

APPLICATION OF RHIZON SAMPLERS TO OBTAIN HIGH-RESOLUTION PORE FLUID RECORDS DURING GEOCHEMICAL INVESTIGATIONS OF GAS HYDRATE SYSTEMS

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Obtaining accurate, high-resolution profiles of pore fluid constituents is critical for characterizing the subsurface geochemistry of hydrate-bearing sediments. Tightly-constrained downcore profiles provide clues about fluid sources, fluid flow, and the milieu of chemical and diagenetic reactions, all of which are used to interpret where and why gas and gas hydrate occur in the natural environment. Because a profile's quality is only as good as the samples from which the data are obtained, a great deal of effort has been exerted to develop extraction systems suited to various sedimentary regimes. Pore water from deeply buried sediment recovered by scientific drilling is typically squeezed with a hydraulic press (Manheim, 1966); whereas pore water in near-surface, less consolidated sediment is more efficiently pushed from the sediment using compressed gas (Reeburgh, 1967) or centrifugation.

Rhizon samplers, simple devices developed by the soil science community, have recently been adapted to sampling pore fluids in marine sediments (Seeberg-Elverfeldt, *et al.*, 2005), including cores recovered on Integrated Ocean Drilling Program (IODP) Expedition 302 (Dickens, *et al.*, 2007). A Rhizon sampler consists of a microporous tube (0.1 μm nominal pore size) connected to a standard syringe via PVC tubing and a luer-lock fitting. Retracting and securing the syringe plunger with a spacer after inserting the microporous tube into the sediment creates a vacuum that pulls pore fluids into the syringe body (Figure 1).

The time required to collect fluid using the Rhizon is similar (~ 1-2 hr) if not longer than that required by other methods, and the total volume of fluid recovered (<10 ml) by Rhizon sampling is less than that obtained by traditional squeezing methods (<35 ml). The Rhizon sampling technique, however, offers several advantages: 1) the geometry of the Rhizon samplers makes it possible to obtain samples at higher spatial resolution along a sediment core; 2) minimal exposure to air means pore waters are subjected to less chemical alteration during the collection process; 3) Rhizon sampling is non-destructive, meaning the sediment record is maintained; and 4) in contrast to sediment compaction during the squeezing process, pulling fluid from the sediment matrix by vacuum extraction is less likely to alter the chemical composition of some analytes. In spite of these striking advantages, Rhizon samplers are

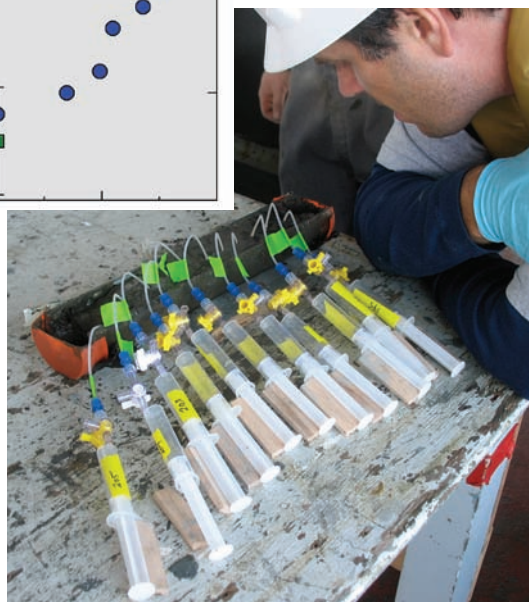
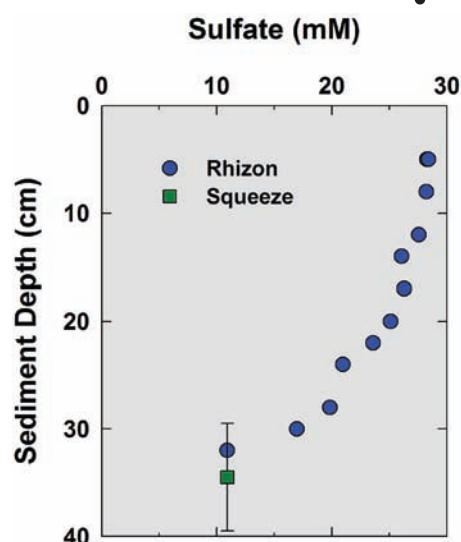


Figure 1: High-resolution Rhizon sampling of a core section collected at Barkley Canyon. The close spacing of the Rhizon samplers was required to obtain the high-resolution sulfate profile for this core section (inset). For comparison, a 10-cm section (indicated by vertical bar) from the base of the core was processed by the traditional compressed gas squeezing method after the Rhizon samplers were removed (inset, green square with vertical bar denoting sample length). Similar results were obtained by each method. Without the high-resolution sampling; however, the obvious curvature in the sulfate profile would be obscured, and subsequent interpretation of its implications would be limited.

- only beginning to gain widespread acceptance for pore water sampling in gas hydrate-bearing and other deep water marine sediment systems.
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- During Cruise 2008-007-PGC along the northern Cascadia Margin (see “Investigating Gas Hydrate as a Factor In Accretionary Margin Frontal Ridge Slope Failures and Cold Seep Biogeochemistry,” this issue.), we utilized Rhizon samplers as a component of our pore water sampling program, which also included traditional squeezing of whole round core sections using compressed gas. Based on results from the analysis of sulfate and chloride concentrations, we demonstrated that Rhizon samplers provide a level of resolution not possible by sediment squeezing (Figure 1), and that analytical results from samples acquired by both methods are comparable (Figure 2). Furthermore, the non-destructive aspect of the Rhizon sampling allowed us to develop a sampling program that was integrated with the studies of our fellow sedimentologists, geophysicists, and microbiologists. At sites where small volumes of pore water were sufficient to address the research questions at hand (<8 ml), we used Rhizon samplers exclusively. In other instances, particularly at seep sites where large pore water volumes exceeding 25 ml were required to satisfy the sample requests, we utilized both Rhizon sampling and squeezing techniques. Additional comparative studies from other inorganic and organic pore water constituents will allow us to more rigorously evaluate the advantages and pitfalls of each technique.

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Given the exceptional performance, simplicity, and portability of the Rhizon samplers, we consider them an essential component in the toolbox of any gas hydrate geochemist investigating pore water profiles in shallow subseafloor sediment.

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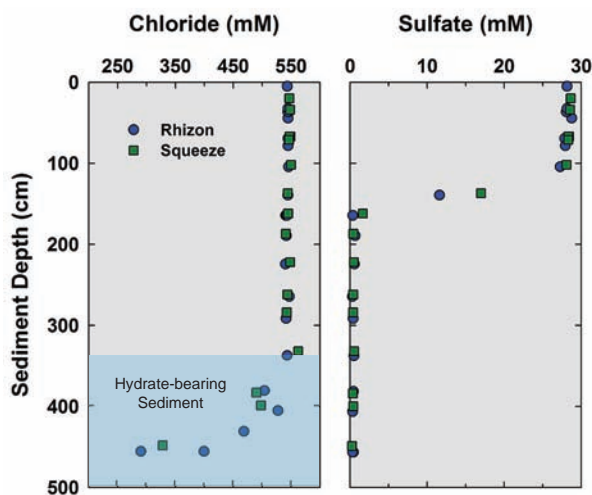


Figure 2: (A) Implementation of Rhizon samplers within the cruise 2008-007-PGC core processing factory. Team members (clockwise from left): Bill Waite (USGS), Kelly Rose (USDOE), John Pohlman (USGS), Greg Middleton (NRCAN), Michael Riedel (McGill), Laura Lapham (FSU) (B) Comparative chloride (left panel) and sulfate (right panel) profiles from fluids sampled by Rhizon samplers (Blue circles) and traditional compressed gas squeezing (green rectangles) at the Bullseye vent cold seep. Concentrations measured from each sample type are largely indistinguishable. Low chloride values below ~330 cm indicate dissociation of the massive gas hydrate present in the bottom of the core. The slightly lower Rhizon chloride values in the hydrate-bearing section likely reflect incomplete dissociation of gas hydrate during the Rhizon sample extraction timeframe.