HAWAII DEEP WATER CABLE PROGRAM

PHASE II-C

TASK 1

HYDROGEN SULFIDE IN SEDIMENTS ALONG THE PREFERRED
SUBMARINE CABLE ROUTE.

Prepared by
George Krasnick,
Parsons Hawaii

For
Hawaiian Electric Company, Inc.

And the

State of Hawaii
Department of Planning and Economic Development

April 1987

RATIONALE

The technical feasibility of the baseline commercial cable system defined by the HDWC Program is being measured by applying a hierarchy of feasibility criteria which apply to the total system and its respective subsystems. The System Feasibility Criteria (Parsons Hawaii, 1985) specify a minimum design life for all components, and this has been included in design considerations for each hardware component.

For the cable itself, numerous operational and environmental conditions may act to reduce the design life, and these define the requirements for the contents of the Laboratory Testing Program. A very significant potential cause of reduced cable life is corrosion, and this has been and continues to be examined in experiments using cable and cable materials samples. The experience of the cable designer with regard to the expected corrosion resistance of the design cable was summarized in a 1985 report entitled "Study of the Corrosion Resistance of the Hawaii Deep Water Submarine Power Cable" (PCC, 1985). This study identified as an area requiring additional information a review of the cable route for potentially damaging concentrations of hydrogen sulfide, and noted that ". . . H_2S concentrations in excess of a threshold value of the order of 50 ppm can increase corrosion rates."

The purpose of this report is to describe how H_2S acts to increase corrosion rates, to summarize sulfide data from along the preferred cable route, and to assess the probable impact of H_2S on the baseline commercial cable.

SULFIDE CORROSION MECHANISMS

Corrosion in an electrolyte such as sea water is an electrochemical phenomenon. Electricity flows from some areas of a metal surface to other areas through the conducting electrolyte. That portion of the metal surface suffering corrosion is termed the "anode," while the "cathode" is that portion of the metal surface from which current leaves the solution to return to the metal.

At the (corroding) anode, positively charged metal ions leave the solid surface and enter the solution. Negatively charged electrons are left behind to travel through either the metal or the electrolyte to complete the circuit at the cathode where they either form negative ions or neutralize positive hydrogen ions. The latter may combine to form gaseous hydrogen molecules.

Reactions at the anode and cathode must proceed simultaneously and at the same rate. However, that rate may be slowed by a number of processes such as accumulation of hydrogen gas at the cathode.

The type and rate of corrosion varies with the metal or alloy, the presence of inclusions or other foreign matter at the surface, the homogeneity of its structure, the nature of the corrosive medium, environmental factors such as oxygen concentration, temperature, water current velocity, stress, oxide scale and other surface deposits, crevices, galvanic effects between dissimilar metals and "stray" electrical currents. Environmental factors greatly affect corrosion rates. In particular, oxygen concentration plays a major role in corrosion, with deaeration an effective means of corrosion prevention for many metals.

Some microorganisms, especially common sulfate reducing bacteria, inhibit cathodic reactions allowing corrosion to proceed even in anaerobic conditions. The hydrogen sulfide they produce accelerates corrosion of metal alloys by the substitution of sulfides for the more protective oxidized corrosion products which form on the alloys under aerobic conditions.

Oxygen contributes to the cathodic reaction in the following way:

$$O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$$
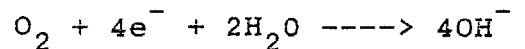
When there is a difference in oxygen concentrations at two points on a metal surface, the point with the higher concentration becomes cathodic to areas exposed to lower concentrations. This is an "oxygen concentration cell."

In aerated environments, most metals develop an oxide film which can provide substantial protection against further corrosion. This is particularly true for aluminum.

From the above it can be seen that oxygen can initially accelerate but ultimately retard corrosion. Development of a very thin oxide film may render metals such as iron and stainless steel "passive." When protected by this film, corrosion resistance is orders of magnitude greater than for the "active" metal. In general, oxidizing environments tend to preserve the passivity of stainless steels. It could be expected that this would also be the case for the galvanized steel armor of the HDWC Program design cable, although oscillations of the cable over a hard surface due to thermal cycling, tidal rhythms, ocean currents or vortex shedding could repeatedly abrade away the oxide film, exposing newly "active" surfaces of the armor wire to rapid corrosion.

In the marine environment, oxygen concentrations are typically highest near the air/water interface, where wind and wave-induced turbulence may maintain slightly supersaturated conditions. The "mixed layer," extending downward from the sea surface to depths of 50-100 meters in Hawaii, generally has uniform, saturated oxygen concentrations. Just below the mixed layer may be another narrow layer where oxygen is supersaturated due to photosynthesis by a concentrated layer of phytoplankton. Farther below the mixed layer and extending to as much as 150 m in Hawaiian waters, is the "thermocline," a region of rapidly decreasing temperature (and density). Oxygen concentrations decrease through the thermocline to a near-zero minimum at depths ranging from 300-700 meters. Below this minimum, concentrations gradually increase to the bottom. Typically, ocean currents carrying oxygenated water across the bottom sediments allow diffusion to aerate the upper layers of the porous sediments. However, where sufficient organic matter has accumulated on the bottom and oxygen demand for decomposition exceeds the supply provided by diffusion , high concentrations of sulfides may be produced by anaerobic sulfate-reducing bacteria.

Because oxygen plays a predominant role in cathodic reactions and contributes to the development and preservation of passivity on stainless steels and the formation of protective oxide films on metals such as aluminum and titanium, its content in seawater is of major importance in the corrosion of metals.

Where oxygen concentrations are lowest, corrosion of most metal alloys is lowest. Aluminum alloys however, suffer their highest corrosion rates where oxygen is depleted, presumably due to weakening of the protective oxide film.

Where anaerobic conditions are established in the marine environment, differential aeration may accelerate the corrosion of partially exposed metals.

High sulfide concentrations enhance corrosion, especially of copper-based alloys. The sulfide films that develop as corrosion products in oxygen-deficient waters improve resistance to impingement attack so long as they remain intact, but when they break down locally they promote severe pitting.

Sulfate-reducing bacteria thrive in the anaerobic conditions created under heavy accumulations of marine growths and promote corrosion at rates similar to those in aerated conditions. The organic reduction of sulfate to sulfide accommodates the electrons released by the anodic reaction. These bacteria can also directly consume hydrogen released in cathodic reactions. Sulfide films are cathodic to the base metal, and a secondary effect of the bacteria can be to promote pitting at discontinuities in the sulfide films.

SULFIDE CONCENTRATIONS IN LOCAL SEDIMENTS

Significant concentrations of hydrogen sulfide are found in two types of marine environments: near volcanic vents and in organic-rich sediments. There is no known hydrothermal venting along the preferred cable route (A. Malahoff, pers. comm.). The only active vents in Hawaii are located off the southeastern coast of the island of Hawaii associated with Loihi Seamount, an active submarine volcano.

Organic-rich sediments are often found under waters of relatively high productivity. Where inorganic nutrient concentrations are high, phytoplankton productivity is high, and the entire food web is enriched. Where water circulation is restricted, fecal matter, skeletal material and carcasses accumulate and decomposition depletes the available oxygen. Under these conditions, anaerobic bacteria develop and utilize oxygen bound in sulfates for oxidation of organic substrates. Concomitantly, gaseous hydrogen sulfide is liberated and dissolves in sea water. In sediments, the hydrogen sulfide combines with heavy metals, particularly iron, to form dark-colored sulfides. Where this occurs, a normal aerobic flora and fauna is not possible.

The upper layers of the ocean offshore of Hawaii are extremely poor in dissolved inorganic nutrients, leading to the common designation of this mid-ocean band as a "biological desert." Typically, low concentrations of dissolved nitrogen forms limit the growth of phytoplankton populations and the resulting low concentrations of cells in the water affords great visual clarity. Near to shore, however, nutrient subsidies from terrestrial runoff, ground water seepage and point-source discharges of sewage effluents and other nutrient-rich wastes may act as fertilizers, stimulating algae at the base of the food web and promoting growth of populations at higher trophic levels. In environments where flushing is restricted, such as Pearl Harbor or Kaneohe Bay, biomass may accumulate to very high levels in the water column and oxygen depletion of the organically-rich sediments may occur. In open coastal waters, this biostimulation normally does not result in an accumulation of organic matter in the sediments because lateral advection by water currents continuously renews the supply of oxygen necessary for decomposition to occur.

A review of literature revealed that locally, researchers have only rarely surveyed concentrations of hydrogen sulfide in sediments. This is primarily because, in most local environments, aeration of at least the upper layers of sediment is adequate to avoid sulfide formation. Measurements in Kaneohe Bay, an estuary with restricted flushing, have been on the order of 1×10^{-3} to 1×10^{-4} moles/l (F. Mackenzie, pers. comm.), or about 3 to 30 ppm, below the threshold value established by Pirelli. Values an order of magnitude lower were recorded near

a deep ocean outfall site at Barbers Point, Oahu (Dollar, 1986).
Values along the proposed baseline commercial cable route should
be lower than in either of these reference environments.

With site-specific quantitative data unavailable and new field
surveys prohibitively expensive, we investigated qualitative
evidence of sulfide formation along the preferred submarine
route.   For this, we enlisted the assistance of Mr.   Bruce
Tsutsui, curator of the Hawaii Institute of Geophysics, Sediment
Core Laboratory. His facility stores, analyzes and catalogs all
sediment core samples taken during University of Hawaii
oceanographic expeditions.   A search of lab records for
locations of past cores in proximity to the preferred cable
route revealed only a few of possible relevance. The locations
are plotted on Figure 1. The three cores off Kawaihae Bay are
south of the intended route, but representative of general
conditions on the Kohala Terrace.   The fourth core is
representative of conditions throughout the central flat portion
of the Alenuihaha Channel.

The lithology of the two Kohala Terrace cores is described in
Theyer and Mato (1983). These descriptions are reproduced in
Appendix A.   More complete discussions of all three cores are
found in the report for the OTEC-1 anchor site survey (Campbell
and Erlandson, 1979). Their descriptions are as follows:o

KANA KEOKI Cruise 78-10-30

    Station 2 - Piston Core 1

        The core, 70 cm long, contained material of fine to
    coarse sand-size with a few fragments coarser than
    sand-size.   Splits of the coarse and fine-sized material
   were made and are described separately.

        The coarse material was predominantly benthic
    foraminifera but also contained micro-mollusks, echinoid
    spines, pteropods, volcanic glass, fresh volcanic rock
    fragments and fragments of feldspar and olivine crystals.

        The finer split was primarily planktonic foraminifera
    with some benthic foraminifera, volcanic glass, both brown
    and green palagonite, sponge spicules, pteropods, diatoms,
    radiolarians and a bryozoan fragment.

    Station 7 - Piston Core 2

        Piston Core 2 came back with a core approximately 33 cm
    long.   A sample was taken from the lowest 5 cm and quickly
    sieved.   The fractions are described below. A quick look
    through the liner suggests that the sample described is
    representative. The 4mm+ fraction is by far the largest.

FIGURE 1
SEDIMENT CORE LOCATIONS
NEAR THE CABLE ROUTE
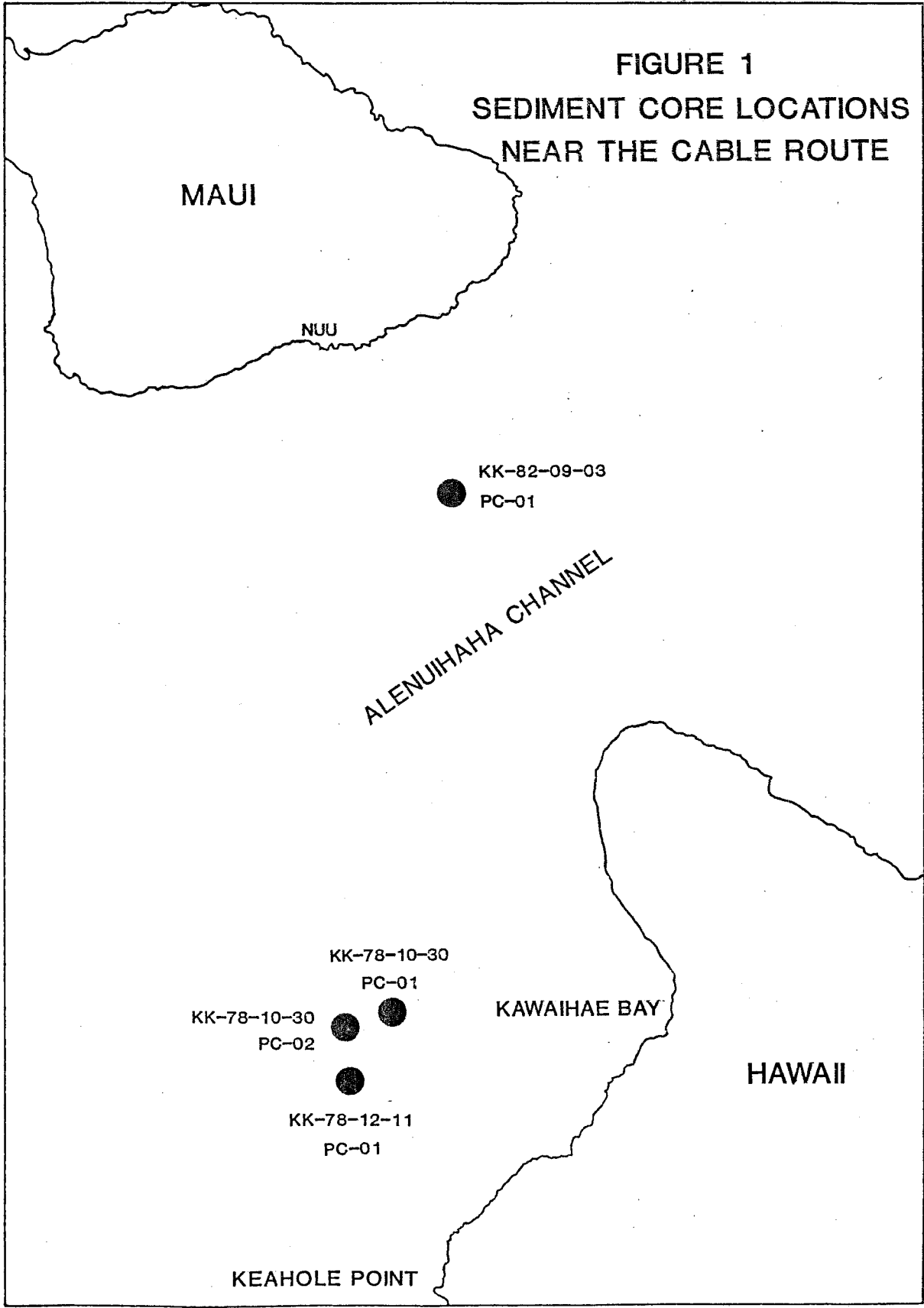
MAUI

NUU

KK-82-09-03
PC-01

ALENUIHAHA CHANNEL

KK-78-10-30
PC-01

KK-78-10-30
PC-02

KAWAIHAE BAY

HAWAII

KK-78-12-11
PC-01

KEAHOLE POINT

>4 mm. Fragments, up to 5 cm long, of coral, clumps of encrusting coralline algae, mollusk shells (whole and fragments); some encrustation by algae and serpulid worms. Shell natural and coral still aragonitic.

<4 mm >1 mm. Foraminifera (both serial and coiled benthonic), molluscan fragments, coral fragments, echinoid spines, juvenile gastropods, algal fragments, rare volcanic rock fragments and single crystals (olivine), some glassy bryozoans.

<1 mm >.35 mm. Foraminifera (coiled forms and rare miliolids) molluscan fragments, echinoid spines; volcanic rock fragments and single crystals of olivine. Very much like the 4-1 mm fraction. Grains in general are angular to subrounded.

<35 mm>.124 mm. Foraminifera (including planktonic-globigerenids?) sponge spicules. Black-brown volcanic rock grain and crystals of olivine. Small, glassy gastropods. Most are indeterminant shell debris.

KANA KEOKI Cruise 78-12-11

Station 1 - Piston Core 1

This 105-cm long core contained fine-grained sand to clay-sized material composed primarily of planktonic and benthic foraminifera, volcanic glass, palagonite, diatoms, radiolarians, sponge spicules and calcareous muds. Mixed in with the lowermost 5 cm of the core were small glassy chips of basalt.

The ubiquitous presence of aerobic fauna in these cores indicates that these sediments are not oxygen depleted and the presence of hydrogen sulfide is not indicated.

The single core taken in the Alenuihaha Channel is also described in Appendix A. These sediments have a very low organic content (B. Tsutsui, pers. comm.). Because of this, oxygen demand likely is also very low and there is no reason to suspect development of anoxic conditions and hydrogen sulfide.

Of the remainder of the route, the area most likely to contain relatively high concentrations of organic matter would be the shallow areas in the lee of Maui and Molokai. Core data from this area are not available, but surface sediment samples have been collected with a pipe dredge (Campbell, et al., 1971). Although the sampling methodology and the sample analyses were not selected with the present question in mind, the authors do not indicate anoxic conditions anywhere in this area.

CONCLUSIONS

1. The preferred baseline commercial cable route does not pass through areas of active hydrothermal venting and therefore hydrogen sulfide from such sources will not affect the submarine cable.

2. Concentrations of hydrogen sulfide from _in situ_ decomposition of organic matter along the preferred route are expected to be at least two orders of magnitude below the threshold established by Pirelli for concern about accelerated corrosion.

References

Campbell, J.F. and D. Erlandson, 1979. OTEC-1 Anchor Site Survey. Final Rept., Prep. for Global Marine Development, Inc. and the U.S. Dept. of Energy. Hawaii Inst. of Geophysics Rept. No. MIG-79-6. 55p.

Campbell, J.F., B.R. Rosendahl, W.T. Coulbourn and R. Moberly, Jr. 1971. Reconnaissance Sand Inventory: Off Leeward Molokai and Maui. National Sea Grant Program Rept. UNIHI-SEA GRANT-TR-71-02. Hawaii Inst. of Geophysics Rept. No. MIG-71-17.

Dollar, S.J. 1986. Response of Benthic Erosystems to Deep Ocean Sewage Outfalls in Hawaii: Nutrient Fluxes at the Sediment-Water Interface. Ph.D. dissertation. Dept. of Oceanography. Univ. of Hawaii. 217p.

Parsons, Hawaii. 1985. Hawaii Deep Water Cable Program, Phase II: System Feasibility Criteria. Prep. for Hawaiian Electric Co., Inc. and the U.S. Dept. of Energy.

Pirelli Cable Corporation. 1985. Hawaii Deep Water Cable Program, Phase II: Study of the Corrosion Resistance of the Hawaii Deep Water Submarine Power Cable. Prep. for The Ralph M. Parsons Company, Hawaiian Electric Company, Inc. and the U.S. Dept. of Energy.

Theyer, F. and C. Mato. 1983. Sediment Core Descriptions: R/V Kana Keoki 1977 through 1981 North Pacific Ocean Cruises and R/V Wekoma 1980 Southeast Pacific Ocean Cruise. Prep. for National Science Foundation and Office of Naval Research. Hawaii Inst. of Geophysics Rept. No. MIG-83-2. 9p + 123p App.

APPENDIX A

Descriptions of Cores Collected
in Sediments Close to the
Preferred Cable Route

Depth in
core (cm)   LITHOLOGY

0
10
20
30
33

BTM
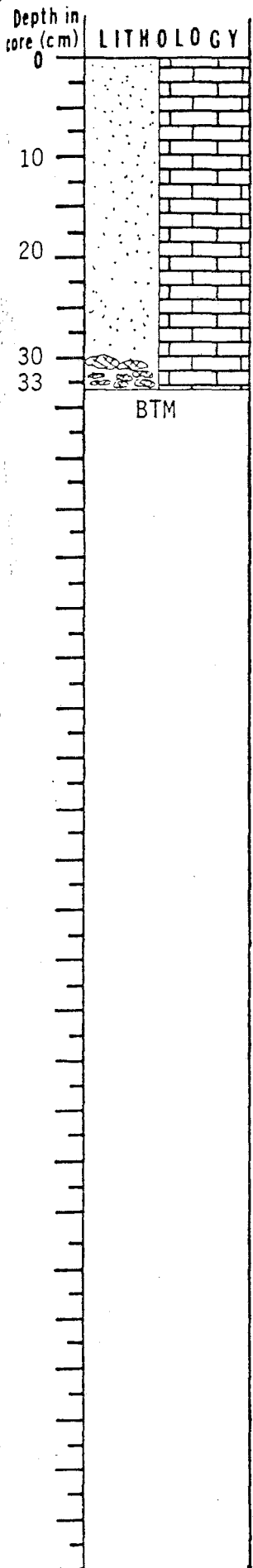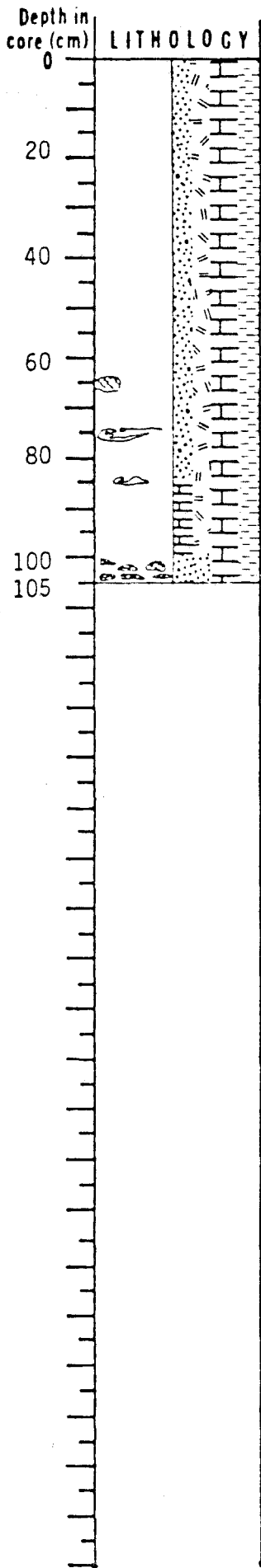
Core ID   :   KK78-10-30   Sta. 07
             :   PCOD 02
Latitude   :   19° 58.8' N
Longitude   :   156° 09.1' W
Water depth :   1164 m
Geoprovince :   Kohala Terrace

0-33 cm   very pale brown (10YR7.5/3.5)
             FORAM OOZE
             50-55% biocalcareous frag, 30-40% foram,
             3-5% iso min, 3% clay, 2-3% aniso min

             Entire core is unconsolidated
             Sandy and pebbly

KEY

FORAM
CORAL

*Bottom age   Quaternary

SEDIMENT   DESCRIPTION

Core ID   :   KK78-12-11   Sta. 01
            :   PCOD 01
Latitude   :   19° 56.0' N
Longitude   :   156° 09.0' W
Water depth: 1400 m
Geoprovince :   West of Kohala

0-85 cm   light gray (2.5Y7/2) to
                 very dark grayish brown (2.5Y3/2)
                 MINERAL VOLCANIC GLASS PALAGONITE RICH FORAM CLAY
                 21-40% clay (sized), 20-30% foram,
                 12-25% volcanic glass and palagonite,
                 10-12% aniso min, 2-10% nanno, 3-15% biocalcareous
                 frag, 2-5% iso min, 1-3% opaque min,
                 1-4% rad, 1-3% diatom, tr-3% biosiliceous frag,
                 tr-2% sponge

85-100 cm   dark gray (10YR4/1)
                 VOLCANIC GLASS PALAGONITE NANNO RICH FORAM CLAY
                 31-33% clay (sized), 20-22% foram, 12% nanno,
                 10-15% volcanic glass and palagonite,
                 7-8% aniso min, 2-3% diatom, 2% iso min,
                 2% biosiliceous frag, 1-2% benthic foram,
                 1% sponge

100-105 cm   very dark gray (5Y3/1)
                 CLAY RICH FORAM MINERAL SILT
                 30% aniso min, 30% foram, 22% clay (sized)
                 3% benthic foram, 3% iso min, 3% opaque min,
                 3% volcanic glass and palagonite,
                 2% biocalcareous frag, 2% nanno

Mottling

Moderate to slight mottling of gray (5Y4/1) at 74-76 cm and
85-86 cm.

  0-9 cm   graded bedding
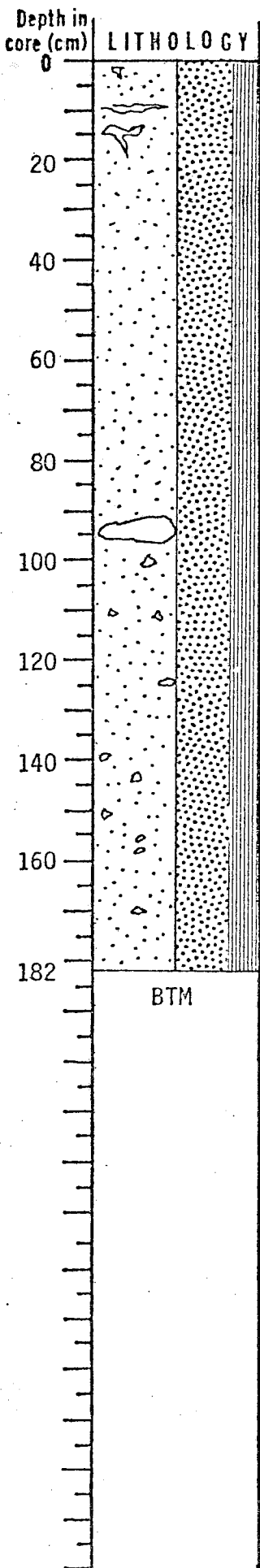
 59-61 cm   small void; coring induced

100-105 cm   rock (basalt?) chips found

KEY

CLAY
FORAM
MINERAL
VOLCANIC GLASS AND PALAGONITE
NANNO
ROCK   *Bottom age   Quaternary

Depth in core (cm)	LITHOLOGY

Core ID : KK82-09-03   Sta. 06
PC 01
Latitude : 20° 29.1' N
Longitude : 156° 02.8' W
Water depth : 1975 m
Geoprovince : Central Alenuihaha Ch.

0-95 cm   black (7.5-10YR2/1)
VOLCANIC GLASS RICH MINERAL CLAY
34% clay, 25% volcanic glass, 20% aniso min,
7% iso min, 7% opaque min, 5% foram, 1% nanno,
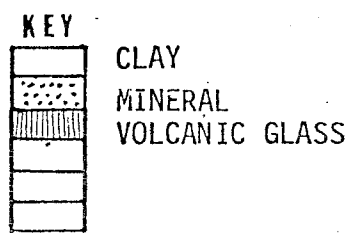1% zeolite

95-182 cm   black (7.5-10YR2/1)
VOLCANIC GLASS RICH CLAY MINERAL
33-35% clay, 25% volcanic glass, 20-25% aniso min,
10-15% opaque min, 5% iso min, 2% foram

Mottling

Very slight mottling scattered sparsely in core;
dark brown (10YR3/3).

12 cm   dark brown (10YR3/3)
MINERAL RICH VOLCANIC GLASS CLAY
30% clay, 30% volcanic glass, 15% aniso min,
10% foram, 5% iso min, 3% opaque min, 2% diatom,
2% nanno, 2% zeolite, tr ceratolith

91-96 cm   semi-indurated sediment found
dark grayish brown (2.5Y4/2)
VOLCANIC GLASS RICH MINERAL CLAY
32% clay, 20% aniso min, 20% volcanic glass,
10% foram, 5% iso min, 5% opaque min, 3% nanno,
2% diatom, 1% rad, 1% sponge, 1% zeolite,
tr ceratolith, tr gastropod

96-182 cm   glassy rock fragments 1-2 cm diameter,
black (10YR2/1)

KEY

	CLAY
	MINERAL
	VOLCANIC GLASS