Wood Downhole Logging: Collett, Ladd In Situ Temperature Measurements: Ruppel Synthesis and Significance: Matsumoto, Paull

Section 4 (this volume) contains summary core descriptions and photographs of each core.

SHIPBOARD CORE HANDLING AND ANALYSIS

General core handling procedures are described in previous *Initial Reports* volumes and the *Shipboard Scientist's Handbook* and are summarized here. The standard procedures were modified slightly so that gas hydrate samples, which are unstable under surface conditions, could be sampled as rapidly as possible. As soon as cores arrived on deck, whole-round sections that were thought to contain gas hydrate were immediately taken for both shipboard and shore-based analyses (see "Gas Hydrate" section, this chapter). Gas voids in the remaining cores, when present, were then sampled by means of a vacutainer for analysis as part of the shipboard safety and pollution prevention program. Core-catcher samples were taken for biostratigraphic analysis. When the core was cut in sections, whole-round samples were taken for shipboard interstitial-water (IW) analyses and for shore-based studies of organic geochemistry, microbiology, and physical properties. In addition, headspace gas samples were immediately taken from the ends of cut sections and sealed in glass vials for light hydrocarbon analyses. One section per core was commonly taken and sealed in a tube equipped for measuring core temperature and the total volume and composition of gas evolved from decomposing hydrate (see "Gas Hydrate" section, this chapter).

Many cores recovered during Leg 164 contained abundant gas that caused the cores to expand. When expansion was observed in a core as it arrived on deck, holes were punctured through the core liner at regular intervals, particularly at voids (presumably where there is gas), to minimize disturbance to the core. When gas caused the sediments to extrude from the core liners, core liner extensions were attached to the 1.5-m-long core sections (or where IW samples were taken) to maintain the stratigraphic position of the sediment. In some cases, this additional core liner affected some of the hole-core passthrough measurements. After the core was split, the original liner and the extension were sealed together with acetone.

Unsplit core sections were run through the multisensor track (MST), and thermal conductivity measurements were performed on sections relevant for heat-flow studies. The cores were then split into working and archive halves, from bottom to top, so investigators should be aware that older material could have been transported upward on the split face of each section. The working half of each core was sampled for shipboard analyses, such as physical properties, carbonate contents, and mineralogical determinations by bulk X-ray diffraction, and for shore-based studies. The archive half was described visually, using smear slides for lithologic classification. Most archive sections were run through the cryogenic magnetometer. Both blackand-white and color photographs were taken of the archive halves, a whole core at a time, and close-up photographs (black-and-white) were taken of particular features for illustrations in the summary of each site. Cores recovered using the pressure core sampler (PCS) were sampled for IW and physical properties analyses and then described and photographed.

Both archive and working halves of the core were then put into labeled plastic tubes, sealed, and transferred to cold storage space aboard the ship. At the end of the leg, the cores were transferred from the ship into refrigerated trucks and to cold storage at the Bremen Core Repository of the Ocean Drilling Program, Universität Bremen, Bremen, Federal Republic of Germany.

Numbering of sites, holes, cores, and samples followed the standard ODP procedures. For example, a sample identification of "164-991A-2H-1, 10–12 cm" represents a sample removed from the interval between 10 and 12 cm below the top of Section 1, Core 2, of Hole 991A during Leg 164. All ODP core and sample identifiers indicate core type. The following abbreviations are used: H = hydraulic piston core (also referred to as APC, or advanced hydraulic piston core); X = extended core barrel (XCB); and P = PCS. APC, XCB, and PCS cores were cut during Leg 164.

¹Paull, C.K., Matsumoto, R., Wallace, P.J., et al., 1996. Proc. ODP, Init. Repts., 164: College Station, TX (Ocean Drilling Program).

²Shipboard Scientific Party is given in the list of participants that precedes the Table of Contents.

Cored intervals are referred to in meters below seafloor (mbsf); these are determined by subtracting the rig floor height above sea level (as determined at each site) from the total length of drill pipe measured from the rig floor.

LITHOSTRATIGRAPHY

The following methods are described in this section:

- 1. Procedures used during Leg 164 to classify sediment;
- Methods used to visually describe sediment cores and the procedure followed to condense these data into computergenerated summary sheets for each core using the ODP visual core description (VCD) program;
- X-ray diffraction methods used to analyze the mineralogy of selected sediment samples;
- Methods used to take routine measurements of sediment color using a spectrophotometer; and
- Methods used to prepare thin sections of samples taken from cores.

Classification of Sediments

The sediment classification scheme used during Leg 164 is descriptive, using composition and texture as the only criteria to define lithologies. Genetic terms such as pelagic, hemipelagic, turbidite, debris flow, mixed sediments, and so on, do not appear in this classification. The term "clay" is used for clay minerals and other siliciclastic material less than 4 μ m in size. Biogenic components are not described in textural terms. Thus, a sediment with 55% sand-sized foraminifers and 45% siliciclastic clay is called a foraminifer clay, not a foraminifer clayey sand.

Rules for Classification

The principal name is determined by the component or group of components (e.g., total biogenic carbonate) that comprise(s) at least 60% of the sediment or rock, except for subequal mixtures of biogenic and nonbiogenic material (Fig. 1). The main principal names are as follows:

- Nonbiogenic: If the total of a nonbiogenic component is greater than 40%, the main name is determined by the relative proportions of sand, silt, and clay sizes when plotted on a modified Shepard (1954) classification diagram (Fig. 1). Examples of nonbiogenic principal names are clay, silt, silty clay, or sand.
- Biogenic: If the total of biogenic components is greater than 60%, the principal name is "ooze" (e.g., nannofossil ooze) (Fig. 1).
- 3. Mixed sediments: In mixtures of biogenic and nonbiogenic material in which the biogenic content is 40%–60%, the principal name consists of two parts: (1) the name of the major fossil(s), hyphenated, if necessary, with the least common fossil listed first, followed by (2) the textural name appropriate for the siliciclastic components (Fig. 1). If nannofossils form 40%–60% of a sediment that contains nothing else but clay, then the name is nannofossil clay, even if nannofossils are somewhat more abundant than clay. When a component makes up 10%–40%, it qualifies for minor modifier status and is hyphenated with the word "rich" (e.g., nannofossil-rich clay). When a component makes up only 5%–10% of the sediment, it can be indicated with a minor modifier that consists of the component name hyphenated with the word "bearing"



Figure 1. A. Textural classification scheme for siliciclastic sediments, modified from Shepard (1954) by subdivision of the central triangular field into muddy sand and sandy mud. The sand-, silt-, and clay-sized fractions are defined using the Wentworth (1922) grade scale. The patterns used on the Shepard triangle are explained in Figure 2. B. Classification for naming mixtures of biogenic and siliciclastic materials. Names for microfossil components and the siliciclastic fraction are examples only (i.e., placeholders); they can be replaced by any valid textural name (for siliciclastic fraction) or microfossil name. Examples are foraminifer silty clay and nannofossil-rich sandy mud. The asterisks in the scheme for biogenic-clastic mixtures indicate an unusual component, such as plant debris, present in amounts of 5%– 10%; use of the "-bearing" category is optional.

(e.g., nannofossil-bearing clay). Where two minor components are present, the most abundant accessory component appears closest to the principal name. Major and minor modifiers are listed in order of increasing abundance before the principal name.

Examples:

In cases of subequal mixtures of calcareous microfossils, the modifiers "calcareous" or "carbonate-rich" can be substituted for the microfossil names.

- Chemical sediments and diagenetic beds or nodules: Sediments composed of minerals formed by inorganic precipitation such as evaporites and carbonates are classified according to mineralogy, texture, and fabric.
- 5. Lithified sediments: The suffix "-stone" is affixed to the principal names sand, silt, and clay when the sediments are lithified. Chalk is partially lithified sediment composed of more than 60% calcareous biogenic components.

Visual Core Description and the Barrel Sheet Program "VCD"

Information from megascopic description of each core was recorded manually section by section on VCD paper forms (one form per section). This information was then condensed and entered into ODP's VCD computer program, which generates a simplified, onepage graphical core description. These graphical core descriptions are presented with whole-core photographs in Section 4 (this volume).

The lithology of the recovered material is depicted on the computer-generated core-description forms by symbols representing up to three components (Fig. 2), separated by vertical lines, in the column titled "Graphic Lithology." Leg 164 sediments are generally biogenic, siliciclastic clays and muds, where mud is defined as a mixture of silt and clay (grain-size divisions for sand, silt, and clay are those of Wentworth, 1922). A sediment type is represented by a single "Siliciclastic Sediment" symbol if it is homogeneous in texture, or by two "Siliciclastic Sediment" symbols if texturally distinct siliciclastic sediments are interbedded (e.g., interbeds of sand and silty clay forming sand-mud couplets). The relative width of the columns indicates the relative proportion of each type of siliciclastic sediment in the interbedded section.

Leg 164 sediments are predominantly mixtures of variable percentages of biogenic particles (e.g., nannofossils, diatoms, foraminifers, and spicules) that are dispersed in the siliciclastic clays or muds (Fig. 2). For sediment with a biogenic fraction greater than or equal to 10%, the biogenic component is plotted as a vertical strip on the "Graphic Lithology" column, with the implication that the biogenic grains are dispersed in the coexisting clayey or muddy sediment (e.g., pelagic and hemipelagic sediments). Constituents accounting for <10% of a given lithology (or others remaining after the representa-



Figure 2. Key to patterns used to represent lithology in the "Graphic Lithology" column of the computer-generated core-description forms, which are presented with the whole-core photographs.

tion of the three most abundant lithologies and components) cannot be shown in the "Graphic Lithology" column but are listed in the "Lithologic Description" section of the core description form (see below).

Clay conglomerates composed of large sedimentary clay clasts and blocks form a special component of some units and are represented in the "Graphic Lithology" column by a special symbol (Fig. 2). These conglomerates commonly contain structures that indicate they were formed by soft-sediment deformation processes. Rudaceous carbonate rocks composed of intraclasts (e.g., cemented calcareous clay) and/or bioclasts (e.g., shell fragments) of carbonate material are rare, but form another special component of some units, and are classified as calcirudites or biocalcirudites in the "Graphic Lithology" column (Fig. 2).

Chronostratigraphic units were identified by the shipboard paleontologist and paleomagnetists and are recorded in the "Age" column of the core description form. Boundaries are indicated as follows: sharp boundary = straight line; unconformity or hiatus = line with + signs above; and uncertain boundary = line with question marks.

The "Structure" column is used to indicate a wide variety of structural features that characterize the sediment, such as bed thicknesses, primary sedimentary structures, soft-sediment deformation structures, and diagenetic features (Fig. 3). The symbols are schematic and are placed as close as possible to their proper stratigraphic position; for exact positions of sedimentary features, copies of the detailed section-by-section paper core-description forms can be obtained from ODP. The "Structure" column is divided into three vertical windows and shows:

- Symbols indicating thickness of sand-mud or silt-mud couplets, distinctness of lithologic boundaries, and synsedimentary contorted bedding (Using a scheme simplified from Ingram [1954], thick bedding refers to couplets thicker than 30 cm, medium bedding to couplets 10–30 cm thick, and thin bedding to couplets thinner than 10 cm; laminae are thinner than 1 cm.);
- Information on grading types, the locations of fining- and coarsening-upward sequences that involve a number of beds, and the nature of the bases of beds (e.g., basal scours); and
- Symbols for sedimentary structures (e.g., lamination, fluidescape features, burrowing intensity, and scours) and other components of special interest in the sediments (e.g., concretions, plant debris, and microfaults).

Deformation and disturbance of sediment that clearly resulted from the coring process are illustrated in the "Drilling Disturbance" column, using symbols shown in Figure 3. Blank regions indicate the absence of coring disturbance. Categories of coring disturbance are distinguished in the following manner: slightly deformed = bedding contacts are slightly bent; moderately deformed = bedding contacts are extremely bowed, but not disrupted; highly deformed = bedding is completely disrupted, with local diapirlike or flow structures; and soupy = water-saturated intervals that have lost all aspects of original bedding. Both highly deformed and soupy intervals can result from flow-in of sediment during piston coring, commonly associated with incomplete strokes of the APC corer.

"Drilling biscuits" are short, disjointed, and rotated core segments that are commonly ubiquitous in sediment recovered with the XCB. In clay and silty clay sequences, the biscuits are recognized as segments, generally 1–10 cm thick, separated by thin to thick (generally >1 μ m to <1 cm, thinnest near the center of the core), black to gray pseudo-laminae or beds that, at least in part, consist of injected drilling slurry. The character of both the biscuits and the laminae vary with the lithology and strength of the sediment (see Flood, Piper, Klaus, et al., 1995, pp. 51–52, for detailed discussion).

Expansion of methane gas during core recovery disrupted the sediments in many of the Leg 164 cores. Some sediment was lost from Structure symbols



Figure 3. Key to symbols used to represent sedimentary structures, components, and drilling disturbance in the "Structure" and "Drilling Disturbance" columns of the computer-generated core-description forms, which are presented with the whole-core photographs.

the core sections as a result of extrusion through holes drilled in the liner to bleed off the gas. This sediment loss, combined with displacement of intervals of more consolidated clayey sediment along the core liner as gas pressure was released, resulted in as much as tens of centimeters of void space within a 150-cm core section. On a few occasions, gas caused end portions of cores to be blown out of the core liners onto the drilling floor. Only gas voids >20 cm in length are documented in the core descriptions in this volume. The whole-core photographs in this volume record the full extent of disruption of the cores, including voids, and the detailed section-by-section paper core-description forms can be obtained from ODP.

The locations of all samples taken for shipboard analysis are indicated in the "Samples" column by the following codes: D = X-ray diffraction (XRD) sample; I = interstitial-water sample; S = smear slide; T = thin section; C = carbon analysis (organic and/or carbonate carbon); W = whole-round sample; and M = micropaleontology sample. In places where large (>10 cm) whole-round sections of core were removed for scientific study, a gap in the graphic lithology is shown. Generally, two or more samples were routinely taken for XRD analysis from each core at each site. Sufficient carbonate samples (generally one or two per core) were taken to characterize sedimentary units and calibrate carbonate content against color-reflectance measurements (see "Spectrophotometry" section). The hue and value/chroma attributes of color were recorded in the "Color" column based on visual comparisons with Munsell Soil Color Charts (Munsell, 1975). Color transparencies of each whole core are available from ODP.

The lithologic description in each of the computer-generated core description forms consists of three parts:

- A heading that lists all the major sediment lithologies in the core;
- 2. A heading for minor lithologies; and
- 3. A more detailed description of the sediments, including color, composition, sedimentary structures, trace fossils identified, and other notable characteristics. Descriptions and locations of thin, interbedded, or minor lithologies that could not be depicted in the "Graphic Lithology" column are presented where space permits.

Smear Slides and Thin Sections of Core Samples

Petrographic analysis of the sediment was primarily based upon smear-slide descriptions (Folk, 1980). Tables summarizing data from smear slides appear in Section 5 (this volume). These tables include information about the sample location, whether the sample represents a dominant (D) or a minor (M) lithology in the core, and the estimated percentage ranges of sand, silt, and clay, together with all identified components. We emphasize here that smear-slide analysis provides only crude estimates of the relative abundances of detrital constituents. Finer grained particles are difficult to identify petrographically, and sand-sized grains tend to be underestimated because they cannot be incorporated into the smear evenly. The mineralogy of smear-slide components was validated by XRD.

Thin sections of the few lithified nodular sediments were made by impregnation under vacuum with Epo-tek resin as needed.

X-ray Diffraction

Each sample was freeze-dried, ground, and packed with a random orientation into an aluminum sample holder. The main minerals within each sample were determined using the Philips model PW-1729 Xray diffractometer with CuK α radiation (Ni filter). Instrument conditions were as follows: 40 kV, 35 mA, goniometer scan from 2° to 70° 2 θ for bulk samples, scan speed at 1.2° 2 θ /min, step size 0.01° 2 θ , count time 0.5 s. Peak intensities were converted to values appropriate for a fixed slit width. Minerals were identified on the basis of peak positions and relative intensities. An interactive software package (MacDiff 3.0, R. Petschick, 1994) was used on a Macintosh computer to identify the main minerals and to measure peak areas. Relative abundances of various minerals were established on the basis of integrated peak intensity. The locations of the peaks used for mineral recognition and abundance estimates are presented in Table 1.

Because of the ubiquitous nature of quartz in the sediments recovered during Leg 164, quartz was chosen as an internal standard to correct the peak positions. Semiquantitative estimates of mineral percentages are presented for quartz, calcite, and dolomite. Weightpercentage calibration for quartz was based on peak areas in four reference mineral mixes containing varying amounts of quartz, calcite, dolomite, and mixed clay minerals. Weight-percentage calibrations for calcite and dolomite were made by measuring the percentage CaCO₃ in Leg 164 samples with only one carbonate phase present (as determined by XRD) and by plotting peak area (of the respective carbonate mineral) vs. percentage carbonate. Percentage CaCO₃ was converted to weight percentage dolomite in the dolomite calibration. Calibration lines are shown in Figures 4 through 6.

Relative abundances of the remaining minerals are presented only as relative changes in the peak areas of the diagnostic minerals. Clay minerals are represented collectively and are not distinguished individually as illite, chlorite, smectite, kaolinite, and so on. Because

Table 1. Positions of diagnostic peaks used for the identification of minerals and estimates of their abundances in X-ray diffractograms.

Mineral	Peak (20)	Peak (Å)	hkl
Quartz	20.85, 26.65	4.26, 3.34	100, 101
K-feldspars	26.91-27.50	3.31-3.24	220, 202, 002
Plagioclases	27.77, 28.13	3.21, 3.17	202,002
Aragonite	26.22, 33.15, 45.86	3.40, 2.70, 1.98	111, 012, 221
Calcite	29.45	3.03	104
Dolomite	30.96	2.89	104
Siderite	32	2.79	104
Ankerite	30.79	2.9	104
Rhodochrosite	31.47	2.84	104
Pyrite	33.04, 56.29	2.70, 1.63	200, 311
Halite	31.69	2.82	200
Barite	25.84, 28.75	3.45, 3.10	021, 121
Gypsum	11.59, 20.73	7.63, 4.28	020, 021
Anhydrite	25.44	3.5	002,020
Clay minerals	19.3-20.2	4.6-4.4	hkl
Clinoptilolite-heulandite	9.80-9.56	8.90-9.25	020

most clays have varying hkl (026, 116) diffractions at ~4.5 Å, their abundances in the sediment can be estimated on the basis of the peak area throughout the range 4.4–4.6 Å. It should be emphasized that the precision of this method is much better than the accuracy, but that relative abundances are useful for general characterization of the sediments. In addition, the (104) peak position of the carbonate minerals was presented to give the degree of substitution, either by larger or smaller cations. This was supplemented by the position of (113), (018), and (116) peaks to determine the substitution of Fe for Ca and Mg in the dolomite. The original diffractograms and the primary computer data files are available from ODP.

Spectrophotometry

Color and reflectance of core sediments were routinely measured downhole using a Minolta Spectrophotometer CM-2002. The purpose was to establish semiquantitative relationships between lithology and spectral reflectance for visible wavelengths, provide a continuous stratigraphic record of color variations downhole, and compare the color spectra measured on board with color spectra determined from core samples using a laboratory-grade spectrophotometer in a shore-based study.

Spectrophotometer readings were taken before cleaning the surface of the working half of the cores. Strips of very thin, transparent plastic film (Glad Cling Wrap, a brand of polyethylene food wrap) were used to cover all core intervals measured to alleviate frequent cleaning of mud from the spectrophotometer. Routine measurements were made at several evenly spaced intervals of each section, generally 10 or 30 cm; sometimes, however, the exact positioning of measurements was dependent on section length and the position of voids within the section. The measurement spacing was occasionally reduced to <10 cm for core intervals with distinct color variations or changes in lithology over short distances.

Before and after obtaining measurements from each core, the spectrophotometer was calibrated for white color reflectance by attaching its white calibration cap. (Note: The white calibration cap was not covered with plastic Glad Wrap during calibration because the Minolta instrument receives calibration values from the white cap during this process.) In addition, the instrument calibration was checked using a white barium sulfate plate, which is the standard used for calibrating laboratory-grade spectrophotometers. These white color calibrations were made to avoid variations in color readings dependent on the laboratory environment (temperature, humidity, and background light) and instrument deviations.

The spectrophotometer readings were recorded using the Spectrolog Program 3.0 on a Macintosh computer. Each reading consists of 31 separate determinations of reflectance in 10-nm-wide spectral



Figure 4. X-ray diffraction calibration line for quartz.



Figure 5. X-ray diffraction calibration line for calcite.



Figure 6. X-ray diffraction calibration line for dolomite.

bands between 400- and 700-nm wavelengths that cover the visible range. Reflectance measurements down some holes are shown in the site chapters.

GAS HYDRATE SAMPLING

Gas hydrate is unstable under surface conditions, making it necessary to employ several unusual sampling strategies to document the habit of the gas hydrate and to assess the amount of gas hydrate occurring within the cores. As cores were received on the catwalk, they were inspected to determine if they contained appreciable gas. If so, gas samples were taken from visually detected gas pockets within the cores. The cores were further inspected for indications of gas hydrate such as gassy, self-extruding cores and anomalously cold sediment with lighter coloration. If gas hydrate was thought to be present,



Figure 7. Apparatus used to measure small-scale variations in core temperature to understand fine-scale distribution of gas hydrate.

whole-round sections were immediately cut out on the catwalk and distributed for various shipboard experiments or preserved as quickly as possible for shore-based studies.

Previous drilling (e.g., Leg 146) has indicated that sediment temperature anomalies are associated with gas hydrate-bearing cores (Westbrook, Carson, Musgrave, et al., 1994). Because gas hydrate decomposition is endothermic (Sloan, 1990), low-temperature thermal anomalies should be associated with gas hydrate-bearing sediments. Thus, a variety of thermal measurements were made on recently recovered cores during Leg 164. However, the interpretation of these measurements is difficult because gas-charged sediments will also be cooled during core recovery (because of gas venting from the pore waters and adiabatic expansion of the gases) and because of the complicated temperature history of the cores. Although the absolute temperature measurements are impossible to interpret, the relative ones are useful. We infer that the local (intercore) variations are produced by gas venting, gas expansion, or gas hydrate decomposition.

Catwalk temperatures were taken by drilling a small hole in the liner, inserting a high-resolution thermocouple probe through the liner and waiting ~30 seconds for the temperature to stabilize. Variations in the techniques are described in gas hydrate sections for each site. Also, thermal measurements were made as described in the "Core Temperature Measurement" and "Gas-Collection Chambers" sections below.

Core Temperature Measurement

Temperature paths of core samples from their in situ temperatures (see "In Situ Temperature Measurements" section, this chapter) to the conditions on board the drillship are complicated and, thus, core temperatures are not frequently measured. During the drilling process, frictional heat will warm the cores by an undetermined amount, even though the bit is being cooled by seawater that is pumped down the hole at near-bottom-water temperatures (<4°C). During core recovery, the sediments are first exposed to cooler temperatures, with the minimum being those of the ocean bottom water (<4°C). Significant warming does not start until the cores pass through the ocean's thermocline on the way to the surface, and continued warming occurs once a core arrives on deck. Surface seawater and ambient air temperatures were ~26°C and 21° ± 5°C, respectively. Because the process of core retrieval is fairly uniform, the temperatures at which neighboring cores arrive on the catwalk should be relatively consistent unless there are additional heat sources or sinks.

Accordingly, temperature measurements of cores on the catwalk generally were in the range of 10° to 15°C. However, unusually low temperatures were recorded in some cores. These anomalies can be explained as a result of heat absorption by endothermic dissociation of hydrate in the sediment.

To investigate surface-temperature heterogeneity of sediments caused by dissociation of disseminated gas hydrate, selected 20-cmlong intervals of whole-round cores were split in half. The surface of the working half was measured by a 30-channel thermocouple digital thermometer within 10 min of the core being split. The instrument consisted of 30 thermocouple probes connected to the ETO DENKI THERMODAC 5001A 30-channel analog digital converter-data logger, controlled by a laptop personal computer (PC) with serial cabling. Each of the probes was supported by a plastic holder with an independent spring, allowing all the probe heads to touch uneven areas on the sediment surface of the split core (Fig. 7). The 30 probes were spaced in a moveable grid of five rows across six columns spaced at 10-mm intervals along the section. The data-acquisition system automatically recorded the temperature at each of the 30 probes every 2.0 s for a total of 40 s. The surface of the 20-cm-long core was measured by moving the probe array so that the operation was repeated in three positions, giving 90 discrete temperature measurements.

The resolution and accuracy of the probe are 0.1° and 0.5° C, respectively. The precision of the probes within the temperature range from 0.3° to 5.8° C is $\pm 0.2^{\circ}$ C. The least significant temperature difference is 0.4° C. An independent portable digital thermometer, SATO MFG. SK-1250MC, was used to monitor the temperature ~2 cm below the surface as an overall indicator of sediment temperature.

Gas Hydrate Dissociation Chamber

The gas hydrate dissociation pressure system (Parr Instrument Co.) consists of a sample holder (23 cm³), gauge block, pressure gauge, and manifold assembly (Fig. 8). Gas hydrate samples were placed in the sample container, and the entire manifold assembly was evacuated in 1 s. The samples were dissociated at room temperature, releasing gas into the gauge block. After thermal equilibrium and complete decomposition, the resulting pressure and temperature were measured, and the gas was sampled through the sample port. The composition of the gas was determined by gas chromatography, and the resulting water was analyzed for dissolved constituents. Any residual gas was trapped in a pre-evacuated stainless steel cylinder for shore-based studies.

Gas-Collection Chambers

Chambers were used to collect the gases that evolved from core sections and to monitor the temperatures as the cores warmed (Fig. 9). Sections of the core that were cut into the normal 1.5-m sections on the catwalk were placed in 1.54-m tubes that are slightly larger in diameter than the core liners. The tubes were constructed from standard polyvinyl chloride schedule-40 pipe sections (~3.5 in) with end caps that were machined so that they would seal on both ends with O-





ring-fitted plates that could be bolted on quickly to make a gas-tight seal. Thus, all the gas that was evolved within the cores after they were sealed in the tubes could be collected and measured.

Gas volumes were measured in three ways. At one end of the gascollection tube, the sealed end caps were fitted with a port through which gas could flow out of the tubes into Tygon tubing that ran through an OMEGA (Series 1800) flow meter calibrated to measure flow rates of 0-2 L/min. The output of the flow meters was recorded every 2 s (using a Lab View program that recorded the output from D100 series Omegabus Digital Transmitters). Thus, the flow meters provided a continuous monitor of the rate at which gas was passing out of the tubes. The rate was integrated over the time period that flow was detected. The gas tubes then passed into overturned 1-L graduated cylinders that floated in baths of salt-saturated water. The cylinders filled with the gas as the gas exited the tubing. Because the cylinders initially were completely water filled, the volume of water that was displaced by the gas could be measured directly. The cylinder tops were fitted with luer-lock fittings that allowed the gas to be collected in 60-mL syringes. This gas was then available for compositional analyses.

Temperature measurements were made by inserting a thermistor from 4 to 8 cm into the cored sediment through a predrilled hole in the normal core end caps. Thus, temperature was monitored within the cored sediments inside the gas-collection tubes. The temperature measured on each probe was automatically recorded every 2 s (using OMEGA D100 Series OMEGABUS Digital Transmitters that were integrated with a Lab View program).

Gas Hydrate Sampling for Post-Cruise Analyses Pressurized and Frozen Samples

To confirm the crystal structure, composition, and cage occupancy of natural gas hydrate, samples of gas hydrate were collected and stored in containers for post-cruise analysis. Pressure vessels (Parr Series 4760, 2.5-in ID and 300-mL volume; 3000-psi pressure limit; Fig. 10), consisting of a gauge block, Teflon gasket, pressure gauge, pressure transducer, and manifold were used to ship samples to Japan. To minimize the decomposition of gas hydrate during storage and shipping, the dead space within the pressure vessels was filled with fine glass beads (1-mm ID). The pressure vessels were stored in



Figure 9. Schematic diagram showing the gas-collection chamber used to monitor both the temperature and gas-flow rates of selected cores as they warmed in the core lab.

a refrigerator at -20° C and shipped in an Igloo brand cooling box filled with dry ice. Individual gas hydrate samples were also wrapped in aluminum foil, stored, and later shipped in liquid nitrogen to Denver, Colorado.

Samples For GHASTLI Testing

Whole-round sediment sections containing significant gas hydrate were cut into lengths of either 13-14 or 27-28 cm using an ODP handheld rotary core-liner cutter and a wire saw. The liner was immediately capped on each end and was quickly transported four decks below to the Second Look Laboratory, where the sample was placed into a thick-walled stainless-steel pressure vessel (PV) that measured 7.62-cm ID × 27.9-cm inside length. In situ pressure was restored to the sample by pushing ultra-high-grade (99.9999 pure) helium into the PV with a gas booster. The repressurization technique required ~10 min to complete. After pressurization in the PVs, the stored samples were refrigerated for shore-based tests within a laboratory apparatus called GHASTLI (Gas Hydrate And Sediment Test Laboratory Instrument) at the United States Geological Survey (USGS) facility in Woods Hole, Massachusetts. GHASTLI has the capability of recreating subseafloor pressure and temperature conditions while measuring gas pressure generation, acoustic velocities, permeability, electric resistivity, and shear strength (Booth et al., 1994; Winters et al., 1994).

BIOSTRATIGRAPHY

Introduction and Time Scale

Preliminary age determinations of Leg 164 sediments are based on biostratigraphic analysis of calcareous nannofossils. Age assignments were made primarily on core-catcher samples, but additional samples from key intervals were used to refine the biostratigraphy. The primary zonation used is that of Okada and Bukry (1980), with a slight modification by Bukry (1981). Zonal markers of Martini (1971) and other supplementary biostratigraphic events reported in Poore et al. (1984), Backman et al. (1990), Rio et al. (1990), Olafsson (1991), Flores et al. (1992), Gartner (1992), and Takayama (1993) were used whenever possible. All of these biostratigraphic events have been compiled and correlated to the magnetic time scale of Cande and Kent (1992) by Young et al. (1994). Numerical ages for each event were interpreted by correlating the summary chart of Young et al. (1994) to the geomagnetic polarity time scale of Cande and Kent (1995). The biostratigraphic events and numerical ages used during Leg 164 are illustrated in Figure 11.



Figure 10. Parr pressure vessels used to store and ship gas hydrate.

Methods

Smear slides are prepared directly from unprocessed samples and examined with a light microscope at a magnification of about 1000×. The abundance code of calcareous nannofossils is as follows:

- V (very abundant) = >50 specimens per field of view;
- A (abundant) = 10-50 specimens per field of view;
- C (common) = 1-9 specimens per field of view;
- F (few) = 1 specimen per 2-50 fields of view; and
- R (rare) = less than 1 specimen per 50 fields of view.

The qualitative evaluation of the preservation of calcareous nannofossils is recorded as follows:

- G (good) = specimens exhibit little evidence of dissolution and/or overgrowth;
- M (moderate) = specimens exhibit moderate dissolution and/or overgrowth, a significant proportion (up to 20%) of the specimens cannot be identified to species with certainty; and
- P (poor) = specimens exhibit severe dissolution and/or overgrowth; more than 20% of the specimens cannot be identified at the species level.

These categories were determined on the basis of the "average" state of preservation of the calcareous nannofossils examined in the smear slides. Degrees of etching (E) and overgrowth (O) were determined following the criteria proposed by Roth and Thierstein (1972) and modified by Roth (1973). We recognized the following states of dissolution and overgrowth:

E-0 and O-0 = no sign of dissolution and overgrowth;

E-1 and O-1 = slight dissolution and overgrowth;

E-2 and O-2 = moderate dissolution and overgrowth; and

E-3 and O-3 = severe effects of dissolution and overgrowth.

Species abundances within the nannoflora, excluding the lowerphotic taxa *Florisphaera profunda*, are defined as follows:

D (dominant) = >50%; A (abundant) = 10%-50%; C (common) = 1%-10%; F (few) = 0.1%-1%; R (rare) = less than 0.1%; and B (barren).

Because of the consistent dominance of *F. profunda* within the Quaternary and Neogene flora, its abundance within the total nannoflora is registered separately from other taxa by applying the same abundance criteria as above.

PALEOMAGNETISM

Both paleomagnetic and rock-magnetic studies were conducted aboard the JOIDES Resolution during Leg 164. Paleomagnetic analysis was directed toward establishing magnetostratigraphy, and it involved routine pass-through measurements and alternating-field (AF) demagnetization of natural remanent magnetization (NRM) of the archive half of most cores. Because demagnetization to remove coring-related overprints often reduced remanence to below the effective sensitivity of the cryogenic magnetometer (see below), a subset of discrete samples was measured on a Molspin spinner magnetometer. Demagnetization on the cryogenic magnetometer was limited to a maximum of 25 mT by the design of the in-line AF coils. Discrete samples were stepwise demagnetized to higher AF levels, usually to a limit of 50 mT. Primary remanences (i.e., stable components thought to be depositional or early postdepositional) were used to construct a magnetostratigraphy, which was correlated with the nannofossil biostratigraphy and dated by reference to the geomagnetic polarity time scale of Cande and Kent (1995).

Rock-magnetic studies were primarily conducted to investigate the diagenetic response of the magnetic mineralogy (Fe oxides and sulfides) to the availability of methane and sulfide and the control that gas hydrate places on this. Rock-magnetic studies also supported the magnetostratigraphic study by clarifying the mineralogy of carriers of the primary remanence and overprints. Low-field magnetic susceptibility of unsplit cores was measured using the MST. Rockmagnetic analysis included low-field susceptibility of discrete samples. Measurements of the anisotropy of magnetic susceptibility (AMS) of discrete samples were taken to determine the magnetic fabric of the sediments.

Core Orientation and Discrete Samples

Core orientation was performed on APC cores using the Tensor tool, which provided a declination for the double-line fiducial mark on the core liner (see below). For a description of the Tensor tool, see Shipboard Scientific Party (1994). Oriented discrete samples were taken in standard ODP square prism plastic boxes (volume = 7 cm³). We followed the sample orientation method of previous cruises (e.g., Shipboard Scientific Party, 1991), in which the z-axis is defined as being downhole parallel to the core, and the x-axis forms a line perpendicular to the split face of the core and directed into the working half toward a reference mark (a double line) along the center of the core liner on the working half. Discrete sample boxes were marked with an arrow in the negative-z (uphole) direction on the face representing the split surface of the core.

NRM Direction and Intensity

Measurement of remanence in complete sections from the archive half of the core was conducted with a 2-G Enterprises (Model 760R)



⊥ First occurrence Last occurrence



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pass-through cryogenic rock magnetometer. An AF demagnetizer capable of alternating fields up to 25 mT is aligned along axis with the magnetometer. Demagnetization of archive sections was routinely conducted at one or two steps to a maximum of 20 or 25 mT. Both the cryogenic magnetometer and the AF coils are encased in a μ -metal shield, and an automated sample-handling system moves the core sections through the AF coils and the magnetometer sensor region.

Some discrete samples also were measured on the cryogenic magnetometer. However, the small moment of discrete samples limits the minimum remanence that can be reliably measured with the cryogenic magnetometer to ~0.5 mA/m. Most discrete samples were measured on a Molspin spinner magnetometer, with a sensitivity limit of ~0.1 mA/m for standard ODP 7-cm³ samples. This instrument also was used for all rock-magnetic remanence measurements. Demagnetization of discrete samples was conducted with a Schonstedt GSD-1 AF demagnetizer; samples were demagnetized along each of three orthogonal axes at each demagnetization step in this single-coil, non-tumbling device.

Bias in Cryogenic Magnetometer Measurements

We noted that when intensities were less than ~0.5 mA/m, cryogenic magnetometer pass-through measurements of core sections were clearly biased (see, for example, the "Paleomagnetism" section in the "Sites 991/992/993" and "Site 994" chapters). At these weak magnetizations, declination measurements along each core (before orientation to geographic coordinates) grouped along 180° (i.e., the negative x-axis, in core coordinates), and inclinations were generally low (close to 0°). Measurement of the empty "boat" (the holder for core sections that transports the section through the magnetometer) confirmed an instrument bias. The "boat" was demagnetized at 20 mT and measured; this measurement was then entered into the controlling program as the "holder correction" for subtraction from subsequent measurements, as is the usual practice. On one such run, declinations were consistently near 180°, and inclinations near 0°. On another run, declinations alternated between 0° and 180°, and inclinations were scattered. Although it is not clear why such a bias should also appear when cores are measured, we considered it wise to treat apparently consistent declination and inclination data from pass-through measurements of sections with remanence <1 mA/m with caution.

Magnetic Susceptibility

Low-field magnetic susceptibility was continuously measured for each unsplit APC core and longer pieces of XCB core. We measured unsplit cores on the MST with a Bartington MS2 susceptibility meter with a MS1/CX80 whole-core sensor at 0.465 kHz (see "Physical Properties" section, this chapter). Measurements were performed at 3- to 10-cm intervals. Conversion of raw susceptibility data to SI volume ratios for a core assumed to be a cylinder with a diameter of 68 mm was achieved by multiplying the raw data by 0.63×10^{-5} (Shipboard Scientific Party, 1993).

Anisotropy of Magnetic Susceptibility

The second-rank tensor derived from AMS measurements provides the three-dimensional preferred orientation of para- and ferromagnetic grains (the "magnetic fabric"). Foliation in this fabric should normally increase with compaction; undercompaction caused by hydrate occupancy of pore spaces should manifest as a reduced foliation.

We used standard foliation and lineation parameters ($F = k_2/k_3$ and $L = k_1/k_2$, where k_1 , k_2 , and k_3 are the maximum, intermediate, and minimum eigenvalues of the susceptibility tensor, respectively) as described in Ellwood et al. (1988). Given the limitation of sensi-

tivity for the AMS device (a Geofyzika Brno Kappabridge KLY-2) imposed by the shipboard environment (~10⁻⁶ SI), we concentrated on determining foliation.

Rock-Magnetic Properties of Sediment Samples

Magnetic mineralogy, abundance, and grain size were investigated by rock-magnetic techniques. Instruments available on the *JOIDES Resolution* were AF and thermal (Schonstedt TSD-1) demagnetizers; a Bartington MS2 bulk susceptibility meter with a MS1B discrete sample sensor, allowing measurements at either 0.47 or 4.7 kHz; an ASC IM-10 impulse magnetizer for the application of isothermal remanence (IRM) up to ~1.3 T; and a DTECH system, used in conjunction with the Schonstedt AF demagnetizer, for imparting partial anhysteretic remanence (pARM).

Bulk Susceptibility

We determined bulk susceptibility (k) for discrete samples either directly with the Bartington meter or as the mean of the AMS eigenvalues (i.e, $[k_1+k_2+k_3]/3$) for samples measured on the Kappabridge. When using the Bartington meter on the 0.1 SI scale, the meter was zeroed before each individual sample measurement, and each measurement was repeated to test for consistency. Bulk susceptibility for discrete samples was normalized for sample mass. The mass of samples in plastic boxes was determined on a SCIENTECH/CAHN balance (see "Physical Properties" section, this chapter), and the mass of a standard plastic box (4.85 g) subtracted; the resulting precision is approximately ± 0.05 g.

Partial Anhysteretic Remanence and Isothermal Remanence

A subset of discrete samples, which had already been AF-demagnetized, was exposed to a bias field of 0.1 mT in AF acquisition windows 10 mT wide, centered on steps of 5 mT up to a maximum of 85 mT; the resulting pARM was measured at each stage on either the Molspin magnetometer or the cryogenic magnetometer. The bias field was applied parallel to the z-axis (downcore). A final bulk anhysteretic remanent magnetization (ARM) was imparted over a complete 90-mT demagnetization cycle, after which the samples were again AF demagnetized in 10-mT steps to 90 mT. Acquisition of bulk pARM gives information about the alternating-field coercivity spectrum of the samples, which clarifies the interpretation of AF demagnetization behavior and helps identify the presence of separate populations of magnetic minerals. Stepwise demagnetization of ARM can be compared with similar demagnetization of NRM (Lowrie and Fuller, 1971; Johnson et al., 1975) to test for the relative proportions of single-domain (SD) and multidomain (MD) magnetic grains.

Saturation IRM (SIRM) was imparted to a second subset of samples at 1200 mT. We measured IRM on the Molspin magnetometer. The IRM-inducing field was initially oriented in the positive z-axis (downcore) direction. Samples then had an IRM imparted in the –z direction at 300 mT (IRM_{-0.3T}). From this we determined the parameter $S_{-0.3T} = \{[(-IRM_{-0.3T}/SIRM) + 1]/2\}$ (Bloemendal et al., 1992). Saturation IRM was also normalized for sample mass, and the ratio SIRM/k calculated.

Isothermal remanence also was imparted in a series of increasing steps, and the partial IRM acquired over each step (pIRM) was determined from the difference in remanence between successive steps.

A further test of the combined thermal stability and IRM coercivity was conducted by imparting a multicomponent IRM (mIRM) in fields of 1.2, 0.4, and 0.2 T along the z-, y-, and x- sample axes, in turn, and then thermally demagnetizing the samples (Lowrie, 1990). The mIRM technique allows for the identification of magnetic minerals through a combination of their coercivity and thermal stability properties, resolving ambiguous interpretations of magnetic mineralogy based on saturation IRM properties alone. Thermal demagnetization was initially performed over 20°C steps from 60° to 100°C, allowing time for the sample to dry adequately. Thermal demagnetization then continued at 50°C steps to 650°C. Samples contained in plastic boxes were carefully removed for each thermal treatment and wrapped in aluminum foil to prevent their disintegration. Samples were returned to their plastic boxes for measurement.

MICROBIOLOGY

Bacteria play a dominant role in the degradation of organic matter within sediments and, as a consequence, drive chemical changes and early diagenesis. The presence of a deep bacterial biosphere in marine sediments only recently has been established (Parkes et al., 1994; Cragg et al., 1992). Those studies demonstrated the activity of bacteria to depths in excess of 500 mbsf and their direct involvement in methane cycling within these sediments.

The aim of this work is to estimate total bacterial numbers and bacterial activity rates, to investigate methane cycling in deep-sea sediments containing gas hydrate, and to confirm that our results from the Cascadia Margin (ODP Leg 146) are representative of other gas hydrate sites.

Sediment Sampling for Microbiological Analysis

Three types of samples were taken for microbiological analysis:

1. Sediment in 1-cm³ samples was taken for direct determination of bacterial numbers. These samples were taken from the end of selected 1.5-m core sections immediately after the sections were cut on the catwalk and before the sections were sealed with an end cap. Potentially contaminated sediment was first removed using a sterile scalpel. Then, using a sterile 5-cm³ plastic syringe with the luer end removed, a 1-cm³ minicore sample was taken. This was sealed with a sterile suba-seal stopper. In a clean area of the laboratory, the 1-cm³ sample was extruded into a sterile serum vial containing 9 mL of filter-sterilized (0.2 μ m) 4% formaldehyde in artificial seawater. The vial was crimped and shaken vigorously to disperse the sediment particles and then stored at 4°C. Clean 1-cm³ pieces of solid gas hydrate were treated in the same way, with the additional step of inserting a sterile hypodermic needle through the septum to allow the escape of gases caused by gas hydrate decomposition.

2. Whole-round core samples were taken and stored intact for shore-based laboratory analysis. These were cut from 1.5- or 3-m core sections on which the core end caps had not been sealed with acetone. The core sections were removed from the catwalk and brought into the core reception area, where they were cleaned, wiped with ethanol, and placed into a special sterile cutting rig (Cragg et al., 1992) that was constantly flushed with sterile oxygen-free nitrogen (OFN) to maintain anaerobic conditions around the core. One end of the whole-round core was cut with a sterile hacksaw blade, removed from the rig, and immediately capped with a sterile core end cap while being flushed with OFN from a sterile gassing jet. The core end cap was then taped to the liner. The cutting rig was cleaned and alcohol washed, and the process was repeated with the other end of the whole-round core. If a whole-round core from a sediment core contained gas hydrate, specially modified core end caps with a gasrelease valve were used. These allowed gas to escape out of the core but prevented any gas entering. Cores were sealed within a gas-tight laminated plastic/aluminum bag containing a chemical oxygen scrubber (Anaerocult A, Merck-BDH) to produce anaerobic conditions. Sealed, anaerobic core sections were stored at 4°C before being analyzed on shore.

3. Sediment samples were taken to measure sulfate reduction and methane oxidation rates at Sites 994, 995, and 996 using radio-tracer techniques. The study was designed to compare microbial reaction rates occurring at the sulfate-methane interface and within the upper sulfate reduction zone with those inferred from pore water gradients. In addition, these samples were taken to compare microbial reaction rates at sites where diffusive processes are operating (Sites 994 and 995) with a site where methane-charged fluids are advecting from below (Site 996). Whole-round sections of core were stored anoxically at in situ temperature until subsampling. At Sites 994 and 995, subsamples were concentrated immediately above and below the base of the sulfate reduction zone (~21 mbsf), but they also occur throughout the sulfate reduction zone. Instruments and materials were sterilized ashore by irradiation, and cores were cut using the sterile cutting apparatus described above. Sediment was subsampled at decimeter intervals using 5-cm3 samples, transferred to the Cape Hatteras, and immediately injected with ³⁵S and ¹⁴C for incubation. Pore waters were extracted from sediment immediately adjacent to the microbiology samples.

DOWNHOLE TOOLS AND SAMPLING Pressure Core Sampler

The ODP Engineering and Drilling Operations Department accelerated development activity on the PCS in March 1995. The lack of consistent recovery from the PCS on previous legs (e.g., Davis, Mottl, Fisher, et al., 1992; Westbrook, Carson, Musgrave, et al., 1994; Behrmann, Lewis, Musgrave, et al., 1992) made development activity on this tool a high priority. Development activity focused on enhancing PCS core recovery primarily by developing new cutting shoes, core catchers, and inner barrels. Pressure retention, which is a requirement for successful recovery, is largely dependent on keeping grit out of critical seal areas. The most effective way to achieve this is to clean the tool thoroughly before each run.

Cutting Shoes

Three new cutting shoes were designed and built simultaneously in preparation for Leg 164 (Fig. 12). One, the "modified piloted cutting shoe" (ODP part number OC0992), is a shortened version, with several minor modifications, of the previous shoe (OC0990). The second is an "auger" shoe (OC0991) that has large, continuous, spiral teeth running the length of the shoe. This design is clearly different in appearance and is meant to pull cuttings away from the core and up the hole along a path that is as direct as possible. The third new design is a "push-in" shoe (OC0993) that is conceptually similar to the APC cutting shoe but has a much smaller bore that corresponds to the smaller core diameter of the PCS. With this shoe, the entire coring system is spaced as much as 36 3/8 in (92 cm) lower in the bottomhole assembly (BHA), locating the cutting shoe up to 41 in (104 cm) ahead of the main bit. During deployment of this shoe, the BHA is slowly lowered until the main bit hits bottom. No rotation or circulation need occur while using this shoe. The "push-in" shoe was designed primarily for recovering core from soft formations that can be piston cored.

Core Catchers

New core catchers also were designed and built before Leg 164. One is a basket core catcher (OP6390) with numerous flexible fingers. This core catcher basket is made from 0.007-in stainless steel sheet stock. A softer version of the basket catcher (OP9396), made



Figure 12. Photographs of three new types of PCS cutting shoes used during Leg 164. A. The "auger" shoe. B. The "modified piloted cutting" shoe. C. The "push-in" shoe.

with 0.005-in stock, also was prepared for the leg. These designs are based on similar core catchers used in the mining industry. A third option was a two-flapper core catcher (OP6391). This is similar to the four-flapper core catcher used extensively in the XCB and RCB systems.

Inner Barrels

Some PCS inner core barrels (OP6234) were prepared with a Xylan coating on the inside surface. This small change was intended to slicken the inner surface of the core barrel to discourage core jamming inside. Both types of inner barrel were shipped to Halifax, Nova Scotia, Canada, for use during the leg.

Pressure Core Sampler Manifold

The PCS manifold (PCS-M) is a module composed of various high-pressure tubes, tube connections, gauges, valves, filters, regulators, and a gas sampler(s). From a scientific perspective, the overall purpose of the manifold is to step down high pressures collected in the PCS for gas sampling at low pressure and to determine the total gas volume released from the PCS.

Four different PCS-M configurations were used before and during Leg 164 (Fig. 13A–D). The progression of these designs reflects a variety of technical problems that were encountered with the use of the PCS-M. We document the changes made to the PCS-M and the reasons for these changes in this section because the design of an appropriate PCS-M for the scientific community has been a contentious issue (Pettigrew, 1992).

The Leg 164 Shipboard Scientific Party inherited the PCS-M1 (Fig. 13A) several months before cruise departure. Some of the history behind this PCS-M design is presented in Pettigrew (1992). The PCS-M1 design consisted of a regulator, a filter cascade, a left manifold, a right manifold, and a vacuum line. In theory, gas entered the

back-pressure regulator directly from the PCS via a valve. The backpressure regulator allowed for a controlled volume of gas at high pressure to be passed downline at a lower pressure. Gas then passed into the filter cascade. The purpose of this filter cascade was to remove sediment that could enter and clog the manifold system. This manifold system consisted of a series of valves and gauges that permitted further lowering of gas pressure and gas sampling into preevacuated gas cylinders at a desired pressure. The manifold design also permitted alternation of sample cylinders in such a way that continuous gas sampling could occur. After complete degassing of the PCS, the PCS-M1 was evacuated via a vacuum line. A cryotrap on the vacuum line prevented contamination of gas samples by hydrocarbon vapors originating from vacuum pump oil.

The PCS-M1 was tested using the GHASTLI at the USGS at Woods Hole (see description in Booth et al., 1994) before the ship's departure on Leg 164. The purpose of these GHASTLI tests was to examine potential carbon isotope fractionation in the PCS-M during its use. The PCS-M1 did not fractionate carbon isotopes. However, the GHASTLI tests also showed that the regulator rapidly clogged with fine-grained sediment and that such clogging quickly made the PCS-M1 inoperable.

The PCS-M2 (Fig. 13B), a modified version of the PCS-M1, was primarily designed to prevent sediment clogging of the regulator. The filter cascade was switched from a downline position of the regulator to an upline position. Further GHASTLI tests demonstrated, however, that this simple modification was insufficient in preventing sediment clogging of the regulator. Thus, a vertical sediment trap with an inner diameter of 0.9 cm was placed in front of the filter cascade. The length of this trap was made adjustable because, in theory, a wide range of gas volumes could evolve from the PCS during shipboard operations. Because a vacuum cannot be pulled through a backpressure regulator, a bypass loop was placed around the regulator to allow for evacuation of PCS-M sections upline from the regulator.

An additional concept behind the PCS-M2 was that the manifold should be compatible with other high-pressure devices located on board the *JOIDES Resolution*. Thus, the entry port into the PCS-M2 was equipped with a "quick-connect."

Total volumes of gas evolved from the PCS were to be determined via pressure-temperature-volume relationships as incremental volumes of gas passed through the PCS-M1 or PCS-M2. For example, if the valve between the PCS and trap (of known volume) were closed and the pressure and temperature within the trap were known, the amount of gas in the trap could be estimated. This procedure then could be repeated until all gas had been released from the PCS.

Successful PCS deployments at Sites 994 and 995 rapidly altered all views on how a PCS-M might be designed. Core 164-994C-27P was the first PCS run of the leg to recover sediment at near in situ pressure conditions. A single gas sample was collected via the PCS-M2 manifold before the filter cascade (Fig. 13B) became completely clogged and gas no longer could pass through the manifold. Removal of the filter cascade showed that much of the clogging resulted from sediment caking on the 60-µm filter. The filter cascade was then replaced with a gas sampling bottle (Fig. 13C). All of the gas sample bottles taken during this manifold configuration contained a significant amount of sediment.

A sample of slurry was collected from the base of the trap during manifold operations conducted while drilling Core 164-994C-66P. The purpose of taking this sample was to understand how much sediment might flow through the manifold. After centrifuging the slurry to clarity, the 50-mL sample contained 16 cm³ of fine-grained sediment.

During (or before) manifold operations on Core 164-994C-36P, the vacuum line became blocked with white crystals and sediment. A new vacuum line was installed before Core 164-994C-45P. However, because an essential tube connector part was not available on ship,



Figure 13. Schematic diagrams of the four pressure core sampler manifolds used before and during Leg 164.

the vacuum line had to be placed at the base of the trap. This manifold configuration, PCS-M3 (Fig. 13C), had a recurring problem with vacuum line blockage.

The use of the pressure-temperature-volume relationships to estimate the amount of gas within the manifold was determined to be impractical after initial gas volume estimations for Cores 164-994C-36P and 53P. The primary reason is that the volume in the manifold changes during and between PCS runs because significant quantities of sediment and water enter the manifold. The temperature within the PCS also differs from that in the manifold. Thus, a bubbling chamber was added to the manifold (Fig. 13C) before drilling Core 164-994C-70P. This bubbling chamber consisted of a graduated (at 10-mL increments) cylinder that was inverted in a plexiglass tube filled with seawater.

The overall size and mass of the original manifold (PCS-M2) presented additional problems. The manifold required firm mounting onto a structure. However, because the PCS also required mounting, a flexible high-pressure line had to be placed between the manifold and the PCS. This line often clogged with sediment. In addition, when sediment clogging was a problem, the bulkiness of the manifold precluded simple and rapid cleaning.

Core 164-995A-9P contained 1 m of very gassy and unconsolidated sediment at in situ pressure. Upon connecting Core 164-995A-9P to the PCS-M3, a significant portion of the core extruded through the sampling port on the PCS and into the manifold. The extrusion of sediment blocked the flexible high-pressure line and all ¹/₈-in connections on the PCS-M3. Development of the PCS-M4 grew out of the problems encountered while drilling Core 164-995A-9P.

The PCS-M4 (Fig. 13D) was a free-standing sediment trap with a pressure transducer that was connected directly to the PCS. A bubbling chamber and a He tank were then connected to the manifold via plastic tubing. The purpose of the He tank was to purge the PCS-M4 of air before degassing the PCS. Although significant quantities of sediment and water passed through the PCS-M4 on certain PCS runs,

this manifold design clogged much less frequently than the other three PCS-M designs.

Water-Sampling Temperature Probe

The water-sampling temperature probe (WSTP) is a downhole tool that allows for measurement of in situ temperature and collection of a water sample on a single deployment. Descriptions of the tool and its use have been presented in previous ODP *Initial Reports* volumes (e.g., Westbrook, Carson, Musgrave, et al., 1994) and in the "In Situ Temperature Measurements" section (this chapter).

An important use of the WSTP during Leg 164 was to collect in situ interstitial water. However, because the tool rarely collects pure interstitial water, we had to account for contamination from borehole and coil waters. The amount of initial coil water remaining can be determined by adding a tracer to the initial coil water and measuring the concentration of the tracer after deployment.

A 10-ppm solution of methylene blue was used at Site 994 to fill the coil before tool deployment. However, the concentration of methylene blue was strongly reduced by adsorption on the large amounts of sediment particles found inside the coil. The sampling coil thus was filled with a 1000-ppm Li⁺ solution at Sites 995, 996, and 997. Concentrations of Li⁺ in the samples were determined by flame emission spectrophotometry, with a relative standard deviation of 0.7% in the concentration range 10–1000 ppm, and 1.2% in the concentration range 2–10 ppm.

The WSTP was deployed only at depths below the SO_4^{2-} reduction zone. Concentrations of SO_4^{2-} , therefore, were used to estimate the amount of borehole water (surface seawater) contamination in WSTP water samples.

Fisseler Water Sampler

The Fisseler Water Sampler (FWS), a prototype water sampling tool designed by Patrick Fisseler of the ODP Engineering and Drilling Operations Department, was sent to Halifax for testing during Leg 164 to evaluate the quality of the water sample in comparison to samples taken by the existing WSTP. This tool was designed to accomplish three things:

- Draw a sample from the formation at or near formation pressure (The existing WSTP design subjects the sample to pressures as low as 75 psi during the sampling process. This is thought to compromise the integrity of some water samples by removing dissolved gasses from interstitial waters as the sample is drawn into the tool.);
- Incorporate a tip profile that tapers more gently, thereby reducing the tendency to crack the formation and allow borehole fluid to contaminate the water sample and the temperature measurement; and
- Split the assembly into components to make the tool simpler to maintain and prepare for the next run.

Because the tool is filled with deionized water in the Downhole Tools Lab before deployment, sample fluid (i.e., interstitial water) must displace this water as it enters the tool. The heart of the design, intended to meet the first objective, is a differential-area piston (Fig. 14). This piston has sample chamber pressure on the lower side. Most of the upper side is vented to the water column ensuring hydrostatic pressure on the upper side. A small ¼-in (6.35 mm) rod extends into a chamber having atmospheric pressure. Because of this differentialarea design, the piston cannot move until the pressure on the sample side reaches a level near hydrostatic. Thus, near-hydrostatic pressure must be reached inside the tool before sample fluid can enter.

Several rod sizes— $\frac{1}{4}$ in (6.35 mm), $\frac{3}{8}$ in (9.53 mm), and $\frac{1}{2}$ in (12.70 mm)—were tested before being deployed during Leg 164, and the $\frac{1}{4}$ -in rod size appears to be suitable for a very broad range of wa-



Figure 14. Schematic diagram of the Fisseler Water Sampler.

ter depths. A metering valve located between the sample coil and the differential-area piston serves as a final calibration of the system. The valve can be adjusted to draw ~100 mL of formation fluid over several minutes in water depths from ~700 to 3500 m. Significantly deeper sites may require very low metering valve settings, an even smaller rod size, or other minor design changes.

The tip profile incorporates a very shallow (5°) taper to reduce disturbance of the formation as the tool is pushed in by the drill string BHA. The electronics section is at the top of the tool, separate from the other components. The intent of this design is to make setting the timer and connecting the electronics to the rest of the tool the last steps in preparing the tool for a run, allowing for more advance preparation.

ORGANIC GEOCHEMISTRY

The shipboard organic geochemistry program for Leg 164 included (1) real-time monitoring of volatile hydrocarbon gases; (2) measurement of the inorganic carbon concentration to determine the amount of carbonate in the sediment; (3) elemental analyses of total carbon, total nitrogen, and total sulfur; and (4) characterization of organic matter by Rock-Eval pyrolysis. All methods and instruments used during Leg 164 are described in detail by Emeis and Kvenvolden (1986) and in the "Explanatory Notes" chapter of the Leg 156 *Initial Reports* volume (Shipboard Scientific Party, 1995).

Hydrocarbon Gas Sampling

During Leg 164, the compositions and concentrations of hydrocarbons and other gases in the sediment were generally monitored in every core. Two methods of gas collection were used: (1) headspace (HS) and (2) vacutainer or syringe (V or S) of gas voids in the core liner.

In the HS method, gases released by the sediment were collected with the following technique: Immediately after retrieval on deck, a calibrated cork borer was used to obtain a measured volume of sediment, usually ~5 cm³, from the end of a section of core. The sediment was placed in a 21.5-cm³ glass serum vial that was sealed with a septum and metal crimp cap. When consolidated or lithified samples were encountered, chips of material were placed in the vial and sealed. The vial was heated to 60°C in an oven and kept at this temperature for 30 min before gas analysis. A 5-cm³ volume of the headspace in the vial was extracted with a standard glass syringe for each analysis by gas chromatography.

The V and S methods of gas analysis were used when gas pockets or expansion voids occurred in cores as they arrived on deck. Vacutainers are pre-evacuated septum-sealed glass tubes (20 cm³). To obtain a gas sample, a special core-liner piercing tool was employed to penetrate the core liner (Fig. 15). This tool, equipped with a valve and needle, was used to transfer gas from the core into the vacutainer. When gas pressures were high, some vacutainers shattered. A variation of this method was the use of 60-mL plastic syringes as seen in Figure 15. The needle was replaced with a syringe equipped with a three-way valve. This method was very useful in obtaining gas from cores that were under high pressure. Syringes were used exclusively to sample gas from Sites 994 through 997. Gas from the syringes was directly injected onto the gas chromatographs and analyzed.

Hydrocarbon and Other Gas Measurement

Compositions and concentrations of hydrocarbon and other gases were measured using two different gas chromatographic systems: (1) a Hewlett-Packard 5890 Series II (HP) and (2) a Hewlett-Packard 5890A Natural Gas Analyzer (NGA), modified by John Booker and Co., Austin, Texas.

The Hewlett-Packard 5890 Gas Chromatograph

The HP is a standard packed column gas chromatograph equipped with a flame ionization detector (FID) configured with a Hewlett-Packard ChemStation 3365 II that allows the single measurement of gas concentrations over 6 orders of magnitude after appropriate calibration. The HP is designed to accurately and rapidly measure the concentrations of methane, ethane, and propane in ~7 min. Ethene is resolved from ethane and can be quantified. The HP was equipped in the following way: sample introduction was via a 1.0-cm³ sample loop with manual column backflush, a FID detector was used, and the oven was programmed from 100° to 120°C, with helium used as the carrier gas.

Natural Gas Analyzer

The NGA is a modified Hewlett-Packard Model 5890A gas chromatograph with three valves and three columns and equipped with a thermal conductivity detector (TCD) and an FID. A Hewlett-Packard ChemStation was used to collect data from both detectors. This gas chromatography (GC) analysis system uses automatic valve switching to direct flows through various sample loops and columns. Three GC columns were used sequentially to provide a rapid partitioning and measurement of N₂, O₂, CO₂, H₂S, and C₁ through C₇ hydrocarbons.



Figure 15. Photograph of the syringe method of sampling a free gas from core liners. A 60-mL syringe fitted with a three-way valve was attached to the core-liner piercing tool by a luer-lock fitting. The use of syringes offered more control in sampling high-pressure gas trapped in the core liner or drawing gas out of a core with no visible gas pockets. Contamination by air during sampling was nearly eliminated using this method.

The NGA employs a multicolumn system composed of (1) a 0.32cm × 0.2-m stainless steel column packed with Porapak T (50/80 mesh) in line with a 0.32-cm × 0.9-m column packed with Molecular Sieve 13× (60/80 mesh); (2) a 0.32-cm × 1.8-m stainless steel column packed with 80/100 mesh HayeSep R (acid washed); and (3) a 60-m × 0.32-mm capillary column coated with a 1-mm film thickness of DB-1 (J&W Inc.). Samples were introduced via three 0.5-cm3 separate sample loops, which were flushed with a 5-cm3 gas sample in one step. The chromatographic separation on the TCD portion of the NGA system was conducted isothermally at 40°C, whereas the hydrocarbon separation on the FID portion of the GC system was conducted by programming from 40° to 80°C at 4°C/min. Helium was used as the carrier gas. The TCD injector and detector temperatures were 100° and 150°C, respectively, and the corresponding temperatures for FID were 150° and 250°C, respectively. Chromatographic response was calibrated against preanalyzed standards, and the gas contents are reported in parts per million by volume.

Inorganic Carbon

Inorganic carbon was determined using a Coulometric 5011 carbon dioxide coulometer. Approximately 10 mg of freeze-dried, ground, and weighed sediment was used for each measurement. Carbonate percentages were calculated from the inorganic carbon (IC) content, assuming that all carbonate occurs as calcium carbonate, as follows:

$$CaCO_3 = IC \times 8.33.$$

Elemental Analyses

Total carbon, nitrogen, and sulfur content of the sediment samples were determined using a Carlo Erba Model NA1500 carbonnitrogen-sulfur (CNS) analyzer. Total organic carbon (TOC) content was calculated by the difference between total carbon (TC) and IC:

TOC = TC - IC.

Organic Matter Characterization and Determination of Maturity

The origin of the organic matter in the sediments can be characterized using organic carbon/nitrogen (C/N) ratios (Bordovskiy, 1965; Emerson and Hedges, 1988). Organic matter type, thermal maturity, and hydrocarbon-producing (S_1 , S_2 , S_3 , and S_4) potential were assessed using a Delsi-Nermag Rock-Eval II pyrolysis system. For details of operation, see the "Explanatory Notes" chapter of the Leg 156 *Initial Reports* volume (Shipboard Scientific Party, 1995).

Collecting Gases from Hydrate by Using Gas Bags

Small pieces of gas hydrate $(1-2 \text{ cm}^3)$ or gas hydrate–bearing sediment were placed into Linde gas bags with open tops. After emplacement of the sample, the open tops were folded and sealed with tape. Because of the decomposition of the hydrate, the bags expanded. One or more vacutainers or syringes then could be filled through the septum of the bag and used for immediate analysis of the gas or for storage for shore-based analyses.

INORGANIC GEOCHEMISTRY

Shipboard interstitial-water analyses were performed on water squeezed from whole-round sections (Manheim and Sayles, 1974), on interstitial and chamber water collected by the PCS, and on water retrieved by the WSTP. Deviations from the standard ODP sampling scheme are given in the separate site chapters. Chloride, salinity, alkalinity, pH, sulfate, ammonium, dissolved silica, and phosphate were analyzed according to the methods described in ODP Technical Note 15 (Gieskes et al., 1991). Potassium, calcium, and magnesium were analyzed by ion chromatography using a DX-100 ion chromatograph fitted with a CS12 column. Strontium was analyzed by atomic absorption spectroscopy (AES) using an air/nitrous oxide flame and 1% lanthanum as an ionization suppressor. Sodium was estimated via charge balance considerations except at Site 996, where Na⁺ concentrations were determined by AES. The precisions of the methods are given in Table 2.

PHYSICAL PROPERTIES

Introduction

Physical properties were measured on unsplit cores and on the undisturbed parts of split cores. The MST was used for nondestructive measurements of wet bulk density, compressional wave velocity, magnetic susceptibility, and natural gamma radiation in unsplit cores. Needle-probe thermal conductivity measurements also were conducted on unsplit cores. Undrained shear strength, unconfined compressive strength, and three-component compressional wave velocity were measured on split sections. Portions of split cores that were undisturbed by drilling and sampling, gas expansion, bioturbation, cracking, pocking, and large voids were used to obtain specimens for index properties measurements (wet bulk density, grain density, dry bulk density, water content, void ratio, and porosity).

The specific sampling strategy for the various physical properties measurements depended on (1) the rate of undisturbed core recovery, (2) the specific interests of shipboard and shore-based scientists, (3) the resolution required to validate the gross variations in physical properties revealed by downhole logging runs, (4) the frequency with which downhole tools (e.g., Adara APC temperature shoe) were deployed, (5) the degree of inhomogeneity in lithology, texture, or structure of the sediments, and (6) the amount of gas hydrate presumed to be present in the sediments under in situ conditions.

Although the major goal of the physical properties measurement program is to determine in situ conditions, drilling and core recovery may alter some sediment properties. This may particularly be a problem where sediments are characterized by high concentrations of gas or gas hydrate under in situ conditions. As a rule, zones of obvious disturbance were avoided when conducting physical properties measurements to reduce the likelihood of sampling sediment properties that were far removed from the in situ conditions.

Multisensor Track

The MST includes four physical properties sensors: the magnetic susceptibility meter (MSM), gamma-ray attenuation porosity evaluator (GRAPE), *P*-wave logger (PWL), and the natural gamma-ray (NGR) detector. Individual, unsplit core sections were placed on the MST, which automatically moves the section through the four sensors on a fiberglass track. MST data are not always continuous as a function of depth because whole-round sections were sometimes removed immediately after coring and because sediment recovery was poor in gas-rich zones.

MST data were sampled at discrete intervals, with the sampling rate chosen to optimize the resolution of the data and the time necessary to run each core section through the device. GRAPE and magnetic susceptibility data were collected at 3- to 4-cm spacings. *P*wave velocities were logged every 1 to 4 cm, and NGR was sampled at 25-cm intervals.

Magnetic susceptibility was measured on all sections using the 1.0 range on the Bartington Model MS2 meter with an 8-cm-diameter loop. The close sampling interval for magnetic susceptibility was

Table 2. Relative standard deviations for analyses of dissolved species in pore water during Leg 164.

	SD	
Analyte	(%)	Standard
CI-	0.18	IAPSO
Alkalinity	2.1	IAPSO
SO42-	1.6	IAPSO
SO42-	3.2	Interstitial water containing 2.1 mM SO42-
K+	2.8	IAPSO
Mg ²⁺	2.1	IAPSO
Ca ²⁺	3.8	IAPSO
Sr ²⁺	1.2	IAPSO
NH4 ⁺	5.9	Standard curve (0.5-30 mM)
SiO,	3.1	Standard curve (100-1000 µM)

Notes: SD = standard deviation. IAPSO = International Association for the Physical Sciences of the Ocean.

chosen to increase the possibility of correlating data between holes and to provide a high-resolution data set for rock-magnetic studies.

GRAPE measurements of wet bulk density were made by comparing the gamma-ray attenuation of the sediments with the degree of attenuation through an aluminum standard (Boyce, 1976). The GRAPE device was calibrated approximately every 24 hr.

NGR analysis, which is a function of the random and discrete decay of radioactive atoms, was made with scintillation detectors according to the procedures outlined by Hoppie et al. (1994).

To determine if the physical properties of the sediments changed during the breakdown of gas hydrate, unsplit cores were occasionally run through the MST twice at the beginning of the cruise. The first MST run was conducted while cores were cold, just after they were cut into sections. The second MST run, which represented the normal MST run, occurred after the cores had thermally equilibrated. No other physical properties measurements could be conducted on the newly retrieved and thermally equilibrated cores.

P-wave Measurements

P-wave velocities were measured with the high-resolution PWL mounted on the MST and with the Digital Sonic Velocimeter (DSV). The PWL continuously measured *P*-wave velocity orthogonal to the long axis of unsplit core sections. The Dalhousie University/Bedford Institute of Oceanography DSV (Mayer et al., 1988; Courtney and Mayer, 1993) was used to measure *P*-wave velocity at discrete locations on split core sections.

The PWL transmits 500-kHz compressional wave pulses through the core at a rate of 1 kHz. The transmitting and receiving transducers were aligned perpendicular to the core axis while a pair of displacement transducers monitored the separation between the compressional wave transducers. Variations in the outside diameter of the liner do not degrade the accuracy of the velocities, but sediment must fill the liner completely for the PWL to provide accurate measurements.

The PWL requires two types of calibrations, which were performed at the beginning of the leg. First, the displacement transducer was calibrated using a standard core liner and a block standard. Then, a one-point velocity calibration was done with the water standard.

P-wave velocity was measured on split core sections using transducers on the DSV device. The T1 transducer pair has a fixed separation of 7.0 cm and is inserted along the axis of the core in soft sediments to measure velocity orthogonal to bedding. The T2 transducer (separation of 3.5 cm) measures velocity roughly parallel to bedding and is inserted perpendicular to the core's axis.

The velocity calculation is based on the traveltime of an impulsive acoustic signal between the piezoelectric transducers inserted in the split sediment cores. The transmitted signal is a 0.1-µs square wave with a period of 0.2 ms. The return signal is stored by the computer, and the first arrivals are handpicked. The DSV software then automatically calculates sediment velocity.

When the material became too consolidated to insert the DSV transducers, measurements were made through the core-barrel liner with the Hamilton Frame System. The velocity estimate is based on the traveltime between two contact transducers (T3 pair). One is placed on the cut surface of the core. The other is directly underneath, in contact with the core-barrel liner. Sample thickness is usually measured by a vertical offset gauge. Freshwater was used to improve the acoustic contact between the sample and the transducers.

Thermal Conductivity

Thermal conductivity data were collected using the full-space needle-probe method of von Herzen and Maxwell (1959). Cores were first passively equilibrated to room temperature (nominally 17°C) for at least 3 hr. The needle probes were then inserted into the core through holes drilled in the liner. Care was taken to avoid insertion of the needle probes into visible voids or into liquid parts of the core.

All five thermal conductivity needles were used simultaneously whenever possible. On each run, four needles measured thermal conductivity in the cores while the fifth needle was in a black rubber standard. Each of the five available needles was systematically rotated through different holes in the standard during sequential runs.

The collection of thermal conductivity data was controlled by a preprogrammed microprocessor, the Thermcon-85. Before taking any data measurements, we conducted a drift survey to measure temperature changes for a minimum of 120 s. Thermal conductivity data collection proceeded only when drift no longer exceeded 0.04°C/min for any of the needle probes. During the data-collection phase, the microprocessor applied constant heat to each needle for 6 min. Reference voltage, the resistance measured by each of the probes, and the current were sequentially logged by the Thermcon unit. A dedicated PC attached to the Thermcon unit stored the data.

To determine thermal conductivity, the measured resistances are first converted to temperatures using calibration constants and drift corrections for each needle. Apparent sediment thermal conductivity adjacent to a given needle probe is approximately proportional to the ratio of temperature and the natural logarithm of time once a linear correction for drift has been included (von Herzen and Maxwell, 1959). Most thermal conductivity determinations were made using data collected between 60 and 240 s from the beginning of the heating interval. For each needle, the data were fit using a least-squares regression procedure that yields both the thermal conductivity and the rate of temperature change. Errors are typically between 5% and 10%. No corrections for temperature or pressure conditions were made as part of the thermal conductivity collection procedure (Ratcliffe, 1960).

Shear Strength

Motorized Vane Shear Device

Undrained shear strength (S_u) was determined in fine-grained plastic sediment by using the ODP motorized miniature vane shear machine according to American Society for Testing and Materials (ASTM) D4648-87 guidelines (ASTM, 1987) and Boyce (1977). A 1.27-cm-diameter \times 1.27-cm-high four-bladed vane was inserted into the working half of the split core and attached to a rotation sensor at each end of a coiled spring. The top of the spring was rotated at a constant rate of 89°/min until the calculated torque decreased or failed to increase with additional rotation.

The shear strength was calculated assuming that failure occurred on a right, circular cylinder equal in surface area to the cylinder inscribed in the sediments by the vane during one continuous revolution. The vane blade constant (K) was calculated by using the following equation:

$$\mathbf{K} = 2/\{\pi \cdot D^2 \cdot H \cdot [1 + (D/3H)]\},\$$

where *D* and *H* are the vane diameter and height in meters, respectively, and K is units of m⁻³. Torque (*T*) (N – m) was calculated from the measured differential spring rotation (D) and the spring calibration constant b:

$$T = \mathbf{b} \cdot \Delta$$

The undrained shear strength, in kPa, was then determined using:

 $S_u = T \cdot \mathbf{K}.$

Residual shear strength was recorded unless a significant postpeak decrease in stress did not occur with additional vane rotation. Errors associated with vane shear testing include (1) partial relief of pore pressure if the vane angular rotation rate is too slow for the sediment permeability and (2) cracking of the sediment during vane rotation at higher shear strengths. Unfortunately, much of the vane shear strength value data had to be discarded because the results may have been affected by problems with the electrical connections.

Penetrometer

A Soiltest CL-700 handheld penetrometer was used to provide additional strength information. The instrument is a flat-footed, cylindrical probe that is pushed 6.4 mm into the split core surface. The resulting resistance is the unconfined compressive strength (c_u) . The mechanical scale reading was converted to undrained shear strength (S_u) by the DSV software using:

$$S_u$$
 (kPa) = $c_u/2$ (kg/cm²) · 98.07 [kPa/(kg/cm²)].

The maximum unconfined compressive strength that can be measured with the penetrometer is 4.5 kg/cm², which is equivalent to a shear strength of 220 kPa.

Index Properties Measurements

Water content, wet bulk density, dry bulk density, and grain density were routinely determined using 10- to 15-cm³ specimens collected from split cores. Other related properties, such as porosity and void ratio, were calculated from phase-relation equations. Immediately after we collected the samples, wet sediment mass (M_i) , and wet sediment volume (V_i) were measured. Dry sediment mass (M_d) and dry sediment volume (V_d) were determined after the samples had dried for 24–36 hr at a temperature of $105^\circ \pm 5^\circ$ C.

Wet and dry sample masses were determined to a precision of ± 0.01 g using a Scientech electronic balance. The sample mass was counterbalanced by a known mass to ensure that only mass differentials of ~ 10 g were measured. The Quantachrome pycnometer determines volumes to an approximate precision of ± 0.02 cm³ based on the helium-displacement principle (see ASTM standard D 5550-94; ASTM, 1994). A reference volume was run periodically (at least once per site) in each chamber to check for systematic errors. Calibrations, if needed, were performed between sites.

Calculations

Calculations of index properties were performed by the shipboard computer program "IP/4D." Although new software was used to complete index properties calculations during Leg 164, the correction factors and equations are similar to those employed during previous legs (e.g., Shipboard Scientific Party, in press). Six different parameters are calculated by the software. Five of them are determined in two ways: by either Method B, which uses the wet total volume of the specimen, or Method C, which uses the dry volume of sediment. The tabulated data shown in the site chapters correspond to the following methods: wet bulk density (wet Method B), grain density (dry Method C), dry density (wet Method B), porosity (wet Method B), and void ratio (dry Method C).

The computer program corrected M_d and V_d to account for residual pore-water salt left behind by drying. The calculations were performed using the evaporated mass of pure water (M_w) and an assumed salinity (s) of 0.035, corresponding to a pore-water density (ρ_{pw}) of 1.024 g/cm³ and salt density (ρ_{salt}) of 2.257 g/cm³. The mass of salt (M_{salt}) in the sample is given by

$$M_{salt} = [s/(1-s)] \cdot M_w$$

and the corrected mass of pore water (M_{pw}) , volume of pore water (V_{pw}) , mass of solids excluding salt (M_s) , volume of salt (V_{salt}) , and volume of solids excluding salt (V_s) are, respectively:

$$\begin{split} M_{pw} &= M_w + M_{salt} = M_w/(1-s), \\ V_{pw} &= M_{pw}/\rho_{pw}, \\ M_s &= M_d - M_{salt}, \\ V_{salt} &= M_{salt}/\rho_{salt}, \text{ and} \\ V_s &= V_d - V_{salt} = V_d - M_{salt}/\rho_{salt}. \end{split}$$

Water Content

Wet water content (w_i) is expressed as the ratio of M_{pw} to wet total mass (M_i) , and dry water content (w_s) is the ratio of the M_{pw} to M_s , respectively (ASTM Standard D 2216–80; ASTM, 1980):

$$w_t = M_{pw}/M_t = (M_t - M_d)/[(1-s) \cdot M_t]$$

or

$$W_s = M_{mw}/M_s = (M_t - M_d)/[M_d - (s \cdot M_t)].$$

Wet and Dry Bulk Densities

Wet bulk density (ρ_i) was calculated from

$$\rho_t = M_t / V_t = (M_s + M_{pw}) / (V_s + V_{pw}).$$

Wet bulk density also was measured using the GRAPE component of the MST (see "Multisensor Track," above).

Dry bulk density (ρ_d) is used to estimate the mass accumulation rate for a given depth interval and is defined by

$$\rho_d = M_s / V_t = M_s / (V_s + V_{pw}).$$

Grain Density

Grain (solid) density (ρ_s) was calculated from

$$\rho_s = M_s/V_s.$$

Porosity and Void Ratio

Porosity (η) and void ratio (*e*) were calculated assuming that all original sediment voids (V_{ν}) were filled with pore water. Porosity and void ratio were respectively calculated from

$$\eta = V_v / V_t = w_t \cdot \rho_t / \rho_{p_t}$$

and

$$e = V_v/V_s = w_s \cdot \rho_s/\rho_{pw}$$

GEOPHYSICS

Zero-Offset and Walkaway Vertical Seismic Profiles

A vertical seismic profile (VSP) entails clamping a geophone at different depths in a borehole and recording the seismic wavefield generated from a source at the surface (Balch et al., 1982; Hardage, 1983; Shipboard Scientific Party, 1989). When the lateral distance between the source and receiver (offset) is small or zero, analysis of the downgoing waves yields accurate *P*-wave interval velocities. Upgoing waves can be processed to yield a seismic trace comparable to that of a conventional single-channel seismic line.

A walkaway VSP (W-VSP) entails firing the source at a series of offsets via a second ship, providing a range of incidence angles (Shipboard Scientific Party, 1986). *P*-waves reflecting at non-normal incidence generate converted *S*-waves, which propagate at velocities that differ from *P*-waves and, thus, carry additional information about bulk sediment properties. To help distinguish between *P*- and *S*-wave arrivals, we used a three-component geophone, sensitive to motion in three orthogonal directions.

Leg 164 VSPs were acquired at three sites (994, 995, and 997). Zero-offset (ZO) VSPs were acquired at all three sites, whereas walkaway VSPs were acquired at Sites 994 and 995. For ZO-VSP acquisition, the seismometer was clamped at 8- to 10-m intervals from the base of the hole (750 mbsf) to near the seafloor, providing ~85 traces. At least 10 shots each of a 300-in³ Bolt Model 3500C air gun and a 400-in³ Seismic Systems Model S-88 water gun were fired for each sonde depth from the *JOIDES Resolution* and stacked to form the ZO-VSP. A Norwegian float was used to maintain constant gun depth.

Walkaway VSPs were shot by the *Cape Hatteras* at ~72-m intervals in the hole. The source used for the W-VSP was a 150-in³ GI (generator-injector) gun, which is a two-chamber air gun with a suppressed bubble pulse signature.

The sondes used were two Woods Hole Oceanographic Institution (WHOI) three-component borehole seismometers manufactured by Geospace, Inc. (Models WLS 1000 and WLS 1100). A fourth channel recorded the pressure wavefield from a hydrophone suspended 170 m below the ship; this hydrophone provided a measurement of the downgoing source waveform. Data were digitized at 500 samples/s and recorded on SCSI hard disks using a Reftek Model 72A-08/G Digital Acquisition System (DAS) supplied by the IRIS/ PASSCAL Instrument Center at Lamont-Doherty Earth Observatory (LDEO). Two independent DASs record in parallel to provide data redundancy. The Reftek recording system allows for continuous time-series recording and later assembly of SEG-Y record sections using logged shot instants; no a priori knowledge of shot instants is required.

All shooting and recording systems were synchronized to a common GPS time base. Each Reftek DAS had an external GPS clock with an antenna mounted on the helipad of the *JOIDES Resolution*; continuous satellite locks provided microsecond timing accuracy. Shot instants were logged using identical systems on both ships. A trigger from the air gun blast phone was sent to a Seascan SAIL clock driven by an Efratom Model FRK Rb oscillator and synchronized to GPS time. The SAIL clock latched the time of the trigger event, which was logged to hard disk on a PC using the "shot-log" program developed by J. Dolan and K. Peal of WHOI.

Accurate navigation was required for the walkaway survey to compute source-receiver distances. This was accomplished by two independent approaches: (1) a P-code receiver aboard the *Cape Hat*-

Table 3. Approximate vertical resolution of	f various logging tools used during	Leg 1	164.
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Tool	Tool Vertical resolution	
Phasor dual induction tool (DITE) Deep resistivity (ILD) Medium resistivity (ILM) Shellware forward (SEL)	200 cm, 88 cm, 59 cm 150 cm, 88 cm, 59 cm	1.5 m 76 cm
Shallow focused (SFL)	59 cm	S8 cm
Natural gamma-ray spectrometry tool (NGT)	46 cm	15–30 cm
High-temperature lithodensity tool (HLDT) Density, photoelectric effect		Variable 15–60 cm 49 cm (6-in sampling) 35 cm (2-in sampling) 20 cm, Alpha processing 30 cm, Alpha processing (2 in)
Sonic digital tool (SDT/LSS)	30 cm Special processing, 15 cm	Variable 10–60 cm
Induced gamma-ray spectroscopy tool (GST)	75 cm	Variable 12–20 cm
Aluminum activation clay tool (AACT)	25 cm	Variable 12–20 cm
Dual porosity compensated neutron tool (CNT-G)	55 cm (6-in sample)	Variable and porosity dependent (15–60 cm) 33 cm, Alpha processing (6-in sample) 25.4 cm, Alpha processing (2-in sample)
Formation MicroScanner (FMS)	6 mm	5–25 cm
Lamont dipole shear sonic tool (LDEO-SST)	30 cm Special processing, 15 cm	Variable 10–60 cm
Lamont temperature-logging tool (LDEO-TLT)	 (1) fast-response (1-s time constant reading)/s (2) slow-response, high-accuracy reading (10-s time constant)/10 s; vertical resolution depends on logging speed. 	

Notes: Standard sampling is at 15-cm (6-in) intervals. High-resolution sampling is at 5.5-cm (2-in) intervals. Alpha processing is a special high-resolution processing routine. Depth of investigation is formation and environment specific; these depths are only rough estimates.

teras logged undithered GPS locations accurate to <10 m and (2) the relative distance between the *Cape Hatteras* and the *JOIDES Resolution* was computed via static differential GPS positions, using identical Ashtech Model XII GPS receivers on both ships. Post-cruise processing will yield relative ship-to-ship offsets accurate to <1 m; the offset between the *JOIDES Resolution* and the hole, which varied as much as ~25 m, was computed using the Winfrog DGPS system on board the *JOIDES Resolution*. Ship-to-ship communication took place via very high frequency (VHF) radio from the Underway Geophysics Lab of the *JOIDES Resolution* to the bridge of the *Cape Hatteras*.

Geophysics Addendum

The issue of noise is important in any scientific measurement, but it is particularly important when recording seismic and acoustic data aboard a noisy ship. The acoustic noise produced by the *JOIDES Resolution* is dominated not by random or white noise but by sharp peaks at several frequencies. This spectrum appears to change with changing sea state (engine loading) and ship activities. Fortunately, the spectral character of much of this noise provides an opportunity to remove it from the broadband signals of interest.

Ships in general are also known for generating strong electric and electromagnetic fields that contribute to the electronic noise in any electronic equipment on board. There is also an issue of ship's ground. Different portions of the structure and hull will have various dynamic levels of ground because of complicated time-variant paths of electric currents. A more detailed discussion of these and other noise factors regarding seismic data, or any data recorded electronically, is given in Hoskins and Wood (this volume).

DOWNHOLE LOGGING

Well-Logging Operations

The Lamont-Doherty Borehole Research Group (LDEO-BRG), in conjunction with the University of Leicester (Borehole Research-Leicester), the Institute Méditerranéen de Technologie (IMT), and Schlumberger Well Logging Services, provided the downhole well logging aboard the *JOIDES Resolution*.

To prepare for logging operations, the completed boreholes were flushed of debris by circulating a "pill" of heavy viscous drilling fluid (sepiolite mud with seawater) through the drill pipe to the mudline. The BHA was pulled up to ~60–100 mbsf, and then it was run down to the bottom of the hole again to condition the borehole for logging. Tool strings comprised of one or more combinations of sensors were then lowered downhole by a seven-conductor wireline cable during sequential runs. A wireline heave compensator (WHC) was employed to minimize the effect of ship's heave on the tool position in the borehole.

During each logging run, incoming data were acquired, archived, and monitored in real time on the Maxis 500 logging computer. The Cyber Service Unit (CSU) computer was used for the geochemical logging string. After logging, data were transferred to a Sun workstation and a Macintosh computer for preliminary shipboard correlation and interpretation.

Logging Tool Strings

Logging sensors continuously monitor geophysical, geochemical, and structural properties of the formation, which are typically record-





Figure 17. Schematic diagram of the LDEO-SST. Tool string is not drawn to scale.

Figure 16. Schematic diagram of Schlumberger logging tool strings used during Leg 164. Tool strings are not drawn to scale.

ed at 15-cm depth increments. The depths of investigation into and vertical resolutions of the formation are sensor dependent, but they are typically between 50 and 100 cm (Table 3). Individual logging tools were combined in five different strings: (1) the seismic stratigraphic combination, (2) the lithoporosity combination, (3) the Formation MicroScanner (FMS), (4) the geochemical combination, and (5) the Lamont-Doherty dipole shear tool (LDEO-SST). Schematic diagrams of these five tool strings are shown in Figures 16 and 17. The seismic stratigraphic and lithoporosity strings also were combined into a single string termed the Quad-combo. The Quad-combo tool string reaches a total length of 31 m (33 m with the Lamont-Doherty temperature-logging tool [LDEO-TLT]), making it difficult to run in short holes or to obtain data from near the bottom of the hole. Splitting the Quad-combo into two separate strings (1 and 2 above) improves the quality of the sonic and neutron porosity logs.

A brief description of the logging tools used during Leg 164 is given below (Table 4). Each tool description includes a review of the potential gas hydrate assessment applications. The presence of natural gas hydrate in the Blake Ridge sediments added further importance to the logging program. Gas hydrate is unstable under surface conditions, which lead to a greater emphasis on downhole measurements that could determine the in situ physical properties of gas hydrate-bearing sediments. The detailed principles of operation of the various logging sensors can be found in Serra (1984), Timur and Toksöz (1985), Ellis (1987), and Schlumberger (1989).

Logging Tools

Natural Gamma-Ray Spectrometry Tool

The natural gamma-ray spectrometry tool (NGT) measures the natural radioactivity of the formation using a sodium iodide (NaI) scintillation crystal detector mounted inside the tool. This tool measures the number of gamma rays and the energy level of each, which permits determination of radioactive potassium, thorium, and uranium concentrations in the formation (Lock and Hoyer, 1971). Gamma

Tool	Acronym	Principle	Synthetic seismogram	Lithology mineralogy	Porosity	Gas hydrate saturation	Used Leg 164	Typical data available on ship
Sonic	LSS/SDT	Traveltime of sound	G	F	G	G	Y	
	BHC SDT C		G	F	G	G	N	Velocity-V
	LDEO-SST		VG	F	G	G	Ŷ	Velocity- V_p , V_s
Resistivity	DITE							120102-000
Shallow	SFL	Focused current	F	F	VG	F	Y	Resistivity
Deep	ILD	Induced current	F	F	VG	G	Y	Resistivity
Gamma ray	GR	Natural gamma-ray emissions	Р	VG			Y	Gamma-ray counts
Caliper	MCD	Hole diameter		Р			N	
Dual laterolog	DLL	Resistivity to current	-	Р		G	N	
Neutron porosity	CNT-G	Absorption of bombarding neutrons	Р	F	VG	-	Y	Porosity
Natural gamma ray	NGT	Natural gamma-ray emissions	Р	VG			Y	K, Th, U abundances
Lithodensity	HLDT	Absorption of bombarding gamma rays	G	G	G		Y	Density
Induced gamma-ray spectroscopy	GST	Capture of bombarding neutrons	F	VG	F	G	Y	Elemental yields
Al activation clay tool	AACT	Absorption of bombarding neutrons	Р	F	Р	—	Y	Aluminum abundance
Formation MicroScanner	FMS	Focused microcurrent	Р	Р	G	Р	Y	Resistivity images
Temperature	LDEO-TLT	Formation temperature	Р	F		Р	Y	Temperature

Table 4. Summary of logging tool specifics and their applications during Leg 164.

Note: Tool acronyms are the same as in Table 3. Additional acronyms: LSS = long-spaced sonic tool, BHC = borehole compensated sonic logging tool, GR = natural gamma-ray logging tool, MCD = caliper tool, and DLL = dual laterolog. VG = very good, G = good, F = fair, and P = poor. Y = yes, and N = no. — = not applicable.

rays are emitted by radioactive isotopes of potassium and by the radioactive isotopes of the uranium and thorium decay series that are present in the formation. Measurements are analyzed by dividing the incident gamma-ray signature into five discrete energy windows that correspond to the main spectral peaks for each element. The total counts recorded in each window, for a specified depth in the borehole, are inverted to give the elemental abundances of K (weight percentage), U (ppm), and Th (ppm). The NGT also provides a measure of the total gamma-ray signature (SGR or [K + U + Th]) and a uranium-free measurement (CGR or [K + Th]). Values are recorded every 15.2 cm and have a vertical resolution on the order of 46 cm.

The NGT is run on all tool strings, except for the LDEO-SST, to provide a common basis for log correlations. The NGT is commonly used to estimate the clay content because of the relatively high abundance of K, U, and Th in clay minerals. The gamma-ray data provided by the NGT also are useful in estimating the organic carbon content of the formation (usually associated with high U counts). The NGT does not yield any direct gas hydrate data; however, its clay typing ability is a critical component of the overall formation evaluation program.

Phasor Dual Induction-Spherically Focused Resistivity Tool

The phasor dual induction–spherically focused resistivity tool (DITE-SFL) provides three different measurements of electrical resistivity. Each measurement has a different depth of investigation into the formation (Table 3): deep induction (IDPH), medium induction (IMPH), and shallow spherically focused log (SFL). The two induction devices (IDPH and IMPH) transmit high-frequency alternating currents through transmitter coils, creating magnetic fields that induce secondary (Foucault) currents in the formation. These groundloop currents produce a new inductive signal, proportional to the conductivity of the formation, that is measured by the receiving coils. The measured conductivities are then converted to resistivity (in ohm-meters). The SFL measures the current necessary to maintain a constant voltage drop across a fixed interval.

Water content and salinity are the most significant factors controlling the electrical resistivity of a formation. Other factors influencing resistivity include the concentration of hydrous and metallic minerals, the volume of hydrocarbons (including gas hydrate), and porestructure geometry.

Gas hydrate-bearing sediments exhibit relatively high electrical resistivities in comparison to water-saturated units, which suggests that the DITE-SFL could be used to determine gas hydrate saturations. There are no reported laboratory resistivity measurements of gas hydrate-bearing sediments; however, there is an extensive body of literature on the electrical properties of partly frozen sediments (reviewed by Pearson et al., 1983). Because ice and hydrate are electrical insulators, the resistivities of permafrost deposits and gas hydrate are largely controlled by unfrozen brine inclusions. Archie's equation (Archie, 1942) is an empirical relationship between water content (saturation) and the resistivity of water-saturated sediments:

$$R = a R_w \mathscr{O}^{-m} S_w^{-n},$$

where

R = formation resistivity (Ω m), a = empirically derived parameter,

 R_w = resistivity of formation water (Ω m),

 \emptyset = porosity (decimal percent),

m = empirically derived parameter,

 S_w = water saturation (decimal percent), and

n = empirically derived parameter.

As gas hydrate forms, the amount of free water decreases, and S_w and R_w are reduced (S_w because some of the available pore space becomes filled with a solid nonconductor [gas hydrate], and R_w because the dissolved salts become concentrated in the remaining unfrozen water). It is possible, however, that the excluded brines are removed from the system by diffusion processes and gravity drainage. If the brine is not near saturation, the effect of gas hydrate formation on R_w is relatively easy to quantify because an increase in salt concentration causes a linear decrease in R_w . Including both the temperature- and salt-concentration effects, the resistivity of a partially hydrated (frozen) brine at temperature (T) is, thus, proportional to (C)⁻⁷ S_w where C is a constant. Substituting this relationship into Archie's equation

and dividing by the resistivity at 0°C, we find that the ratio of frozen (R_i) and thawed (R_i) resistivities is (modified from Pearson et al., 1983):

$$R_f/R_t = C^{-T} S_w^{1-n},$$

where

- R_f = frozen (hydrated) formation resistivity (from log in the gas hydrate-bearing interval, Ω m),
- R_t = thawed (nonhydrated) formation resistivity (from log in the water leg of the gas hydrate–bearing interval, Ω m),
- C = empirically derived parameter,
- n = empirically derived parameter,
- S_w = water saturation (decimal percent), and
- T = formation temperature (°C).

To use this relationship, one must know the empirical parameters C and n, which have been calculated by Pearson et al. (1983). Thus the modified Archie equation can be used to estimate water saturation in a gas hydrate-bearing stratigraphic unit.

During Leg 164, the resistivity logs also were used to calculate sediment porosities. Porosities can be determined from the resistivity logs by using the Archie equation and assuming a water saturation equal to 1 in the hydrocarbon-free sedimentary sections.

Long-Spaced Sonic Tool

The long-spaced sonic tool (LSS) measures the time required for sound to travel through the formation between a transmitter and a receiver. It provides a direct measurement of sound velocity through sediments from the interval transit time measured and is likely to yield measurements free from the effects of formation damage and enlarged borehole from drilling processes. Sound velocity is an indirect measurement of sediment porosity and lithification.

The configuration of the LSS used during Leg 164 was arranged in the sonic digital logging tool (SDT) array. The tool contains two broadband piezoelectric ceramic transmitters spaced 61 cm apart and two piezoelectric receivers spaced 61 cm apart, with the lower receiver located 91 cm above the upper transmitter. In addition, eight wideband ceramic receivers are arranged in an array that is 1.07 m long and 2.44 m above the upper transmitter at the base of the sonde. This configuration provides eight different transit-time measurements. Interval transit times have been converted to compressional wave velocities (km/s). Full waveforms are recorded by the tool, allowing shore-based postprocessing to estimate shear and Stoneley wave velocities, as well as amplitude attenuation. Logs were corrected for cycle skipping caused by enlarged boreholes and, in some cases, bowsprings were used to assure good centralization of the sonic tool within the borehole.

Acoustic transit-time well logs can be used to measure the amount of gas hydrate within a drilled sedimentary unit. Timur developed the first three-phase, time-average equation that can be used to directly calculate the volume of gas hydrate within a rock interval (reviewed by Lee et al., 1993). Since its development, the Timur equation has been modified for numerous geologic conditions. Pearson and others (1983) were the first to apply the Timur equation to gas hydrate– bearing rocks.

Lamont-Doherty Dipole Shear Sonic Tool

The LDEO-SST consists of a piezoceramic monopole compressional wave transmitter (12–14 kHz), a wideband dipole shear wave transmitter (2–4 kHz), and a semirigid receiver array, including four compressional wave and three shear wave receivers (Fig. 17). The transmitters are separated from the receiver string with flexible

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acoustic isolators. The dipole transmitter creates unidirectional flexing of the borehole wall that excites shear waves in contrast to the nondirectional monopole source. The LDEO-SST also includes an orientation module for recording azimuthal orientation of the shear transmitter and receivers.

The LDEO-SST can measure compressional and Stoneley wave velocities, and it can directly measure shear wave velocities in "soft" formations in which the shear wave velocity is equal or less than the velocity of the drilling fluid, such as in water-saturated clays. Full waveforms from the compressional and shear wave receivers are digitally recorded by an industrial log-data acquisition system, which also controls tool operations. Computer software developed for the tool allows for conventional first-motion detection methods for determining wave-propagation velocities. Recorded waveforms can be used for post-cruise analysis to extract additional information, such as sonic wave attenuation and signal spectrums.

The ratio of compressional to shear wave velocities provides information on porosity, lithology, and the dispersion of Stoneley waves, which yields useful permeability and fracture data. Compressional and shear wave ratios also can be used to assess the amount of gas hydrate in a sedimentary sequence (Lee et al., 1993).

High-Temperature Lithodensity Tool

The high-temperature lithodensity tool (HLDT) uses a Cesium radioactive source and two detectors mounted on a shielded sidewall skid that is pressed against the formation by a hydraulically activated arm. The arm also provides a caliper measurement of borehole diameter. The medium-energy gamma rays emitted by the source at an energy of 662 keV lose energy by interacting with the electrons in the formation, causing Compton scattering until absorbed through the photoelectric effect. The number of gamma rays reaching the two vertically spaced detectors yields an energy spectrum for each detector that is directly related to the number of electrons in the formation, which, in turn, is related to the bulk density.

Photoelectric absorption occurs when gamma rays reach a low energy level (<150 keV) after being continually scattered by electrons in the formation. The photoelectric effect (PEF) depends on the atomic number of the elements in the formation; thus, the magnitude of this measurement is nearly independent of porosity. The PEF values, when used in combination with the NGT curves, can provide an indication of the different types of clay minerals in the sediments.

In conventional formation density logging, porosities are derived from the following relation:

$$\emptyset = (\rho_m - \rho_b)/(\rho_m - \rho_f),$$

where ρ_m is the known matrix density, ρ_f is the fluid (water) density, and ρ_b is the formation bulk density (log measured). The densities of natural gas hydrate have not been directly measured; however, it is possible to calculate gas hydrate densities using their unit cell dimensions (Pearson et al., 1983). The estimated bulk density of structure-I methane hydrate is ~0.9 g/cm³. To calculate porosities within a gas hydrate–bearing rock unit, a modified density equation has been developed for a three-component system (water, hydrate, and matrix):

$$\rho_b = (1 - \emptyset)\rho_m + (1 - S_h)\emptyset\rho_w + S_h\emptyset\rho_h,$$

where

 $\rho_b = \text{bulk density,}$ $\rho_m = \text{matrix density,}$ $\rho_w = \text{water density,}$ $\rho_h = \text{hydrate density,}$ For most cases, the true bulk density (ρ_b) of a water-bearing formation is almost identical to the bulk density (ρ_b) of a gas hydrate– bearing formation as determined by the HLDT. As a result, the HLDT yields accurate porosity data in gas hydrate–bearing formations, and the photoelectric effect measured by the HLDT provides information about formation lithologies.

Compensated Neutron Porosity Tool

The compensated neutron dual porosity tool (CNT-G) is used principally for delineation of porous formations and determination of their porosities. The CNT-G uses a 16 Curie Americium-Beryllium chemical source, which bombards the formation and borehole with fast neutrons (4.5 MeV) and two pairs of sensors to detect the number of neutrons (count rates) in the epithermal (0.1-100 eV) and thermal (<0.025 eV) energy ranges. The emitted neutrons interact elastically with the surrounding atoms, and the greatest energy loss occurs with atoms of the small-capture cross section, in particular hydrogen atoms (almost the same mass as one neutron). Thus, the slowing down and capture of the emitted neutrons is primarily controlled by the amount of hydrogen surrounding the tool. The amount of hydrogen in a rock sequence is related to the amount of water and hydrocarbons, including gas hydrate, that are present. Theoretical calculations indicate that the relative effect of gas hydrate on the neutron porosity log is minimal. The epithermal porosity for the pure water and gas hydrate constituents should only vary by ~6.2% (porosity units). Modeling studies also reveal that the capture cross section and neutron decay time for pure gas hydrate and water are almost identical (Collett, 1993). Therefore, the compensated neutron log should yield accurate reservoir porosities in gas hydrate-bearing rock units (assuming no free-gas effect).

Geochemical Logging Tool

The geochemical logging tool (GLT) consists of four parts: (1) an NGT; (2) a CNT-G used as a carrier for a Californium source of neutrons (2 MeV instead of the 4.5 MeV for the Americium-Beryllium source); (3) the aluminum activation clay tool (AACT) used in conjunction with the CNT-G (Hertzog et al., 1989); and (4) the induced gamma-ray spectroscopy logging tool (GST). The lower energy of the Californium source in the CNT-G, compared with the CNT-G tool that uses an Americium-Beryllium source, reduces the number of fast neutron reactions that would interfere with the AACT measurement. The AACT is similar to the NGT, but it measures the gamma-ray spectrum of the activated formation in three additional energy windows. Comparison of the AACT measurements to the NGT measurements obtained from the same tool string provides a measure of the concentration of Al (in weight percentage).

The GST is located at the base of the GLT string and consists of a high-energy pulsed neutron accelerator (14 MeV) and an NaI scintillation crystal detector. In neutron spectroscopy well logging, each element has a characteristic gamma ray that is emitted from a given neutron-element interaction. Specific elements can be identified by their characteristic gamma-ray signature, with the intensity of emission related to the atomic elemental concentration. By combining elemental yields from neutron spectroscopy well logs, reservoir parameters including porosities, lithologies, formation fluid salinities, and hydrocarbon saturations (including gas hydrate) can be calculated. The GST can be operated in two timing modes: inelastic, which mainly measures neutron reactions in the high-energy range (elements quantified: carbon, calcium, iron, oxygen, sulfur, and silicon), and capture-t mode, which measures gamma rays emitted from the neutron capture (elements quantified: calcium, chlorine, iron, hydrogen, sulfur, and silicon). In ODP wells, the GST historically has been operated in capture- τ mode. However, a selected number of inelastic mode measurements were made during Leg 164 (see individual site chapters).

Preliminary interpretation of the geochemical logs aboard ship can be compared to XRD measurements and to core descriptions to infer downhole mineralogical variations. After shore-based processing, the data will be used to make detailed assessments of mineralogical compositions.

The amounts of carbon, oxygen, and hydrogen in a rock sequence are not only controlled by the matrix lithology but also by the amounts of water and hydrocarbons, including gas hydrate, that are present in the rock. By using simple mixing relationships and the output from the GST, it is possible to develop elemental relations (ratios) that yield gas hydrate saturations (e.g., the carbon/oxygen and hydrogen/carbon ratios).

Formation MicroScanner Tool

The FMS produces high-resolution images of the microresistivity character of the borehole wall. The FMS tool comprises four orthogonal pads with 16 button electrodes (6.7 mm in diameter) on each pad that are pressed against the borehole wall (Serra, 1989). The electrodes are arranged in two diagonally offset rows of eight electrodes each. Each pad measures ~8 cm², and one pass of the tool covers approximately 30% of a 25.72-cm borehole. Each individual electrode emits a focused current into the formation. The button electrode current-intensity measurements, which reflect microresistivity variations, are converted to variable intensity color images. Processing corrects the offset rows to one level, providing a vertical resolution of ~0.5 cm at a sampling interval of 0.25 cm (Serra, 1989). The FMS tool string contains a general purpose inclinometry tool (GPIT) that orients the resistivity measurements through the use of an accelerometer and a magnetometer that responds to the declination and inclination of the Earth's magnetic field.

Scientific applications of the FMS images include obtaining information related to texture, sedimentary features, lithology, and diagenesis (Ekstrom et al., 1986; Hiscott et al., 1992). Detailed mapping of fractures, faults, foliations, and other formation structures, as well as determination of strikes and dips of bedding planes, also is possible.

Most well-log calculations assume that simple mixing rules can be applied to evaluate reservoir conditions; however, little is known about the nature of gas hydrate reservoirs. For example, does hydrate occur as a pore-filling constituent or is it only found in massive form? Information about the nature or texture of gas hydrate is needed. The FMS can be used to make an electrical image of the gas hydrate in the well bore, thus yielding information about the nature or texture of the hydrate occurrence in a rock interval.

The Lamont-Doherty Temperature Tool

The LDEO-TLT is a high-precision, low-temperature logging tool that can be attached to the base of any of the above Schlumberger tool strings. Data from two types of thermistors (fast and slow response time) and a pressure transducer are collected every second and are recorded internally. The fast-response thermistor (time constant = -0.4 s; precision = $\pm 0.005^{\circ}$ C) is able to detect small, abrupt temperature excursions in the borehole fluids caused by fluid flow from the formation and can be used to estimate temperature gradients in the formation. The slow-response thermistor also has a precision of $\pm 0.005^{\circ}$ C. Data are recorded as a function of time, with conversion to depth based on the synchronized time-depth record of the wireline cable.

Because gas hydrate exists under a limited range of temperature and pressure conditions, data on formation temperatures are needed to calculate the thickness of the gas hydrate stability zone. Temperature data from the LDEO-TLT can be used to assess the distribution of the theoretical gas hydrate stability field for a given location. The data recorded by the LDEO-TLT may differ somewhat from actual (equilibrated) formation temperatures because drilling and circulation operations disturb the temperature conditions in the well bore. However, with the spatial temperature gradient, it is possible to identify abrupt changes in the gradient that may indicate localized fluid flow between the borehole and the formation.

Log Data Quality

Log data quality may be seriously degraded by rapid changes in the hole diameter and in sections where the borehole diameter is greatly increased or washed out. The result of these effects is to impair logging by causing "bridging" or "tool sticking" and to increase the fluid volume between the formation and the logging tool. Deepinvestigation devices such as resistivity and velocity tools are least sensitive to borehole effect. Nuclear measurements (density, neutron porosity, and both natural and induced spectral gamma ray) are more sensitive because of their shallower depth of investigation. Corrections can be applied to the original data to reduce these effects, except in the case of very large washouts.

By using the NGT on each tool string, log measurements can be depth correlated between logging runs. However, logs from different tool strings may still have minor depth mismatches caused by cable stretch or ship heave during recording. Small errors in depth matching can impair the multilog analyses in zones of rapidly varying lithology. Ship heave is minimized by a hydraulic wireline heave compensator designed to adjust for rig motion during logging operations. Precise depth matching of logs with cores is difficult in zones where core recovery is low because of the inherent ambiguity of placing the recovered section within the cored interval.

Shore-Based Log Processing

Processing, quality control, and display of the logging data were performed at each of the six holes logged during Leg 164 by LDEO-BRG, Borehole Research-Leicester, and IMT, using Schlumberger "Logos" software and additional programs developed by members of LDEO-BRG. Displays of most of these processed data appear with accompanying text at the end of the appropriate site chapters in this volume. Files of all processed logs (including FMS, dipmeter, LDEO-BRG temperature data, high-resolution density and neutron data, and sonic waveforms not shown in printed form) and explanatory text are included on the CD-ROM enclosed in the back pocket of this volume. A directory of the contents of the disk is found in the Table of Contents of this volume.

Shore-based processing of data from each hole consisted of (1) depth adjustments of all logs to a common measurement below the seafloor, (2) corrections specific to certain tools, and (3) quality control and rejection of unrealistic values.

The depth-shifting procedure is based on an interactive, graphical depth-match program that allows the processor to visually correlate logs and define appropriate shifts. The reference log and the log to be adjusted in depth are displayed side by side on a screen, and vectors connect the two logs at positions chosen by the user. The total gamma-ray curve (SGR) from the NGT tool run on each logging string was used, in most cases, to correlate the logging runs. In general, the reference curve is chosen on the basis of constant, low cable

tension and high cable speed (tools run at faster speeds are less likely to stick and are less susceptible to data degradation caused by ship heave). Other factors, however, such as the length of the logged interval, presence of the bottom-hole assembly, and the statistical quality of the collected data (better statistics are obtained at lower logging speeds) are also considered in the selection. A list of the amount of differential depth shifts applied at each hole is available upon request to LDEO-BRG.

Specific tool corrections were performed on the gamma-ray data to account for changes in borehole size and for the composition of the drilling fluid. Processing techniques unique to the AACT and GST tools of the geochemical string are described in detail below.

Quality control was performed by cross-correlation of all logging data. If the data processor concluded that individual log measurements represented unrealistic values, the choices were to either discard the data outright and substitute the null value of "-999.25" or identify a specific depth interval containing suspect values that must be used with caution. The latter are noted in the text that accompanies all processed log displays. Quality control of the acoustic data was based on discarding any of the four independent transit time measurements that were negative or that fell outside a range of reasonable values selected by the processor.

In addition to the standard 15.2-cm sampling rate, bulk density and neutron data were recorded at a sampling rate of 2.5 and 5.1 cm, respectively. The enhanced bulk density curve is the result of a Schlumberger enhanced processing technique performed on the MAXIS system onboard. Whereas in normal processing shortspacing data is smoothed to match the long-spacing data, in enhanced processing this is reversed. In a situation in which there is good contact between the HLDT pad and the borehole wall (low density correction) the results are improved because the short-spacing data have better vertical resolution.

Locally, some intervals of log data appeared unreliable (usually because of poor hole conditions) and were not processed beyond what had been done on board the ship. In general, a large (>12 in) and/or irregular borehole affects most recordings, particularly those that require eccentralization (HLDT) and a good contact with the borehole wall. Hole deviation can also degrade the data; the FMS, for example, is not designed to be run in holes that are more than 10° off the vertical, as the tool weight might cause the caliper to close.

Processing of Leg 164 Geochemical Logging Data^{3,4}

Geochemical Tool String

Logging, including geochemical logging, was conducted at Sites 994, 995, and 997. The geochemical logging tool string (Fig. 16) consists of four logging tools: the NGT, the CNT-G, the AACT, and the GST. The natural gamma-ray tool is located at the top of the tool string, so that it can measure the naturally occurring radionuclides, Th, U, and K, before the formation is irradiated by the nuclear sources contained in the other tools. The compensated neutron tool, located below the natural gamma-ray tool, carries low-energy Californium-252 (252Cf) to activate the Al atoms in the formation. The aluminum activation clay tool, a modified NGT, is located below the ²⁵²Cf source and measures the activated gamma rays in the formation. By combining the AACT measurement with the previous NGT measurement, the background radiation is subtracted out and a reading of formation AI is obtained (Scott and Smith, 1973). The gamma-ray spectrometry tool, at the base of the string, carries a pulsed neutron generator to bombard the borehole and formation and an NaI(Tl) scintillation detector, which measures the spectrum of gamma rays generated by neutron-capture reactions. Because each of the elements in the formation is characterized by a unique spectral signature, it is possible to derive the contribution (or yield) of each of the major elements silicon (Si), iron (Fe), calcium (Ca), titanium (Ti), sulfur (S), gadolinium (Gd), and potassium (K) to the measured spectrum and,

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in turn, to estimate its abundance in the formation. The GST also measures the hydrogen (H) and chlorine (Cl) in the borehole and formation, but the signal for these elements is almost entirely because of seawater in the borehole, and they are, hence, of little value.

The only major rock-forming elements not measured by the geochemical tool string are magnesium (Mg) and sodium (Na); the neutron-capture cross-sections of these elements are too small relative to their typical abundances for the tool string to detect them. A rough estimate of Mg + Na can be made by using the photoelectric effect, measured by the lithodensity tool. This measured PEF is compared with a calculated of PEF (a summation of the PEF from all of the measured elements). The separation between the measured and calculated PEF is, in theory, attributable to any element left over in the formation (i.e., Mg and Na). Further explanation of this technique is found in Hertzog et al. (1987). This Mg + Na calculation was not performed for any of the logs discussed here because of the high variance in the data caused by poor hole conditions.

Data Reduction

Well-log data from the Schlumberger tools are transmitted digitally up a wireline and recorded on the *JOIDES Resolution* in the CSU. The results from the CSU are made available as "field logs" for initial, shipboard interpretation. Subsequent reprocessing is necessary to correct the data for the effects of fluids added to the well, logging speed, and pipe interference. Processing of the spectrometry data is required to transform the relative elemental yields into oxide weight fractions.

The processing is performed with a set of log interpretation programs written by Schlumberger that have been slightly modified to account for the lithologies and hole conditions encountered in ODP holes. The processing steps are summarized below:

Step 1: Reconstruction of Relative Elemental Yields from Recorded Spectral Data

The first processing step uses a weighted least-squares method to compare the measured spectra from the geochemical spectrometry tool with a series of standard spectra to determine the relative contribution (or yield) of each element. Whereas six elemental standards (Si, Fe, Ca, S, Cl, and H) are used to produce the shipboard yields, three additional standards (Ti, Gd, and K) can be included in the shore-based processing to improve the fit of the spectral standards to the measured spectra (Grau and Schweitzer, 1989). Although these additional elements often appear in the formation in very low concentrations, they can make a large contribution to the measured spectra because they have large neutron-capture cross-sections. For example, the capture cross-section of Gd is 49,000 barns; that of Si is 0.16 barns (Hertzog et al., 1987). Gd is, therefore, included in the calculation of a best fit between the measured and the standard spectra. This best-fit analysis was done for the elements in each of the logged holes to include spectral standards for Si, Ca, Fe, Ti, Gd, H, and Cl.

During the processing of Holes 995B and 997B the spectral standards for K and S were not used because these two elements existed in concentrations below the resolution of the tool and including them would significantly increase the noise level of all the other yields. A nine-point smoothing filter was applied to the yields in all holes to reduce noise in the data.

Step 2: Depth-Shifting

The second step in log processing is to depth shift the logging runs to a chosen reference run. A total gamma-ray curve (from the NGT, which is run on each tool string) is usually chosen as a reference curve, based on cable tension (the logging run with the least amount of cable sticking) and cable speed (tools run at faster speeds are less likely to stick). For Hole 994C, the reference NGT run was taken from the Quad-combo (DITE/SDT/HLDT/CNT-G/NGT) run. For Hole 995B, the NGT curve on the geochemical logging tool itself was Table 5. Oxide factors used in normalizing elements to 100% and converting elements to oxides.

Element	Oxide/carbonate	Conversion factor
Si	SiO ₂	2.139
Ca	CaCO ₃	2.497 for Holes 995B and 997E
Ca	CaO-CaCO ₃	1.399-2.497 for Hole 994C
Fe	FeO*	1.358
K	K ₂ O	1.205
Ti	TiO ₂	1.668
Al	Al_2O_3	1.889

Note: * = Computed using an oxide factor that assumes a 50:50 combination of Fe₂O₃ and FeO factors.

used as the reference curve, so no depth shifting was necessary at this stage. For Hole 997B, the reference NGT run was taken from the second (repeat) FMS run. The latter was the most appropriate run because of its greater speed and depth coverage.

Step 3: Calculation of Total Radioactivity and Th, U, and K Concentrations

The third processing routine calculates the total natural gamma radiation in the formation as well as concentrations of Th, U, and K, using the counts in five spectral windows from the natural gamma-ray tool (Lock and Hoyer, 1971). This resembles shipboard processing, except that corrections for hole-size changes are made in the shorebased processing of these curves. A Kalman filter (Ruckebusch, 1983) is applied to minimize the statistical uncertainties in the logs, which would otherwise create erroneous negative readings and anticorrelations (especially between Th and U). At each depth level, calculations and corrections also were performed for K contained in the mud. This K correction is particularly useful where KCl is routinely added to the hole; however, because of dispersion it is difficult to know exactly how much K is in the borehole. The outputs of this program are K (wet weight percentage), U (parts per thousand), and Th (parts per thousand), along with a total gamma-ray curve and a computed gamma-ray curve (total gamma ray minus U contribution). They are displayed as a function of depth in the log summary figures at the end of the relevant site chapters (this volume).

Step 4: Calculation of Al Concentration

The fourth processing routine calculates an Al curve using four energy windows while concurrently correcting for natural activity, borehole fluid neutron-capture cross-section, formation neutroncapture cross-section, formation slowing-down length, and borehole size. Porosity and density logs are needed in this routine to convert the wet weight percentage K and Al curves to dry weight percentage. For Hole 997B, because of the very poor hole conditions, log density data were not used. Instead, a working porosity curve was constructed from physical properties data of bulk and grain density and substituted as a log curve.

A correction is also made for Si interference with Al; the ²⁵²Cf source activates the Si, producing the aluminum isotope, Al²⁸ (Hertzog et al., 1987). The program uses the Si yield from the gamma-ray spectrometry tool to determine the Si background correction. The program outputs dry weight percentages of Al and K, which are used in the calculation and normalization of the remaining elements.

Step 5: Normalization of Elemental Yields from the GST to Calculate the Elemental Weight Fractions

This routine combines the dry weight percentages of Al and K with the reconstructed yields to obtain dry weight percentages of the GST elements using the relationship:

$$W_i = FY_i/S_i$$

where

- W_i = dry weight percentage of the *i*-th element,
- F = normalization factor determined at each depth interval,
- Y_i = relative elemental yield for the *i*-th element, and
- S_i = relative weight percentage (spectral) sensitivity of the *i*-th element.

The normalization factor, F, is a calibration factor determined at each depth from a closure argument to account for the number of neutrons captured by a specific concentration of rock elements. Because the sum of oxides in a rock is 100%, F is given by the following equation:

$$F(\sum X_i Y_i / S_i) + X_K W_K + X_{Al} W_{Al} = 100.0,$$

where

- X_i = factor for the element to oxide (or carbonate) conversion,
- X_{K} = factor for the conversion of K to K₂O (1.205),
- X_{Al} = factor for the conversion of Al to Al₂O₃ (1.899),
- W_{K} = dry weight percentage of K determined from natural activity, and
- W_{Al} = dry weight percentage of Al determined from the activation measurement.

The sensitivity factor, S_{ii} is a tool constant measured in the laboratory, which depends on the capture cross-section, gamma-ray production, and detection probabilities of each element measured by the GST (Hertzog et al., 1987).

The factors X_i are simply element to oxide (or carbonate, sulfate, and so on) conversion coefficients and effectively include the O, C, or S bound with each element. In processing the GLT data, the correct choice of X_i is important in the closure algorithm described above and requires some geological input. In most lithologies, the elements measured by the tool occur in silicates in which the compositions can be expressed completely as oxides. The only choice here concerns the degree of oxidation: Should iron be expressed as FeO or Fe₂O₃?

With carbonate or carbonate-rich lithologies, the measured calcium is more likely to be present as CaCO₃ (X_{Ca} :2.497) than as the oxide (CaO; X_{Ca} : 1.399). A good indication of the choice of calcium conversion factors can often be gained from shipboard XRD and CaCO3 measurements, which estimate acid-liberated CaCO₃. In the absence of suitable shipboard data, a rough rule of thumb was used such that if elemental Ca was below 6% then all Ca was assumed to be in silicate, above 12%, in carbonate. Ca concentrations between these figures were converted using linear interpolation. During Leg 164, XRD and CaCO3 data were available for processing the geochemical logs from Holes 995B and 997B. Although Ca is low over most of the logged section, there are no calcium-bearing silicates present in significant proportions, and the calcium is assumed to be tied up as the carbonate. For this reason, a carbonate factor of 2.497 (CaCO₃) was used for Holes 995B and 997B. A variable carbonate oxide factor was chosen, however, for Hole 994C (see Table 5). With the variable oxide factor, a factor of 1.399 is used if Ca is less than or equal to 6% by weight, a factor of 2.497 is used if Ca is greater than 12%, and the oxide factor is linearly interpolated if Ca is between 6% and 12%.

Step 6: Calculation of Oxide Percentages

This routine converts the elemental weight percentages into oxide percentages by multiplying each by its associated oxide factor, as shown in Table 5. The results are displayed as a function of depth in the log summary figures at the end of the relevant site chapters (this volume). The calcium carbonate measurements performed on board for all three holes are also displayed.

Step 7: Calculation of Error Logs

The seventh and final step in processing is the calculation of the statistical uncertainty of each element, using methods described by Grau et al. (1990) and Schweitzer et al. (1988). This error is strongly related to the normalization factor, F, which is calculated at each depth level. Both the normalization factor and statistical uncertainties are displayed as a function of depth in the log summary figures at the end of the relevant site chapters (this volume). A lower normalization factor represents better counting statistics and, therefore, higher quality data.

Overall, the logs in all three holes are degraded by poor hole conditions (particularly the size and rugosity of the boreholes), but some general trends in chemical variation are apparent that need to be considered in any geological interpretation of the borehole. In Holes 994C and 995B, there is evidence of broad cycles of compositional variation, seen best in the Al₂O₃ curve where some three or four cycles of upwardly decreasing Al₂O₃ occur of over more than 100 m. The variation in Hole 997B is more systematic, with Al₂O₃ gradually decreasing downhole by some 10% and SiO₂ rising by a similar amount to compensate.

IN SITU TEMPERATURE MEASUREMENTS

In situ thermal measurements were made using the Adara APC temperature shoe, the thermal capability of the WSTP, and a prototype instrument under development by E. Davis of Pacific Geoscience Centre and H. Villinger of University of Bremen. The in situ temperature instruments are described below, and the resulting data are described in chapters related to their respective deployments.

Adara APC Tool

The Adara tool consists of electronic components, including battery packs and data logger, and a platinum resistance-temperature device calibrated over a temperature range of 0°–30°C. A photograph of Adara components can be found in Fisher and Becker (1993). The Adara thermal tool fits directly into the cutting shoe on the APC and can, therefore, be used during regular piston coring. The thermal time constant of the cutting shoe assembly into which the Adara tool is inserted is ~2–3 min. To obtain thermal measurements, the only modification required to normal APC procedures is that the corer be held in place for at least 10 min after firing. During this time, the Adara tool tracks the thermal equilibration of the sediments. The specific tools used during Leg 164 were calibrated by Andy Fisher in 1993 and 1995 at WHOI and were chosen for deployment in the Leg 164 thermal program on the basis of their calibration and drift characteristics.

The Adara tool logs data on a microprocessor contained within the instrument. Following deployment, the data are downloaded for processing on PCs. The tool can be preprogrammed to record temperatures at a range of sampling rates. Sampling rates from 3 to 5 s were generally used during Leg 164.

A typical APC measurement consists of a mudline temperature record lasting as long as 10 min, a pulse of frictional heating when the piston is fired, a period of thermal decay lasting 10–15 min, and a frictional pulse upon removal of the corer. APC data tend to be smoother than WSTP data because of the greater stability of the data logger, the relative certainty that the APC tool has firmly penetrated into sediments during firing of the hydraulic assembly, and the fact that the tool accumulates four data records and reports only the average. Before reduction and drift corrections were made, the nominal accuracy of the Adara temperature data was estimated at 0.1°C.

WSTP Temperature Tool

At depths below which the Adara tool could no longer be used, but where the formation was sufficiently competent, in situ thermal measurements were made using the thermal capability of the WSTP. A schematic diagram of the deployment geometry of the WSTP can be found in Fisher and Becker (1993). During deployment, temperatures are recorded by a digital data logger in the WSTP tool for later downloading. However, a loss of power at any time during a single deployment of the WSTP tool (which may comprise several runs) will result in the loss of all of the data stored in the logger. The WSTP records only resistances, which must later be converted to temperatures using the thermistor calibrations stored in the laboratory computer. The thermistors used during Leg 164 were calibrated by Andy Fisher in 1993. All of the thermistors had drift characteristics well within acceptable limits.

The WSTP probe tip extends 3.5 cm beyond the main assembly and has a thermal time constant of 2-3 min. A typical WSTP measurement consists of a mudline temperature record lasting as long as 10 min, a brief interval of frictional heating associated with probe penetration into sediments ~1 m ahead of the drill bit, a period of thermal decay lasting 10-15 min, and a frictional pulse upon removal of the probe. In practice, mudline temperatures measured on descent tend to be poor because of instabilities in the electronics, and the mudline stop is typically accomplished on the ascent, even though the probe is covered with mud and will take longer to reach an equilibrium temperature. A key difficulty with WSTP measurements is the necessity of holding the probe stationary for 10 min or more beneath a heaving ship or in sediments that do not close around the tip. When used in APC/XCB coring, the WSTP is decoupled from the drill string in an attempt to minimize problems with holding the probe stationary.

Several complications peculiar to WSTP measurements limit determination of temperature equilibrium values to an accuracy of only $\pm 0.1^{\circ}-0.2^{\circ}$ C. First, after the first few minutes in the bottom of the hole, the thermal perturbation associated with the tool's departure from uniform cylindricity propagates downward and affects the sediments in the vicinity of the probe tip. Second, the probe tip often cannot be held stationary in the bottom of the hole, or else indurated sediments may crack around the tip. Such complications may result in small, but identifiable, perturbations to the thermal record. Finally, although the probe tip is nominally emplaced 1 m deeper than the bottom of the hole, the true depth of insertion is not known and may vary from 0 to 1 m. If thermal gradients increase with depth, then equilibrium temperature values obtained with the WSTP tool must always be assumed to represent minimum bounds on in situ temperatures.

Scientists have noted considerable degradation in the quality of thermal data collected when the WSTP was in dual water and temperature sampling mode. To avoid this problem during Leg 164, dedicated thermal runs were interspersed with combined water and temperature sampling runs. During the dedicated thermal runs, a specially fabricated solid sleeve was used in place of the filter assembly. The solid sleeve renders the tool's geometry closer to that of an ideal line source and makes it less likely that indurated sediments will fracture upon penetration of the probe tip (Fisher and Becker, 1993).

Davis/Villinger Temperature Probe

A prototype temperature probe, the Davis/Villinger Temperature Probe (DVTP), was deployed for the first time during Leg 164. The probe, has a nearly cylindrical casing that terminates in a pointed tip. In situ temperatures are logged by two thermistors, one located 1 cm from the tip of the probe and the other 12 cm above the tip. A third thermistor, referred to as the internal thermistor, is located in the electronics package. The commercially supplied thermistors used during Leg 164 were matched within 1% (by resistance) and aged at 300°C. Thermistor sensitivity is 1 mK in an operating range from -5° to 20°C, and the total operating range is -5° C to 100°C. The thermistors were calibrated at the factory and on the laboratory bench before being installed in the probe. However, calibrations in constant temperature water baths could not be completed before deployment and were, therefore, conducted after the cruise. In addition to the thermistors, the probe contains an accelerometer sensitive to 0.98 m/s². Both peak and mean acceleration are recorded by the logger. The accelerometer data are used to track disturbances to the instrument package during the equilibration interval.

In most respects, a DVTP deployment resembles a WSTP deployment. Mudline temperatures were measured for 5–10 min before the probe was lowered into the hole for a 5- to 15-min equilibration interval at the bottom. Mudline temperatures also were collected for at least 3 min on ascent to provide a stable baseline value for comparison with the mudline temperature recorded by the Adara tool. The thermal time constant of the DVTP and the decay characteristics of equilibration curves can only be determined empirically after numerous deployments. However, data collected during Leg 164 indicate that the time constants are probably 1 min for the probe tip thermistor and ~2 min for the thermistor at 12 cm from the tip.

The prototype DVTP has several advantages over the WSTP for in situ measurements at XCB depths:

- The probe's geometry is nearly cylindrical over a much longer distance than the WSTP, so that the DVTP more closely approximates a line source.
- The taper of the probe tip is ~5°, which minimizes formation stresses associated with tool insertion.
- 3. The incorporation of two thermistors adds an element of reproducibility to the measurements and theoretically makes it possible to estimate the thermal gradient. In high-temperature settings, the second thermistor can be set to allow measurements over a wider range of temperatures at reduced sensitivity.
- 4. The DVTP electronics are more stable than those in the WSTP, and the logger unit has greater storage capacity. The probe consumes relatively little power compared to the WSTP and has an external communication port, making it unnecessary to open the tool for data retrieval.

Data Reduction

Data reduction procedures are similar for all the temperature tools. The transient thermal decay curves for marine thermal probes are known to be a function of the geometry of the probes and the thermal properties of the probe and the sediments (Bullard, 1954; Horai and von Herzen, 1985). Analyses of WSTP and Adara data require the construction of synthetic decay curves that are calculated based on tool geometry, the sampling interval, and tool and sediment thermal properties. However, it is never possible to obtain a perfect match between the synthetic curves and the data because (1) the probe never reaches thermal equilibrium during the penetration period; (2) contrary to theory, the frictional pulse upon insertion is never instantaneous; and (3) temperature data are sampled at discrete intervals, meaning that the exact time of penetration is always uncertain. Thus, both the effective penetration time and equilibrium temperature must be estimated by applying a fitting procedure, which involves shifting the synthetic curves in time to obtain a match with the recorded data. Data collected more than 20-50 s beyond penetration usually provide a reliable estimate of equilibrium temperature.

Simple processing of clean temperature records can be accomplished largely by using shipboard software written especially for analysis of raw data collected with the WSTP and Adara tools. Variables in the analysis program include the thermal conductivity of the sediments, the time of tool insertion, the delay time between insertion and peak frictional heating, and the length of the thermal decay interval to be fit. The thermal decay curves for the WSTP and Adara tool measurements were fit on board assuming thermal conductivity of 1.0 W/(m·K) for all of the data.

The thermal conductivity values used in determining heat flow were generally those obtained by the needle-probe measurements (see "Physical Properties" section, this chapter), but they were corrected to more accurately reflect the pressure and temperature conditions of the in situ sediments. Laboratory results were corrected assuming an increase in conductivity of 0.5% per 1000 m of water depth and a decrease in conductivity of 0.25% per degree of temperature increase (Ratcliffe, 1960). These corrections do not account for any increase in thermal conductivity associated with compaction caused by overburden pressure at subseafloor depths.

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