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STUDY TITLE: The Fate and Effects of Barium and Radium-Rich Fluid Emissions from Hydrocarbon Seeps on the Benthic Habitats of the Gulf of Mexico Offshore Louisiana

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KEY WORDS: Central Gulf; Louisiana; deepwater; hydrocarbon seeps; fluid emissions; barium; radium; radioactivity; radiation; barites; chimneys; crusts; chemical fingerprints; age dating; radioisotopes; fluxes; benthic chemosynthetic fauna; methanotrophic mussels.

BACKROUND: In addition to hydrocarbons, some of the seeps occurring at upper bathyal depths (510 to 657 m) in Garden Banks-382 (27^{o} 37.77' N; 92^{o} 28.08' W), Garden Banks-338 (27^{o}37.79'N; 92^{o}28.12'W) and Mississippi Canyon-929 (28^{o} 01.46'N; 89^{o} 43.63'W) are also issuing copious amounts of barium and radium-rich fluids. Upon their exit on the seafloor, these fluids are likely to act as the primary source for the extensive radium-rich barite deposits of varied morphological shapes documented on the seafloor. The impact of the excess barium and radium on the benthic habitats is unknown. The deepwater habitats along the slope are relatively pristine. However, as the oil and gas industry is moving its exploration and production main activities to deepwaters, their present pristine status is likely to change. It is therefore of importance to explore the natural processes occurring in deepwaters ahead of the anticipated anthropogenic complications.

OBJECTIVES: The primary objectives of this study were to document products and processes related to naturally occurring barium and radium-rich fluid emissions from hydrocarbon seeps, and assess their impact on the offshore habitats in deepwater Gulf of Mexico.

DESCRIPTION: The barite-bearing seeps have been documented and sampled during submersible dives. The sites are characterized by intense gaseous hydrocarbon and fluid mud venting occurring from numerous cone-shaped mud volcanoes. Subsurface seismic data indicate that shallow salt diapirs are present under the sites and seepage occurs through normal faults associated with the diapirs. Dense communities of methanotrophic mussels (Bathymodiolus sp.), neritid gastropods and galatheid crabs inhabit the flanks of these mud volcanoes.

Specific determinations of barium, radium and selected chemical elements and their isotopes in pore fluids have allowed us to fingerprint the fluid emissions.Measurements of barium, radium and selected chemical elements and their isotopes in solid barites and determinations of radium and barium in both soft tissues and hard skeletons from methanotrophic mussels and heterotrophic fauna provided data relevant to mobility of the elements in the benthic habitats. Radium and barium in growth increments from the barite chimneys were used as an archived history and record of episodic venting whose chronology was derived from the radium-decay series isotopes. External gamma ray and internal alpha radiation (derived by ingestion of radioactive barite) exposure and dose to epifauna inhabiting the barite seeps, consisting of vagrant heterotrophs (crabs and starfishes) and sessile methanotrophic mussels, was estimated from measured radium-decay series specific concentrations.

SIGNIFICANT CONCLUSIONS: Barite ($BaSO_4$) deposits consist of chimneys, crusts blanketing mud volcanoes, and unconsolidated sands infilling gulleys. The chimneys are dominated by the mineral celesto-barite (i.e., Sr-rich barite), whereas the crusts consist of both barite and calcite. The Gulf of Mexico barites are anomalously enriched in Sr, Ca and Ra by comparison with barites from normal marine settings elsewhere. Fluid fluxes from point sources in the Garden Banks and Mississippi Canyon, estimated on the basis of material mass balance, are 250 L/yr and 2920 L/yr, respectively. Assuming that the Ba-Ra-rich seeps cover about 0.1% of the Louisiana upper slope, the annual fluxes of Ba and Ra are estimated to be of the same order of magnitude as their annual discharges from the Mississippi River. The largest possible radiation dose to fauna from Ra-rich barites (0.0128 mGy/day) is substantially lower than the threshold of detrimental radiation effects for aquatic animals. However, the cumulative radiation dose and consequential genetic effects over a mean lifespan of 25 years for mussels could be substantial.

STUDY RESULTS: Formation-water-derived fluids emerging on the seafloor are anomalously enriched in Ra and Ba relative to seawater by factors of up to 4.5×10^4 and 15×10^4, respectively. Their migration time from the source to the seafloor is established to be < 20 years on the basis of the relatively short-lived ^{228}Ra isotope content. Sulfur, oxygen and strontium isotope compositions indicate that the Gulf of Mexico seep barite deposits form by the mixing of sulfate-rich seawater with Ba-, Sr-, and Ca-rich formation fluids seeping with gaseous hydrocarbons, primarily thermogenic methane. The chimneys are erected vertically above the seafloor whereas the crusts drape mud volcanoes and/or form pavements at the sediment/water interface. Both ^{226}Ra and ^{228}Ra are "orphans" in the sense that their respective parents ^{238}U and ^{232}Th are practically absent in the fluids and barites. The "orphan" property of Ra affords radiometric dating of the barites by $^{210}Pb/^{226}Ra$ and $^{228}Th/^{228}Ra$ daughter/parent isotope pairs. The assays indicate that chimney ages range from 0.5 to 6.5 years whereas the crust ages range from 9.0 to 23.1 years. The growth rates of the chimneys vary from 4.4 cm/yr to 9.1 cm/yr. These results indicate that the Ba-Ra-rich fluid expulsion on the seafloor, triggering barite deposition, is a rapid and recent event. The uptake of Ba and Ra by the fauna inhabiting the barite-bearing seeps was found to be proportional to the Ba/Ra ratio in the pore fluids. Mussels harboring methanotrophic endosymbionts average 0.6 dpm/g and 0.5 dpm/g ^{226}Ra for soft tissues and calcareous shells, respectively, which are significantly higher than those reported for shallow marine mussels. Vagrant, heterotrophic, fauna living around the seeps yield ^{226}Ra and Ba up to 10.7 dpm/g and 4319 ppm, respectively. The considerably higher levels of Ra and Ba in the heterotrophs are probably acquired through ingestion of barite particles.

STUDY PRODUCTS: P. Aharon, D. Van Gent, B. Fu, L. M. Scott. 2001. Fate and Effects of Barium and Radium-Rich Fluid Emissions from Hydrocarbon Seeps on the Benthic Habitats of the Gulf of Mexico Offshore Louisiana. A final report by the Louisiana State University for the U. S. Department of the Interior, Mineral Management Service, Gulf of Mexico OCS Office, New Orleans, LA. Contract No. 14-35-0001-30660-19946. 151 pp

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