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LEGACY OF HYDRATE RIDGE: AN ILLUSTRATED ACCOUNT

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ABSTRACT

Hydrate Ridge has the distinction of hosting the first documented subduction-driven cold seep system that supports chemosynthetic life by Anaerobic Oxidation of Methane as well as the most widely researched methane hydrate setting at any active continental margin. Today this site is a vital node of Northeast Pacific regional long-term studies that constitute the most advanced cabled ocean network, the NSF's Ocean Observatory Initiative. The illustrated time-line available as a poster at the 8th International Conference of Gas Hydrate in Beijing documents highlights of field studies, persons involved, themes addressed and key results published from the beginning to the present. It chronicles submersible and ROV-deployments, deep drilling operations and surface ship expeditions and reviews selected results that for the first time addressed fundamental objectives of convergent margin dewatering and gas hydrate research that still persist today.

Keywords: active margin seeps, gas hydrates

INTRODUCTION

Research on Hydrate Ridge at the Cascadia convergent margin has advanced our understanding of fundamentals on cold seepage and gas hydrate formation and behavior as no other effort at comparable study sites. Documenting that legacy is the subject of this review. It is based on illustrating a time-line -- available as a poster at the 8th International Conference of Gas Hydrate in Beijing-- that spans 30 years of diverse research and compiles all available publications. Unlike conventional lists of references, the publications are grouped according to research topics that were conducted over the years. In briefly summarizing the results, the account follows this grouping of the studies conducted, scientific themes pursued, persons involved and key results published from surface ship expeditions, submersible- and ROV-deployments, deep-sea drilling operations and automated continuous recordings of methane hydrate behavior and seepage events.

BACKGROUND

Initially one of a series of accretionary thrust ridges along the Cascadia margin, Hydrate Ridge has the distinction of hosting the first documented subduction-driven methane and cold seep fluid system (Kulm et al. 1986) that supports chemosynthetic life (Suess et al. 1985) by Anaerobic Oxidation of Methane (Boetius et al 2001). Subsequently this site became the most widely researched methane hydrate setting at any active margin (Suess et al. 1999) resulting in advances of fundamental knowledge on natural gas hydrate systems. The name Hydrate Ridge was first used in 1999 after approval by the Advisory Committee on Undersea Features of the U.S. Department of Interior acting on a proposal filed by G. Bohrmann. Research on Hydrate Ridge continued unabated and today has become a vital component of Northeast Pacific long-term studies that constitute the most advanced cabled network, the NSF's Ocean Observatory Initiative (OOI Science Prospectus, 2007).

The discovery of subduction-related seepage on Hydrate Ridge was publicized in the National Geographic Magazine (Gore and Sugar, 1985) in a

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feature on the restless planet Earth. The authors happened on their tour to the Northwest Pacific to talk to scientists at Oregon State University, the University of Washington and the University of California at Santa Cruz who had just observed first hand from the submersible ALVIN what became known as cold seep activity at Hydrate Ridge. Scientific details of this discovery were reported by Suess et al (1985) and Kulm et al (1986). Identical discoveries were then reported from segments of the subduction zone off Japan observed from the submersible NAUTILE (LePichon 1986). With both accounts the global role of fluids, methane, and thereafter of gas hydrate as characteristic components of subduction zone dewatering was recognized.

Convergent margin dewatering

Selecting the sites for submersible deployments and video-guided sampling at seeps and hydrate sites was based on geophysical and bathymetric surveys to understand the convergent tectonic setting of the Cascadia margin. Side-scan sonar, high-resolution mapping, and 3D seismic reflection data were used. The development of fore-arc basins, the distribution of the Bottom Simulating Reflectors (BSRs), the land- and seaward convergence of thrust packages were recognized as well as the intersecting faults identified as possible dewatering pathways. Advanced high-resolution mapping and video-coverage continue today in order to safely place instruments, establish nodes, and run cables in preparation for the Ocean Observatory Initiative.

Cold seepage

The outstanding advance in knowledge --of course-- was the recognition that methane and emanating fluid were the characteristic components of subduction-zone dewatering and that it's seafloor manifestation were cold seeps. Isotopically light carbon (negative $\delta^{13}C$) arising from the Anaerobic Oxidation of biogenic Methane (AOM) was found in seep biota, carbonate crusts, dissolved inorganic carbon (DIC) in pore fluids, and gas plumes in the water column. Tracking $\delta^{13}C$ became the most readily established criteria for cold seepage.

Hydrogeology and fluid flow

Subsequent research at the summit of Hydrate Ridge addressed the subsurface hydrology. Imaging pathways of fluid flow and establishing structural constraints on near-surface seeps and methane hydrate distribution were the objectives. Fluid sources in relation to the seep biota were extensively reported on and initial attempts made to quantify fluid fluxes. "The Mosquito" an *in situ* device capable of metering a wide range of flow rates currently serves the Ocean Observatory Initiative with inferences from 4D seismic surveys in understanding the mechanics of intermittent fluid venting.

Hydrate formation and distribution

Spreading the results of Hydrate Ridge among the scientific community lead to two deep-sea drilling campaigns targeting gas hydrates: ODP Legs 146 and 204. A memoir published by the American Geological Society played a major role in disseminating background knowledge and formulating drilling objectives. During these campaigns the characteristic chloride anomalies in pore fluids from post-drilling release of hydrate water was used to estimate hydrate saturation. With results from other drill sites, this approach lead global estimates of hydrate inventories by up-scaling. Infrared logging of drill cores was introduced to recognize layers of hydrate. This approach took advantage of endothermic hydrate destabilization by visualizing "cold spots".

Hydrates: Energy-climate-geohazards

Combining Cl-anomalies from pore fluids in host sediments and autoclave-core tomography with seismic wave analyses provided a detailed understanding of hydrate saturation. It allowed estimating the reservoir size present under Hydrate Ridge. This resulted in a wave of public attention on methane hydrate as potential energy resource, climate-driver and trigger of geohazards. It was again a popular science publication, the Scientific American and its international issues that provided a major impact by publicizing these issues. It re-captured the attention of science colleagues, administrators, politicians and media as these still are hotly debated societal issues. The environmental impact of gas hydrates including their energy potential had been formulated years earlier by Kvenvolden in 1988 but remained largely dormant.

Hydrate-carbonate-biota association

The hydrate-carbonate-biota association generated the most publications as the most visible manifestation of seepage. Seep biota consuming methane and incorporating methane-carbon via Anaerobic Oxidation of Methane (AOM) prevent methane from entering the oceanic water column. This function –-the benthic filter-- was first recognized at Hydrate Ridge. Different rates of methane emissions determine the community structure of seep organisms. High rates favor mats of microbes at the sediment surface, intermediate rates favor partially buried bivalve assemblages and slow rates favor burrowing and deep-dwelling organisms. Another relationship of the association has intrigued researchers beyond the straightforward tracking of isotopically light carbon (negative $\delta^{13}C$): incorporation of ^{18}O during seep carbonate formation that possibly originates from $\delta^{18}O$-enriched hydrate water. There are however, other more likely sources for heavy water to be incorporated, nevertheless the intimate association between hydrate dissociation and carbonate formation was shown beyond doubt by the matching fabric of hydrate and aragonite phases.

Microbes and biomarkers

Enormous scientific interest was sparked by the discovery of the microbial consortia at Hydrate Ridge that were able to couple sulfate-reduction with methane-oxidation (AOM). The consortia produce characteristic lipids and other diagnostic organic molecules. These biomarkers identify AOM-related processes in sediments, biota and carbonate crusts. A miniaturized sampling scheme first used on authigenic carbonate from Hydrate Ridge found highest concentration of AOM-biomakers in confined areas that resembled biofilms. Indeed *in vivo* biofilms of AOM-consortia were independently identified in young Hydrate Ridge samples.

Knowledge of seep community structure, AOM-related reactions and biomarkers are now used world wide in research of ancient and recent cold seep systems. The library of biomarkers grows steadily and environmental criteria (oxygen and temperature) are beginning to be correlated to biomarkers of different AOM-consortia.

Geochemical characterizing

Several outstanding results on of hydrate and hydrate-associated samples originated first from Hydrate Ridge studies. U/Th-dating of seep carbonates established that periods of increased seepage events coincide with low sea level stands. This suggested that hydrostatic pressure changes with time modulate seep flow. Ages of pore waters determined via the ^{129}I-isotope system from hydrated cores that were extremely enriched in the biophilic element iodine are thought to identify deep and ancient sources for the supply of methane to the hydrate reservoir. The noble gas content of hydrates was first determined on Hydrate Ridge samples. The source of Rare Earth Elements (REEs) in AOM-carbonates was shown to come from mobilization during organic matter decomposition rather than from deeply sourced fluids. Gypsum crystals in hydrate-associated sediments that were initially suspected to be an artifact were later established to result from oxidation of AOM-related sulfides by oxidation fronts that penetrate downward during periods of slow seep activity.

Hydrate structure and fabric

The *in situ* Raman spectroscopy allowed undisturbed hydrates to be analyzed at an outcrop on the Hydrate Ridge. Structure-I characteristics were confirmed and identical cage occupancy as shown for synthetic methane hydrates. Hydrogen sulfide was found to be a trace constituent of the hydrate structure and occluded free methane in macro-pores. The coexistence of free methane with hydrate had earlier been inferred from analogous bubble-fabric seen in hydrate samples and associated carbonates but dismissed as an artifact caused by removing hydrate samples from the gas hydrate stability zone (GHSZ). Since then autoclave-core tomography that visualizes fabric and quantifies free gas content has removed any doubts about bubble fabric in near-surface hydrates and the consequences on hydrate physical properties. The mean size of naturally occurring hydrate crystals were determined by high-energy synchrotron radiation. Crystal size increased with age and differed by an order of magnitude from those produced in the laboratory.

Methane plumes and bubbles

Evidence of methane from seeps had initially been identified in the water column above Hydrate Ridge. In the following years extensive efforts were devoted to mapping and imaging the plumes as well as understanding methane bubble behavior in the water and sediment columns. Acoustic imaging of plumes shows the vertical structure of methane plumes above the seafloor to be limited by the depth of the GHSZ. Resent surveys show intermittent plumes (4D imaging) over Hydrate Ridge. This phenomenon is explained by configuration of subsurface pathways and overpressures generated at the base of the GHSZ.

Video-imaged dissolution experiments on methane hydrate chunks ascending through the water column show an increase in dissolution rate above the depth of the GHSZ. This suggested that "armored bubbles" forming instantaneously at the gas-water interface when bubble streams emanate from the seafloor.

Armored bubbles had been observed from submersible dives at Hydrate Ridge but dismissed as improbable. They were later confirmed by high-resolution video-imaging of an active venting site Einstein's Grotto for the Ocean Observatory Initiative (Interactive Oceans; Expedition VISION'11). This is deemed to be an ideal site to instrument for the characterization active methane seepage by the Ocean Observatory Initiative. It will be instrumented with a digital still camera, mass spectrometer, fluid sampler, seismometers, an OSMO sampler, and current meter.

New methods and technologies

The readily accessible location on Hydrate Ridge has continuously attract expeditions pursuing many different objectives which --more often than not-- attempted and succeeded in deployment of new technologies. These developments and results have been referenced with the respective field of studies as used throughout this account. The latest new approach concerns the persistent question of the coexistence of methane, hydrate and water within the GHSZ. This causes acoustic turbidity zones in the sediment column depending on seismic frequencies used. Several explanations have been advanced to explain this phenomenon. Among these excess salt in pore fluids or lack of water in the sediment pore space could prevent bubbles from converting to hydrate. Deploying new Undersea Electromagnetic Source Instrumentation (DUESI) over Hydrate Ridge show evidence for both models: a subsurface increase of electrical conductivity that would favor the salt inhibition model as well as a decrease that would favor the water-starved model.

Popular science

The legacy of Hydrate Ridge would be incomplete if not recounting the enormous popular attention and interest in gas hydrate issues that was generated by the science fiction novel *Der Schwarm*. It was published 2004 in German and subsequently translated in over 30 languages. It explored the whole spectrum of scientific, environmental, political and human issues – drawing on real science and largely unreal fantasies-- but with an uncanny understanding of the importance of the hydrate topic. An understanding that scientist too close to the topic sometimes miss. Quoting the author Frank Schätzing from the English language edition captures the issue very well: *"It was no secret that deep-sea hydrothermal vents were occupied by numerous exotic species, but when geochemist Erwin Suess arrived at the GEOMAR Centre from Oregon State University in 1989, he told of stranger things - cold seeps surrounded by oases of life, mysterious sources of chemical energy rising from inside the Earth, and vast deposits of a substance that until then had been dismissed as an intriguing but insignificant by-product of natural processes: methane hydrate.*

It was time for the geosciences to break out of the seclusion in which they, like most other scientific disciplines, had worked. Now they tried to make themselves heard. They hoped to develop methods for predicting and averting natural disasters and long-term changes to the environment and climate. Methane seemed the answer to the energy problem of the future. The media sensed a story, and the geoscientists learned gradually how to make use of the new-found interest in their work."

Epilogue

The scientific legacy of Hydrate Ridge was generated from proposal-driven fundamental research by largely academic institutions. The results were to no small degree disseminated by popularizing gas hydrate issues. This sparked new insights and contributed to an evolving view from pursuing methane hydrates as energy reserves (Boswell and Collett 2010; Makogon 2010) to documenting natural hydrate destabilization in the wake of global climate change (Kvenvolden 1988; Phrampus et al 2012; Shakova et al 2010). The latter view now includes the threat of methane release from permafrost and hydrates, a widely debated environmental issue known as "*Arctic Armageddon*" (Carana 2011a,b;). Less sensational but equally profound scientific spin-offs that may be traced back to results from Hydrate Ridge are for example research on the deep biosphere (Jørgensen and Boetius 2007) or on carbon capture and storage (House et al 2006; Haeckel and Suess 2011).

ACKNOWLEDGMENT

This text to accompany the illustrated presentation of a time-line of research that I participated in and observed over many years is not a review in the traditional sense. Rather it traces the impact of knowledge gathered from one well-defined site and its dissemination to a field of Earth system science that may best defined as: geosphere-hydrosphere-biosphere transfer. It focuses on the way *science is done* and the evolution of successively more advanced objectives as results kept flowing in. Above all it focuses on seagoing operation on Hydrate Ridge and the persons behind it. Hence many thanks to numerous former and current colleagues at GEOMAR (Kiel) and CEOAS (Corvallis) who shared the enthusiasm and efforts in this research adventure. This was not a planned long-term adventure it just took off. Special thanks go to Gerhard Bohrmann (MARUM, Bremen) and Marta E. Torres (CEOAS, Corvallis) for their continuous support and carrying on the adventure. I am particularly indebted to Charles K. Paull (MBARI, Monterey Bay), John R. Delaney and Deborah S. Kelley (UW, Seattle) and Karen A. Weitemeyer (SIO, La Jolla) for generously providing images and inspiration to update the illustrated account that is available separately.

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