

2. INTERSTITIAL WATER STUDIES, LEG 15 – NEW PROCEDURES AND EQUIPMENT¹

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INTRODUCTION

Interstitial water samples have been collected on every leg since the beginning of the Deep Sea Drilling Project. Sediment samples were taken from selected core sections and processed as soon as possible after recovery. When it was necessary to store samples for later squeezing, sediments were kept in glass jars with polyseal caps and stored at 4°C in the laboratory refrigerator. While all reasonable precautions were taken to minimize contamination during sampling and processing, the sediments were exposed to the atmosphere and squeezing was carried out at the ambient temperature of the shipboard laboratory.

This section provides a complete description of the specially constructed equipment and an explanation of the new procedures employed in the collection and processing of sediments for the Leg 15 geochemical program. This is the first time that sediments have been processed in an inert atmosphere and samples have been squeezed at different temperatures aboard the *Glomar Challenger*. Interstitial water samples were squeezed at two temperatures from 64 segments of core. Samples of sediment from all three geochemical sites were also packaged under an inert atmosphere in especially designed vessels (kettles) for gas equilibration studies. Whenever practical, pH measurements were made directly on the fresh sediments. Samples of interstitial gases were collected from cores recovered in the Cariaco Trench, and special interstitial water samples were collected at two sites for determination of the dissolved rare gases. Figure 1 is a flow sheet of the sediment sampling and processing procedures.

The Leg 15 special geochemical studies were carried out by a six man team. In addition to the authors, Dr. Joris Gieskes, Scripps Institution of Oceanography, and Messrs. David Bos and Richard DuBois, Deep Sea Drilling Project were participants. The equipment was loaded under the supervision of Horowitz at San Juan, P.R., and installed and tested by Waterman, Bos, and DuBois while the ship was in dry dock at Curacao and while occupying the reentry site (146). The other three members of the team boarded the ship at Curacao following completion of drilling at Site 146.

Selection of sediment samples was made by Broecker and Horowitz. The squeezing, packaging, and storage of pore fluids was carried out by Waterman, Bos, and DuBois.

Sediment samples for gas equilibration studies were packaged by Broecker and Horowitz. The pH and alkalinity measurements on the freshly squeezed pore fluids were made by Gieskes; the pH measurement on the sediments were made by Broecker and Horowitz.

Interstitial gas was encountered at Site 147. Samples were taken by Bos from all gassy cores and analyzed immediately on a gas chromatograph in accordance with the DSDP policy of monitoring methane and ethane during drilling operations. Samples were also taken from many of these cores with a new gas pocket sampler designed by Takahashi, Broecker, and Horowitz for shore-based laboratory studies. The samples of pore fluids for rare gases studies were collected by Horowitz.

SAMPLING

On Legs 1 through 6, samples of sediment for the interstitial water program were taken from core sections at the time they were split by the geologists. On Legs 7 through 14, sediment samples were taken immediately following recovery from the ends of the freshly cut 150-cm sections. Criteria for the selection of samples and detailed sampling procedures have been described by Waterman (1970). On Leg 15, geochemistry sediment samples were obtained by cutting short segments, 15 to 30 cm long, from the 150-cm sections as soon as possible after the core was received from the drill rig. The segments were closed with polypropylene end caps (Caplugs) secured with plastic electrical tape. Sediments were selected principally on the basis of appearance as seen through the plastic core liner and at the freshly cut surfaces. Segments which were not immediately processed were stored in a refrigerator at 4°C.

INTERSTITIAL WATER

A major portion of the Leg 15 geochemical program was directed to the squeezing and packaging of interstitial water samples for chemical analyses in shore laboratories. Sample preparation and low temperature squeezing were carried out in a specially outfitted core storage van located immediately forward of the superstructure, adjacent to the cargo hatch covers. Room temperature squeezing was carried out near the core photography facility and packaging of the pore waters in the thin section laboratory.

All operations attendant to the extraction of the pore fluids were performed in a specially fabricated glove box manufactured by Germfree Laboratories, Inc., Miami, Florida. The unit is equipped with an air lock on one end. Two arm holes in the front panel are fitted with iris ports made from sandwiched layers of neoprene rubber. A

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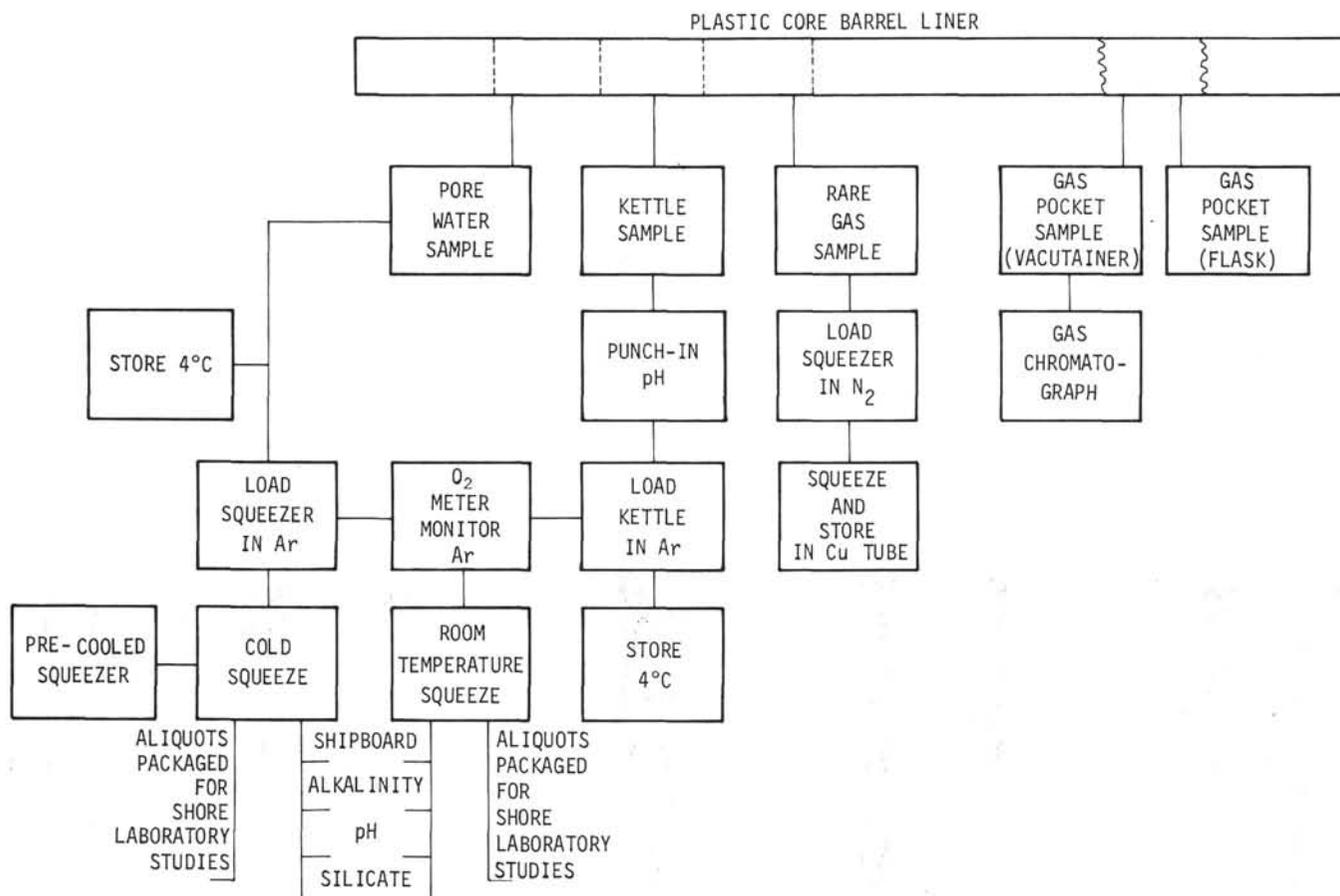


Figure 1. Flow sheet.

similarly equipped port installed in the end of the box, opposite the air lock, is used primarily to introduce the sediments. These closures were designed and fabricated aboard ship by Messrs. David Bos and Richard DuBois. All three ports are fitted with iris diaphragms made of PVC plastic which can be closed to minimize loss of flushing gas. A second glove box, a mirror image of the unit described above, was used to load the kettle samples.

All handling of the sediments was carried out in an inert gas atmosphere. The main chamber and the air lock are each fitted with a pair of stopcocks to provide an inlet and exit for the flushing gas. Argon was supplied via copper refrigeration tubing from a bank of cylinders each containing 7000 liters of compressed gas. Oxygen content of the glove box atmosphere was monitored with a YSI Model 51A Oxygen Meter equipped with a high sensitivity membrane. Although the meter detection limit is approximately 0.3% of the normal atmospheric O_2 level the quantity of argon available and the time required to flush the boxes made it impractical to work at a level below 0.5 to 2 percent, while maintaining a slight positive pressure.

Sample processing and the loading of the squeezers was carried out by a two man team. One end of the plastic core liner section is pushed through the iris port in the end of the chamber and the sediment is manually extruded with a close-fitting ramrod. When stiff clays are encountered, it is sometimes necessary to split the plastic liner longitudinally

to relieve the friction between the sediment and the tube. The sediment is received inside the chamber where it is impaled on the blade of a Teflon-coated spatula. Pieces varying from 3 to 6 cm in length are cut from the extruded core. Holding the individual pieces of sediment vertically and using a second spatula, it is usually possible to scrape off from 1 to 5 mm of the surface which had been in contact with the plastic liner. In many instances a clearly discernible layer of a light-colored slime is apparent on the surface of the extruded sediment. In those instances when it is necessary to split the liner to extrude the sediment, pieces are scraped before using. The cleaned pieces of sediment are placed in the squeezer without further handling. In some instances the sediments are quite soft and the core begins to slump the moment it is extruded. These pieces are not scraped.

As on previous legs, 9 cm (I.D.) stainless steel hydraulic squeezers were used to extract the pore waters. These squeezers are a modification of the design published by Manheim (1966). The squeezers used on Leg 15 were specially manufactured in the Woods Hole Oceanographic Institution instrument shop. They have 3-cm high base plates, a thickness sufficient to accommodate the two thermocouples used in the temperature control apparatus. The base plate and scraper-sealing disks were made from butyl rubber, a precaution against loss of possibly high H_2S concentrations in the Cariaco Trench samples.

A specially designed squeezer cooling system manufactured by Virtis Inc., Gardner, New York, was used to maintain the desired low temperatures during squeezing. The system included (a) a central refrigeration and forced circulation unit, (b) four insulated squeezer cooling jackets with separate temperature controllers, and (c) a multi-channel temperature indicator unit (Figure 2). About 5 liters of a 1:1 ethylene glycol (automobile antifreeze) and water mixture is continually circulated between the refrigerated reservoir and the coils of the cooling jackets. The cooling jackets are fashioned from 2-mm thick copper sheet. Each jacket is made from two 14-cm long half cylinders, joined with a piano hinge, which clamp snugly around the outside of the squeezer cylinder. Cooling is achieved by circulating the liquid through a network of copper refrigeration tubing silver-soldered to the outside of the half cylinders. The jackets are covered with 1.5-cm thick foam rubber insulation. The coolant is circulated between the reservoir and the jackets through silicone rubber tubing encased in Armaflex and lagged with tape.

The reservoir temperature is maintained at -10°C . One of the thermocouples inserted in the base of the squeezer is

connected to the temperature controllers. When the temperature of the squeezer is above the desired setting, coolant is allowed to circulate through the jacket coils. When the desired temperature has been achieved, the thermocouple activates a pair of solenoid valves in the controller unit shunting the cold liquid into a bypass loop. The second thermocouple insert into the squeezer base is connected to the multiple channel indicator and is used for monitoring the temperature of the units. A cutout in the bottom of one of the jacket halves provides clearance for the syringe and the two thermocouples. On Leg 15, two cooling jackets were mounted on the Carver laboratory presses, and two were used for precooling the squeezers prior to loading them with sediment.

Three portions of each sediment sample, two cold and one warm, were routinely squeezed. The squeezers were assembled and placed in the glove box through the air lock. The units to be used for the cold squeezings are pre-cooled and kept in the cooling jackets until a few minutes before use. All three squeezers are readied for use by removing the piston immediately prior to receiving the sediment. Once loaded, two filter paper circles, the Teflon scraper plate,

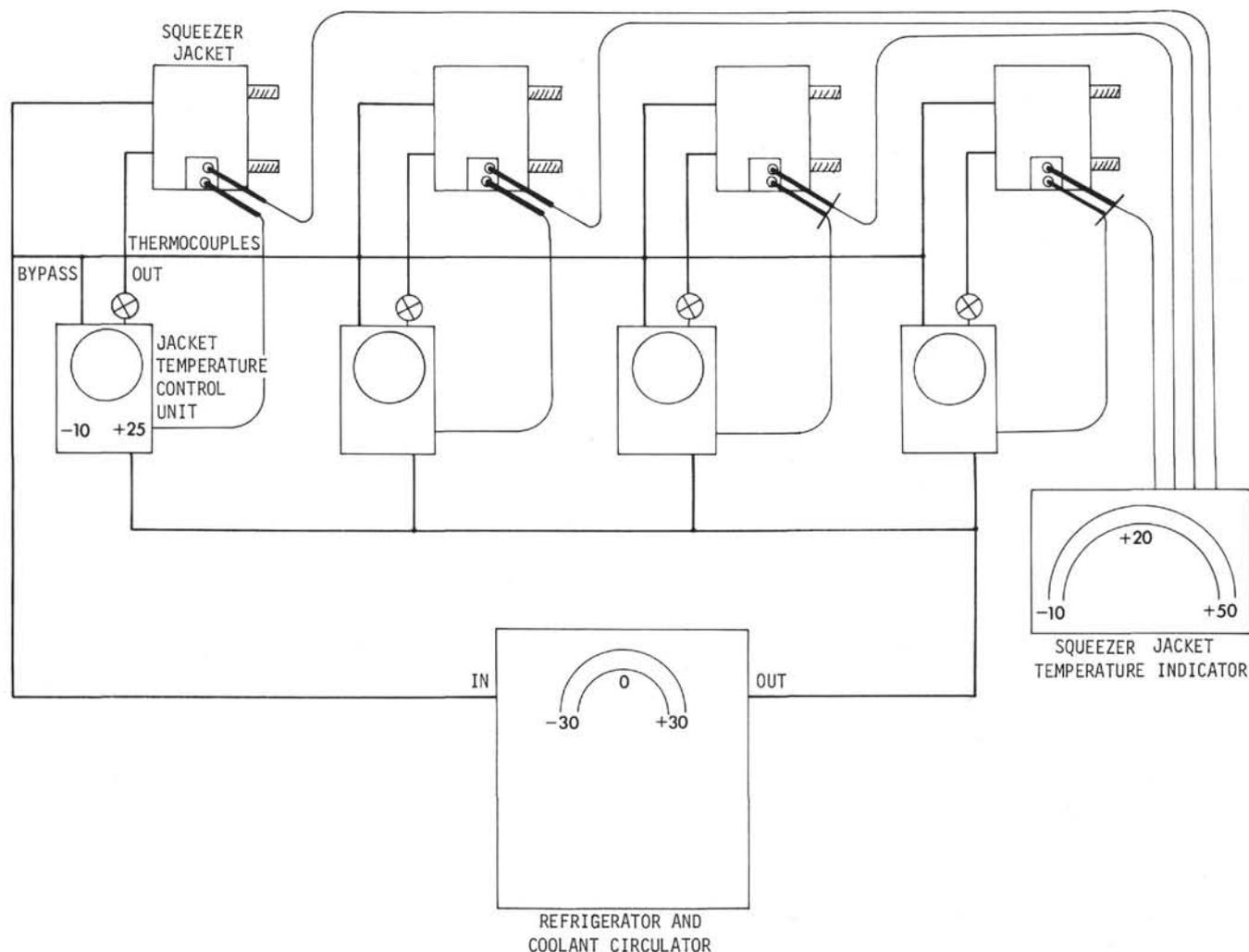


Figure 2. Squeezer cooling system.

and the scraper plate sealing disk are placed on top of the sediment. The pistons are replaced in the cylinders. The tops of the cold squeezer pistons are fitted with foam rubber insulating caps which eliminated cold metal sweating. A 35 ml disposable-type plastic syringe, flushed with the argon atmosphere of the glove box, is fitted into the effluent delivery hole in the base of each squeezer. The squeezers are placed in the air lock for removal. The time necessary to load three squeezers varied from 15 to 30 minutes, depending on the difficulty encountered in extruding the sediments.

Three manually operated, 12-ton hydraulic laboratory presses (Carver Model C) were used for squeezing. The pressing faces of the two units used for cold squeezing are covered with sheets of phenolic plastic to create a thermal barrier. The precooled squeezers are clamped into cooling jackets already installed on the presses, and pressure is gradually applied to initially compress the sediment and expell argon gas from the squeezer. As soon as a drop of pore water is observed at the effluent delivery hole or in the tip of the syringe, the pressure is relieved by momentarily opening the valve in the base of the hydraulic jack. The syringe is removed from the squeezer, the plunger pushed all the way forward to expell gas, then reinserted in the effluent delivery hole.

The initial temperature of a jacketed squeezer following installation in the Carver press varied between 7°C and 15°C. The squeezers were allowed to cool to 4°C before squeezing was started. In most instances this temperature was reached in 5 to 10 minutes; in a few cases 20 to 30 minutes were required. The temperature of the squeezer can be easily maintained to $\pm 0.4^\circ\text{C}$ (precrise laboratory tests). Room temperature squeezing was carried out in an air-conditioned room at an average temperature of 22°C. Squeezing pressures ranged from a total load of 700 kg (11.5 kg/cm²) to 9000 kg (148 kg/cm²). The most frequently used terminal pressure was 4500 kg (74 kg/cm²). Pressures used were nearly the same for both cold and warm squeezings.

Initial squeezing is done at low pressures, i.e. 500 kg total load, with increases not exceeding 500 kg at one time. Low pressures are preferred for clays. Pore water recovery from clayey sediment samples of the size used on Leg 15 is principally dependent on how long one is willing to spend gradually applying pressure. The amount of pore water recovered from each portion of sediment varied from 8 ml to more than 50 ml. Most squeezings, both warm and cold, produced 15 to 25 ml of interstitial fluid. Squeezing times varied from less than one minute for calcareous oozes to more than one hour for stiff clays.

The pH of all three interstitial waters is measured immediately upon termination of the squeezing using a flow-through electrode manufactured by Orion. About 0.2 ml of unfiltered fluid is required for each measurement. The remaining water is Millipore-filtered using a Swinnex-25 filter unit. The two cold squeezes are combined by filtering into the same receiver syringe. The largest single aliquot (10 ml) of pore fluid is routinely taken for a shipboard alkalinity measurement. Alkalinity samples were taken from all of the combined cold squeezes and the majority of the warm squeezes. Analytical results and

interpretations of the pH and alkalinity data are reported by Gieskes elsewhere in this volume. One ml aliquots were sealed in disposable plastic syringes for shipboard silicate analyses. Silicate samples were taken from cold squeezes only at Site 147 and from both cold and warm squeezes at Sites 148 and 149.

The remainder of the pore waters was subdivided and packaged for several shore-based programs. These programs include: major and trace element analysis at W.H.O.I. (Sayles et al.); major and trace element analysis at Texas A&M University (Presley); CO₂ studies at Queens College (Takahashi); hydrogen isotope studies at U.S.G.S., Denver, Colorado (Friedman); H & O isotopic studies at L.D.G.O. (Lawrence); and oxygen isotope studies on SO₄²⁻ at Shell Oil, Houston, Texas (Lloyd). The pore water samples used for major and trace element analysis were packaged in polyethylene tubing and disposable syringes. Pore water samples for CO₂ studies were equilibrated with reference gas in specially fabricated glass containers, then spiked with saturated HgCl₂ solution to prevent biological alteration during storage. Isotopic samples for Friedman (2 ml and 5 ml) were heat-sealed in glass ampoules. Isotopic samples for Lawrence (0.1 ml) were collected by momentarily dipping the ends of capillary tubes in the poly-tubing containing the W.H.O.I. samples and heat-sealing with a micro-torch. Pore water samples for Lloyd (2-8 ml) were treated with saturated HgCl₂ solution and heat-sealed in short sections of poly-tubing. Additional information on containers and packaging can be found in the Interstitial Water Program Shipboard Manual (Waterman, 1970) and in the separate reports of individual investigators elsewhere in this volume.

KETTLE SAMPLES

Samples of sediment collected at all three geochemical sites from 15-cm sections of core liner were transferred to sealed glass containers for special outgassing studies. Samples were held at 4°C in a refrigerator and transferred in batches. All handling of the sediment was carried out inside a glove box in an argon atmosphere.

The kettles were designed by RMH and fabricated by Q-Glass Company, Bloomfield, New Jersey (Figure 3). Each unit was made from two flanged pieces of 75-mm Pyrex sewer pipe manufactured by Corning Glass Works. The body of the vessel is made from one of the pipe sections and sealed off to have a volume of about 500 ml, while the other section is fashioned into a domed top. The flange of the bottom section is grooved and fitted with a butyl O-ring coated with Apiezon H grease. A gas-tight seal is achieved by holding the two pieces together with a Corning sewer pipe clamp. The kettle top is fitted with two Ace stopcocks with easy-action Teflon plugs (0-10 mm). Butyl rubber O-rings are used on the plugs. The stopcocks are designed to use Swagelok tubing fittings to connect to a vacuum line. The kettles were autoclaved before being sent to the ship.

Sediments are extruded from the segments of core liner by the same procedure as described above for interstitial water. The extruded sediment is received directly into the kettle after first discarding about 1 cm of the portion in contact with the end cap. The flange, which must be kept clean to seal properly, is protected during transfer of the sediment by strips of aluminum foil folded over to touch

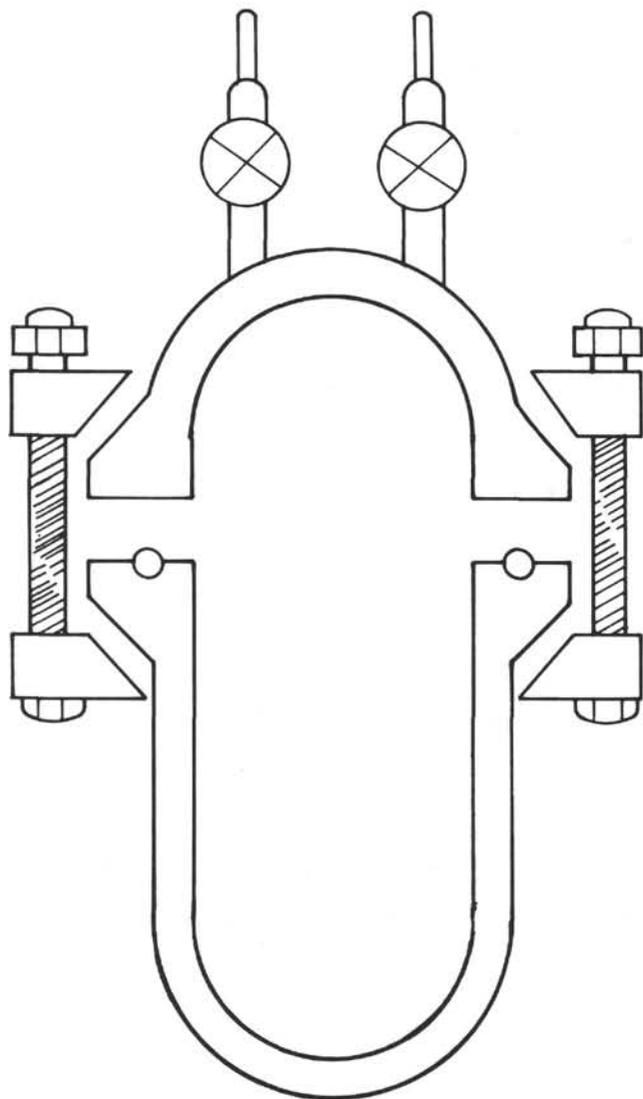


Figure 3. Kettle for sediment samples.

both the inside and outside walls of the container. As soon as the sediment transfer is completed, the top of the container is clamped in place and the kettle connected directly to the argon gas supply and flushed for 10 minutes. The stopcocks are then closed and the kettle removed from the chamber via the air lock. The kettle samples are stored in a core van at 4°C.

pH MEASUREMENTS

Measurements of the pH of freshly squeezed pore fluids have been made routinely since Leg 4 using a combination glass-calomel electrode (Sayles, 1970). About 1 ml of pore water is needed for this procedure. As noted in the section on Interstitial Water, the Leg 15 measurements were made with a miniature flow-through electrode using 0.2 ml of water. The injection of the pore water directly from the syringe in which it is initially collected into the flow-through electrode minimizes atmospheric contamination. Whenever possible, punch-in pH measurements were also made on the fresh sediment. The use of the punch-in

electrodes is limited by the consistency of the sediment since the probes must be used to make their own holes. Sediments were soft enough to permit punch-in measurements on samples taken from the surface to 100 meters at Site 147, to 160 meters at Site 148, and to 150 meters at Site 149.

The punch-in pH measurements were made with an Orion Model 801 digital pH/mv meter using a Beckman #40471 glass electrode paired with an Orion 90-92 double junction reference electrode. Most of the measurements were made in one end of the core segment collected for the kettle samples. The core liner is vertically oriented, and end cap removed, and the two electrodes pushed into the sediment to a depth of 2 to 3 cm. A thermometer is also inserted into the sediment to the same depth. The sample is set in an ice bath. The pH as a function of temperature is recorded, first while the core is cooling and later, out of the ice bath, while warming to room temperature. Data were obtained over a range of 11 to 29°C. At the completion of the run, the electrodes are rinsed with distilled water wiped with laboratory tissue and their performance checked with a pH 6.86 buffer. When not in use the electrodes are stored in this buffer solution. We are indebted to Dr. Robert Berner who advised on the technique and choice of electrodes and made preliminary tests.

INTERSTITIAL GASES

Attempts have been made on several legs to tap the gas pockets which sometimes form in the plastic core liners. Gas samples were collected in rubber-stoppered, evacuated test tubes (vacutainers). Many attempts were thwarted by having the tapping needle clog with sediment or fluid. Also, the CO₂ content of these samples must be considered suspect since it can be demonstrated that new vacutainers contain measurable amounts of CO₂. On Leg 15, interstitial gas samples were collected at Site 147 in vacutainers for immediate chromatographic analysis and in evacuated 125-cc glass sample flasks using a new sampler specifically designed for this leg.

The interstitial gas sampler was designed by one of us (RMH) and fabricated in the Lamont-Doherty Geological Observatory shop (Figure 4). The principal components of the sampler are (1) a two-part machined aluminum block with a cylindrical cavity to hold the core liner, (2) a side-access (catheter type) tapping needle, (3) a sample flask manifold with GE thermistor vacuum gage, and (4) a mechanical vacuum pump. The 125-cc sample flasks were manufactured by Q-Glass Company.

The sampler is operated by clamping the block around the core liner and over a gas pocket. Then the tapping needle assembly is installed in a bore hole in the top section of the block. In the "cocked" position, the needle and sample manifold can be evacuated quickly. The system is pumped down to a pressure of 1 Torr and isolated from the vacuum pump. The gas pocket is tapped manually by forcing the needle assembly downward to puncture the core liner. Neoprene rubber gaskets in the sample block cavity and O-rings in the needle assembly provide a seal. The evacuated flasks are opened one at a time and the interstitial gas admitted to a pressure of 0.8 atm. Up to three such samples can be collected successively from one

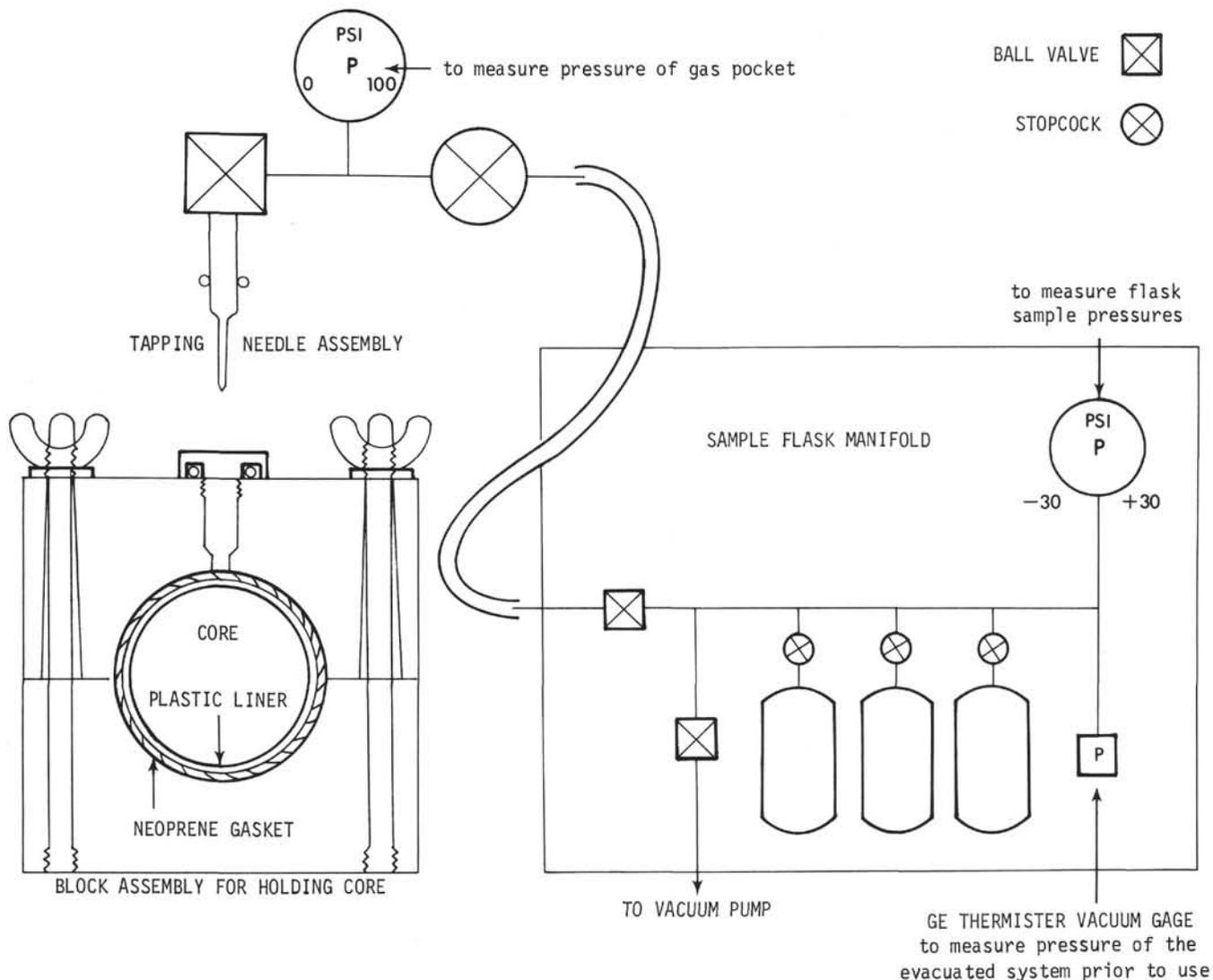


Figure 4. Gas pocket sampler.

gas pocket. The gas pocket pressures encountered on Leg 15 averaged 1.5 atm. and never exceeded 2 atm. Higher pressures are presumably dissipated by opening the gas pockets and by leakage to the ends of the core liner.

RARE GAS SAMPLES

At Sites 148, 149, and 150 special interstitial water samples were squeezed and packaged for the determination of dissolved rare gases (Clarke). The squeezed water was collected and stored in 30-cm sections of 6-mm soft annealed copper refrigeration tubing (Weiss, 1968). The hydraulic squeezer routinely used for obtaining special trace element pore water samples was employed for this subprogram. Loading of the squeezer was carried out in a plastic glove box continuously flushed with nitrogen gas, as these samples were to be analyzed for argon content.

The plastic glove box with its air lock is flushed with nitrogen gas for a minimum of 30 min at a flow rate of 10 l/min before each use. A 15-cm segment of core is taken into the glove box, extruded, and loaded into the squeezer.

The Teflon scraper plate is fitted into the top of the cylinder which is then placed on the hydraulic press and aligned to receive the piston. The Teflon fluid receiver tube is screwed into the base plate and connected to the sample receiving assembly. The squeezer is joined to the sample tube assembly which is flushed with nitrogen. The flushing gas is then cut off and the squeezing started. Pore water displaces the nitrogen gas in the copper sample tube and the overflow collects in a plastic syringe at the top of the assembly. Squeezing is terminated when an amount of water approximately equal to the volume of the sample tube has been collected in the syringe. The pore water is initially sealed in the sample tube with Tygon tubing and Mohr pinch clamps. Permanent crimp seals are then made about 1 cm from each end of the copper tube. The Mohr clamps are removed and the excess pore water discarded from the end sections. The ends of the sample tubes are then filled with distilled water and the hoses again clamped. When duplicate samples are to be collected, two copper tubes are connected in series (one above the other) and filled at the same time. Samples are stored at 4°C.

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