Department of Marine Science
University of South Florida
St. Petersburg, FL 33701

PROGRESS REPORT AND PROPOSAL

TO: U.S. Department of Energy, Ecological Research Division

TITLE: The West Florida Continental Shelf: A Study of Geothermal Flows
and Other Processes Affecting Radionuclides and Trace Metals

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MASTER

Kent A. Fanning
Kent A. Fanning
Associate Professor
Department of Marine Science
University of South Florida
830 First Street South
St. Petersburg, FL 33701
(813) 893-9133

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Robert H. Byrne
Robert H. Byrne
Assistant Professor
Department of Marine Science
University of South Florida
830 First Street South
St. Petersburg, FL 33701
(813) 893-9508

Peter R. Betzer
Peter R. Betzer
Professor
Department of Marine Science
University of South Florida
830 First Street South
St. Petersburg, FL 33701
(813) 893-9502

William M. Sackett
William M. Sackett
Chairman
Department of Marine Science
University of South Florida
830 First Street South
St. Petersburg, FL 33701
(813) 893-9131

A. Riley Maco
A. Riley Maco
Director
Office of Sponsored Research
University of South Florida
4202 Fowler Avenue
Tampa, FL 33620
(813) 974-2897

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Progress Report

Department of Energy

Contract # 80EV05486

✓ (Oct. 1, 1979 - July 1, 1980

ABSTRACT

Our Department of Energy funded studies began as physical and chemical investigations of the single known geothermal discharge on the West Florida Continental Shelf. In the course of these studies it was discovered that the discharge phenomenon is of regional extent and may have considerable impact on the chemistry and biology of the shelf. Enormous enrichments of radionuclides (Ra-226, Rn-222) and biologically active heavy metals (Pb, Cu) have been observed emanating from point sources. Primary productivity in the region we have investigated appears to be depressed.

The origin of the submarine discharges we have observed has been identified as normal seawater which enters the substrata of the Floridian Plateau. In its journey through the plateau, the seawater undergoes considerable modification including considerable calcium enrichment and magnesium depletion, consistent with a dolomitization process.

In the next year's work we plan to investigate several different environments of the West Florida Shelf. Our plans include four transects across the shelf. The immediate goal will be to understand the distributions of important radionuclides and trace metals in those environments because much of the West Florida Shelf is unexplored in that regard. These transects are designed to accommodate our additional goals of expanding the study of geothermal discharges on the West Florida Shelf and also studying the possible transport of high levels of radioactivity seaward from the estuaries. We additionally propose to study the interactions of organisms with metals and radionuclides. The nuclides of greatest interest to us are Ra-226 and Pb-210, and the organisms of greatest initial interest to us are

phytoplankton and zooplankton. Eventually we hope to examine higher levels of the food web. Our results should allow some prediction of the interaction between parts of the food web and pollutant metals and radionuclides.

INTRODUCTION

Our interest in submarine geothermal springs along Florida's west coast grew out of contact with hydrologists and their studies of temperature distributions in wells and the subterranean flow within the Floridan Aquifer. To explain their results, they had to recognize that most of the Floridian Plateau was porous and permeable enough to have hydrological contact with the ocean. Thus, seawater could be flowing into (or out of) the Plateau at many levels where it might mix with fresh groundwater, react with the calcareous framework, and follow a variety of percolation patterns. One such pattern seems to provide a flow of warm, undiluted seawater out of vents and seepage areas in the region of the West Florida Shelf between Sanibel Island and Cape Romano. The best known portion of that flow is at Mud Hole Submarine Spring (MHSS).

Details of the West Florida geothermal activity and of the hydrological studies of its potential importance are presented in Appendix I, which also describes some of our research on the subject.

Our studies have been part of a program funded by the Department of Energy to consider the impact of energy-related activities on the environment. The rationale was that the warm springs might be models for what would occur on continental margins by exploiting coastal subterranean seawater or brines that had been geothermally heated. Such a development would produce the release of large quantities of warm seawater that might be chemically different from the receiving shelf water. Based on our work, it should be possible to make reasonable predictions about the impact of those releases in many coastal areas with a potential for geothermal power development.

An equally important reason for our work is the role of subterranean flows of seawater in the geochemical cycles of the sea. As highlighted dramatically on the Galapagos Spreading Center (Corlis et al., 1979; Edmond et al., 1979), processes associated with subterranean flows may provide the dominant sources or sinks for some solutes. High-temperature coastal flows have also been discovered, with important chemical differences between the effluent seawater and receiving seawater (Vidal et al., 1978). To our knowledge, the thermal flows we have studied are the only well known cases of a large heated discharge of seawater from limestone terrain. Thus, the springs of the West Florida Shelf provide an interesting contrast and help to complete the picture of the impact of subterranean flows on the ocean.

Basically, we set out to answer four questions about the West Florida thermal flows:

1. Was the fluid discharging from the vents originally seawater?

This question is a partial test of Kohout's ideas about subterranean flow in the Floridian Plateau (Appendix I).

2. What is the scale of the phenomenon? This question may be stated another way by asking if MHSS is just an isolated spring, or are there many others along the West Florida Shelf and other carbonate platforms of the Gulf of Mexico, Atlantic, and elsewhere?
3. How was the effluent water altered by flowing through the Floridian Plateau?
4. What are the impacts of the West Florida Thermal springs on the surrounding shelf environment?

Although not complete, our work on those questions has been very successful, and the Progress Report outlines the results.

However, because of our surveys of Ra-226 and Rn-222 in waters of the West Florida continental margin, we have discovered that some of the waters are many-fold enriched in those nuclides compared to other nearshore areas. Further, west Florida's estuaries seem to be order(s) of magnitude richer in Ra-226 and Rn-222 than east coast estuaries. The reasons for the enrichments may or may not involve the thermal springs, but finding those reasons could be as valuable as studying the geothermal flows themselves.

Therefore, our Proposal considers radionuclides as well as the geothermal flows on the West Florida Shelf.

PROGRESS REPORT

Source of the Discharge Water in the Springs

As Appendix I clearly indicates, we have concluded that the effluent from the vents and from the areas of seepage was normal seawater when it first entered the substrata of the Floridian Plateau. Its composition, expressed as chlorinity ratios, is too close to seawater for any other explanation to suffice, particularly in view of the lack of sources of soluble ions in the upper 1000 meters of the Plateau. Further, the seawater most likely to penetrate the Plateau and feed the springs probably did so between 500 and 1000 m below sea level. The deep source water could have come from anywhere around the southern third of the Floridian Plateau; our salinity data from the eastern Gulf of Mexico, from the Straits south of the Florida Keys, and from the water column off Miami indicate chlorinities of 19.3-19.5‰ at all three locations below 500 m depth.

Thus, the information we have gathered is consistent with Kohout's model for the circulation of seawater inside the Floridian Plateau.

Magnitude of the Geothermal Flow

So far, we have definitely identified six geothermal springs, occupying an 85-km² area about 45 km SSW of Ft. Myers, Florida (Appendix I). But, we have indications that the geothermal field is potentially much larger. Figure 1 shows the locations of the six springs: MHSS, Steward Spring (SS), Spring III, Spring IV, Spring V, and Spring VI. Figure 1 also shows areas yielding side-scan sonar returns suggestive of spring-like depressions and sites where computer-enhanced LANDSAT imagery indicated spring-related turbidity

Figure 1. Locations of geothermal springs and spring-like indications on the West Florida Shelf.

(Kohout et al., 1979). The circumstantial indications of springs occupy an area of 500-1000 km².

However, we suspect that the portion of the West Florida Shelf influenced by thermal flows may even be larger than 1000 km², although that suspicion is largely based on unsubstantiated reports. First, Warm Mineral Springs is 90 km NNW of MHSS (Fig. 1, Appendix I); so we know that heated saline waters can reach that far. Similar flows could be offshore to the west. Next, we have made many overflights of the West Florida Shelf, and it is fairly common to see isolated plumes of turbidity at least as far north as Tarpon Springs, Florida which is about 220 km away from MHSS. Also, surveys by underwater television have discovered clouds of high turbidity in bottom depressions near the continental shelf break west of MHSS (David Gettleison, Continental Shelf Associates, Inc., personal communication). Information of the types just described constitutes leads to follow when attempting to define the magnitude of the west Florida geothermal flows. So far, that information has proved to be a surprisingly accurate basis on which to plan expeditions.

Although we intend to keep using such information, as a result of our most recent studies at MHSS, we have a much more valuable prospecting tool in the search for geothermal flows: radon. The details are given later.

Alterations of the Effluent During Transit

Because the water flowing from the springs was apparently once seawater surrounding the Floridian Plateau, the record of the processes affecting it during passage through the Plateau can be revealed by comparing the compositions of spring water and seawater. That comparison is partially presented in Appendix I. The percolating seawater undergoes many changes -- e.g., reduction

processes, a loss of magnesium, a gain in calcium, a loss of phosphate, an acidification, a large gain in silica, and an enormous gain in Ra-226 and Rn-222.

The best explanation we can devise for the changes in calcium and magnesium is that they represent the results of the reaction between the percolating heated seawater and the limestone of the Floridan Aquifer. Secondary dolomite would be a by-product, and dolomite of that sort is found in the lower portions of the Aquifer. We think that this circulation-replacement process may have operated and be operating in many other carbonate platforms around the world. The possibility deserves consideration and investigation.

Another process affecting the percolating seawater is the addition of trace metals (Table 1). It is obvious that, compared to other seawater samples, the effluent from MHSS is extremely enriched in several weak-acid soluble particulate metals. Because the effluent waters are warm, low in pH, and anoxic, they might reasonably be expected to solubilize metals from the strata through which they flow. The fate of the enriched metals after the effluent is discharged to the shelf waters is unknown to us at present.

The effluent from MHSS has few suspended particles -- about 100 particles per ml. We used a computer-controlled scanning electron microscope with EDAX attachment to look at the details of the particle sizes and compositions; the results indicated some interesting changes to the seawater during its transit through the Plateau. Typically, the particles were very fine, with the most abundant size class having a volume of $0.02 \mu\text{m}^3$. The most abundant mineral was probably calcium carbonate, no doubt because of the intimate contact with limestone strata. However, the next most abundant mineral seems to have been a calcium silicate. We do not know exactly why it was there, but

Table I: Trace Metal Composition of the Effluent of
Mud Hole Submarine Spring

<u>Dissolved Metals (µg per liter of effluent)</u>					
<u>Sampling Data</u>	<u>Cd</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Pb</u>
December 77	1.6	1.5	10	1.5	33
October 78	7.6	43	48	6.1	154
Bewers et al. (1976)					
North Atlantic	0.04	----	1.6	0.2	----
Windom & Smith (1978)					
Gulf Stream	----	0.14+0.05	----	---	----
Patterson et al. (1976)					
Pacific	----	----	----	---	0.025* 0.15**

<u>Particulate Weak Acid Soluble Metals</u> <u>(µg per gram of suspended matter)</u>						
<u>Sampling Data</u>	<u>Ca</u>	<u>Cd</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Pb</u>
December 77	167,000	8.5	33	840	29	251
October 78	612,000	1.5	40	1990	84	245
Far Field	3,685	11	39	560	--	90 Surface
(Sarasota)	22,623	11	27	70	--	71 Bottom

* unpolluted

** polluted

a reasonable guess is that the high silica concentration in the effluent may have prompted its formation. The third most abundant mineral was an iron sulfide. Its presence is also believable because there was some sulfide in the effluent water (Appendix I, Table 3) and the trace metal data do show considerable iron present.

A thorough study of all possible alterations to the seawater during its passage through the Plateau has an important benefit, namely that, in addition to knowing what happened to the water, we may be able to learn where it happened. This information can be related to the kind of solid phases the seawater contacted and perhaps to its residence time within different portions of the Plateau. Knowledge of that sort can be used in many ways, not only for evaluating geothermal power possibilities, but also for evaluating the consequences of wastewater disposal in the Aquifer, for considering questions about potable water from the Plateau, and for understanding rates of natural geological processes such as secondary dolomitization.

Impact of the Springs on the Shelf Environment

We found that the discharge of the springs affects their environment in at least three ways: the water circulation, biological distributions, and radionuclide distributions. Because of the very high trace-metal concentrations in MHSS effluent, it is conceivable that there could be a large injection of metals by the springs to their immediate surroundings. Unfortunately, we have not investigated that possibility yet. Therefore, this progress report presents only the three effects for which we have information. The order of presentation is as given above, meaning that what may possibly be the best -- i.e., radionuclides -- is saved for last.

Water Circulation

By inserting a plastic hose into one of the vents in the depression of MHSS, we were able to follow the circulation above the spring as the discharge mixed with the shelf water. The technique was to pump Rhodamine WT dye down the hose and into the discharge stream while it was still in the vent and then follow the dye patch as it appeared on the surface. The patch was photographed from a Coast Guard helicopter hovering above the area and from an anchored vessel.

In the warmer months of the year, the technique worked quite well (Fig. 2). The dye appeared on the surface within 4 minutes of the beginning of the pumping. The patch spread until, between 14 and 19 minutes elapsed time, all the dye was in the water column, and unstained water appeared in the center of the patch. Despite winds and currents, the "doughnut-like" patch grew and maintained its integrity for about an hour and eventually covered over 0.25 km^2 of sea surface. We conclude that, in the warmer months, the pattern of circulation due to the effluent is somewhat like a mushroom-shaped cloud, with the vent discharge rising rather quickly in the center and then spreading in all directions. There may even be a convection cell with diluted effluent sinking again after spreading. But the most important conclusion is that, under these conditions, any component enriched in the effluent is likely to reach the sea surface very quickly and exert its impact up there rather than near the sea bed.

In the winter months, the situation seems drastically different. A strong thermocline ($2-3^\circ\text{C}$ per meter) forms at mid-depths in the water column and seems to place a "cap" over the lower part of the column in contact with the spring. Dye released near bottom in a spring did not reach the surface

TIME SEQUENCE OF THE SURFACE EXPRESSION OF
DYE-LABELED SPRING EFFLUENT. OCTOBER 25, 1978.

Figure 2

after several hours. Further, that intensely stable regime in the water column coincides with the period when the spring depressions seem to collect considerable silt -- e.g., up to 2 meters thick at Spring III. Thus, in winter, finding discrete vents is more difficult, and seepage may be a more important mode of discharge. However, the arrival of warmer weather seems to break down the stable water column, the depressions clean themselves of silt, and discrete vents are more easily spotted and photographed.

Biological Distributions

The springs do exert some kind of influence on the native biota. However, we have not been able to pinpoint exactly what it is. Larger organisms congregate around the vents. As mentioned in Appendix I, sea turtles are found there almost exclusively. However, the SCUBA divers report many large fish like grouper are always found in the depressions. It may be that, by keeping the depressions relatively free of debris, the springs create a favorable habitat for benthic life and organisms that feed on it. The effluents do not provide many nutrients that could stimulate phytoplankton (Table 3, Appendix I). In fact, carbon-14 productivities in the overlying water appear to be depressed ($0.5 - 1.5 \text{ mg C/m}^3/\text{hr}$) compared to what might be expected so close to shore. In keeping with that result, the phytoplankton over the springs are dominantly dinoflagellates which are characteristic more of oligotrophic waters than of normal shelf waters. We have learned that the seasonal change in stability and circulation in the water column can exert a major effect on the benthos. When we first visited MHSS, it had a flourishing benthic community, almost like a sponge reef community. Then the winter season came, and, when we visited it a few months later, the area had collected considerable debris. The community was decimated.

Radionuclide Distributions Near the Springs

As suggested in the Introduction, the study of Ra-226 and Rn-222 in the effluent waters and the West Florida Shelf waters is probably the most valuable one we have performed to date. We first began to realize the potential significance of those nuclides when at our request, Robert Key and David Schink of Texas A & M University determined activities of Ra-226 in vent waters from MHSS. The activities were much higher than any seawater they had ever seen. So, with DOE support, we acquired radon extraction and counting equipment to do our own analyses, and we also sent samples to Willard Moore's laboratory at the University of South Carolina. As explained in Appendix I, the results from all three laboratories agree that the effluents from the springs are 1,000-1,300-fold enriched in Ra-226 and 10,000-13,000-fold enriched in Rn-222 compared to the upper layers of the Gulf of Mexico. Thus, the two nuclides should be excellent tracers of spring water after it leaves the vents. Shelf water could dilute the effluent so much that salinity, silica, temperature, or oxygen could not be used to identify spring water, but the radionuclide signatures should still be detectable.

To find out, we adopted the following plan. Our extraction and counting equipment was ordered at the beginning of the last contract year and arrived by January, 1980. By March, we were ready to go to sea with it, and the cruise left from St. Petersburg (Fig. 3). The first transect was to establish the general background of natural radioactivity on the West Florida Shelf. Thus, we took two stations in Tampa Bay (Stations 1 and 2) and then steamed southwest across the shelf toward the shelf break (Stations 3-8). At most of those stations, we sampled surface and near-bottom waters. Then we steamed to Sanibel Island and conducted the second sampling effort, called transect 2, in the vicinity of the thermal springs (Stations 9-18). At most of those

Figure 3. Cruise Track

stations, surface and deep waters were also sampled, and Station 9 was located at the head of San Carlos Bay in order to see what the local estuaries might be delivering to the shelf waters. Stations 11, 12, and 14 were at MHSS, Station 13 was 600 m away from MHSS, and Station 15 was at Spring V (Fig. 1). Station 18 was an orifice sampling station at MHSS.

Activity data were evaluated by comparison to salinity (Fig. 4). Transect 1 out of Tampa Bay to the shelf bread shows a linear regression of Ra-226 and salinity. That line could be considered the background for the shelf. However, the point for Station 9 does not fall on that regression although the second point on transect 2 -- i.e., for Station 10 -- does. Therefore, on the basis of all samples except those for Stations 1 and 9 and those around the springs, we can say that the background for the shelf quite probably follows the line for transect 1 in Figure 4 when the salinity is greater than 30‰. Thus, the Ra-226 activities in the water column near the springs (Stations 11-15) show strong enrichments over the level of Ra-226 in the shelf background.

The impact of the springs on the radioactivity of the West Florida Shelf shows up even better when we consider the distribution of Rn-222 (Fig. 5). The radon-salinity plot for our March data had roughly the same milieu for the shelf background as the radium-salinity plot. However, the deep waters for Stations 11-15 showed radon activities which were factors of 2-3 larger than the shelf background.

As far as we know, the radon abundances at those spring stations were higher than any reported in continental shelf waters. Work by Biscaye et al. (1980) shows that standing crops of excess Rn-222 in the shelf area around the New York Bight are usually a few tenths of a dpm/cm^2 but that occasionally they increase to 1.0 dpm/cm^2 or slightly higher. Our data (Table 2) also

Figure 4. A comparison of radium-226 activities and salinities for the waters of the West Florida Shelf in March 1980. Station numbers shown by data points. Station locations in Figure 3. Transect 1 extends southwest from Tampa Bay and transect 2 is south of Sanibel Island.

Table II. Standing crops of Ra-226, Rn-222, and excess Rn-222 in the water column of the estuaries and West Florida Shelf between Tampa Bay and Cape Romano, Florida (Stations 11-17 are in the thermal spring area).

<u>Standing Crop (dpm/cm²)</u>				
<u>Station</u>	<u>Water Depth (m)</u>	<u>Ra-226</u>	<u>Rn-222</u>	<u>Excess Rn-222</u>
1	6	1.3	3.7	2.4
2	8	0.8	3.6	2.8
3	7.5	0.5	----	-----
4	7.5	0.5	3.2	2.7
5	31	0.8	1.4	0.6
6	57	1.3	1.1	- 0.2
7	103	1.2	0.7	- 0.5
8	76	0.8	1.1	0.3
9	3	0.3	0.8	1.1
10	6	0.4	1.2	0.8
11	13	1.2	9.7	8.5
12	13	1.2	8.1	6.9
13	14	1.2	9.2	8.0
14	18	1.8	12.6	10.8
15	15	0.8	5.4	4.6
16	20	0.8	----	-----
17	20	---	1.2	-----

Figure 5. A comparison of radon-222 activities and salinities for the waters of the West Florida Shelf in March 1980. Station locations in Figure 3. "s" = surface or upper water column; "d" = deep or near bottom water.

show standing crops of excess Rn-222 of a few tenths, but, in the area around the thermal springs, the standing crops become higher. Rn-222 standing crops become particularly high, such that excess Rn-222 reaches 4-11 dpm/cm². Ra-226 standing crops become somewhat higher around the springs, but the really big increase is for Rn-222.

Therefore, we should easily be able to use Rn-222, and probably Ra-226, to identify important areas of geothermal discharge on the West Florida Shelf. Our system functions nicely at sea aboard a small (65') coastal research vessel so that promising bottom terrain or clouds of turbidity can be investigated as soon as discovered. Further, as Table 4 in Appendix 1 shows, our system gives both high and low activities which agree well with those of established radio-chemists.

The existence of the large abundances of Ra-226 and Rn-222 over the springs suggests the possibility of enrichments of other radionuclides due to the spring effluents. For example, much of the Rn-222 in the water should be decaying to Pb-210 because degassing to the atmosphere is probably far from total. Thus, we might expect to see more Pb-210 in the water over the springs than elsewhere on the shelf. If we do not, then there may be a good stripping mechanism at work. Also, since so much Ra-226 is discharging from the vents, it would be reasonable to look for fairly large quantities of Ra-228 discharging from the vents as well. Zones within the Floridian Plateau that contain the uranium parent for Ra-226 may also contain an abundance of Th-232, the parent of Ra-228. Pb-210 and Ra-228 are only two of many radionuclides that may be discharging from the vents.

Radium-226 and Radon-222 on the West Florida Shelf

To the best of our knowledge, there have not been very many studies of

these two nuclides in the waters over continental shelves. Comparison of our data with anyone else's was accordingly difficult. There are two reports which are suitable: that by Li et al. (1977) on Ra-226 in the areas of the New York Bight and southeast of Cape Hatteras and that by Knauss et al. (1978) on Ra-226 and other nuclides along the western margins of North and South America. Compared to their results, most of our activities (Fig. 4) are much higher. For their samples, a Ra-226 activity of 10 dpm/100 kg or dpm/100 l is a very high value, and, for ours, activities that low are encountered only near the shelf break where open Gulf of Mexico surface water is found. West Florida Shelf waters, even away from areas of known springs are several fold richer in Ra-226 than they report for their respective shelf waters. The differences between estuarine or brackish-water samples are even greater. At salinities of 25-33‰, Tampa Bay has 100-220 dpm/100 l of Ra-226 and San Carlos Bay near Sanibel Island has 80-120 dpm/100 l; by comparison, at those same salinities, the Hudson Estuary has only 10 dpm/100 l according to Li et al. There may be other estuaries around the Gulf that are as rich in Ra-226 as Florida's estuaries; Reid (1979) reports Ra-226 activities of 50-100 dpm/100 kg, in a restricted Texas Bay (Trinity Bay). Reid also claimed that the Northwest shelf of the Gulf was enriching its surface waters in Ra-226.

So why is the fringe of the Gulf of Mexico, and the West Florida Shelf in particular, apparently so enriched in Ra-226 (and possibly Rn-222) compared to other continental margins? We cannot be certain at present, and considerably more shelf samples from Florida and elsewhere in the Gulf must be analyzed before we know that the enrichment is widespread. For Florida at least, it's possible that the flushing of the estuaries puts high levels

of natural radionuclides into the shelf environment. Those nuclides may get into Florida's estuaries in fresh groundwater that percolates through the phosphate beds of central Florida and then into the estuaries. It is also possible that thermal springs contribute Ra-226 and other nuclides by discharging further out on the shelf.

Whatever the cause(s) of the enrichment, obtaining a firm understanding of them in future work is very important. It would help to explain why the Gulf of Mexico seems to be so rich in Ra-226 and Ra-228 (Reid et al., 1979; Reid, 1979). It would be important to an understanding of the radioactive background of the West Florida Shelf against which energy-related activities will be conducted. It would be required in order to determine where the enrichments ultimately go -- e.g., into the biota, into the Florida current and out of the Gulf through the Florida Stratis, into the atmosphere, and into the sediments, to name a few possibilities.

ACCOMPLISHMENT, COMPLIANCE, AND
PERCENTAGE EFFORT

As a result of our efforts under this grant the following publications are completed or in progress:

- a.) Fanning, K. A., Byrne, R. H., Breland, J. A., II, Betzer, P. R., Moore, W., Elsinger, R., and Pyle, T. E., 1980. Geothermal springs of the West Florida Continental Shelf: Evidence of dolomitization and radionuclide enrichment. Submitted to Earth and Planetary Science Letters (Appendix I).
- b.) Byrne, R. H., 1980. Theoretical upper-bound limitations for multi-ligand complexes in solution. Marine Chemistry 9: 75-80. (Appendix II).
- c.) Breland, J. A., II, 1980. Chemical and physical characteristics of a saline geothermal submarine spring off Florida's southwest coast. M.S. Thesis, University of South Florida, Tampa, FL.
- d.) Byrne, R. H. and Kester, D. R. Ultraviolet spectroscopic study of ferric equilibria at high chloride concentrations. Submitted and undergoing revision, Journal of Solution Chemistry.

During the contract year just ended, the principal investigators devoted the following percentages of their time to the project.

K. A. Fanning	2/12
R. H. Byrne	2/12
P. R. Betzer	1/12

Appendix 2 removed - reprint

APPENDIX III

STUDIES OF INORGANIC Pb SPECIATION IN SEAWATER

The pathways of chemicals in the environment are strongly influenced by chemical form. In order to predict the fate and influence of metals injected into seawater by hydrothermal activity, thermodynamic and then kinetic models of chemical behavior must be constructed. The procedure which should be taken to model the behavior of Pb injected on the West Florida Shelf has been initiated. As a first step, careful studies of the chemical complexation of Pb with the major anionic seawater constituents have been undertaken. This analysis is now essentially complete for 25°C and one atmosphere. The results of this study were presented at the spring AGU meeting in Toronto (1980) and are now being prepared for publication.

Many models of Pb speciation in seawater have been constructed. A number of these models are shown in Table 1-III. The diversity of models constructed by various authors is due to a number of effects:

a. The range of stability constants available in the literature is large for any one Pb-ligand complex. This problem is worst for the important complexes PbOH^+ and PbCO_3° .

b. The constants selected have been determined in simple media and must be corrected to seawater conditions. The different correction procedures adopted by different authors increases model diversity.

c. Models for Pb speciation are dependent on the models adopted for the major element speciation of seawater. The range of major element speciation models available (for example: Sipos et al., 1980) generates further diversity.

Most of these difficulties can be minimized using a medium approach. In such an approach trace metal behavior is studied directly in the medium

Table 1-III

Inorganic Lead Speciation Models for Seawater

<u>Species</u>	<u>Dyrssen & Wedborg (1974)</u>	<u>Long & Angino (1977)</u>	<u>Stumm & Brauner (1975)</u>	<u>Turner & Whitfield (1979)</u>	<u>Zirino & Yamamoto (1972)</u>
PbCO_3° PbCO_3Cl^-	< 1	18	40	65	77
PbOH^+ , $\text{Pb}(\text{OH})_2^+$ PbOHCl°	15	5	33	6	1
PbCl_i , Pb^{2+} PbSO_4°	84	73	27	28	21

(Minor species contributions are not shown, causing some sums to total less than 100%)

of interest. In this case the formation of PbCO_3° has been examined directly in seawater. Figure 1-III shows the spectrophotometric behavior of dissolved Pb in 34.7‰ salinity seawater as a function of wavelength and pH. At constant salinity the relative concentrations of Pb complexes in seawater were demonstrated to be controlled principally by the concentration of carbonate ion, $\text{m}_{\text{CO}_3^{2-}}$, in solution.

The net result of the Pb complexation determinations in seawater is a formation constant, $\beta_{\text{PbCO}_3^\circ}$. This constant has the following form and numerical value.

$$\beta_{\text{PbCO}_3^\circ} = \frac{\text{m}_{\text{PbCO}_3^\circ}}{\text{m}_{\text{PbCl}} \cdot \text{m}_{\text{CO}_3^{2-}}} = (10 \pm 0.7) \times 10^3 \left(\frac{\text{moles}}{\text{kg}} \right)^{-1}$$

where $\text{m}_{\text{PbCO}_3^\circ}$ is the concentration of PbCO_3° and m_{PbCl} is the sum concentration of Pb^{2+} , PbCl^+ , PbCl_2° , PbCl_3^- , and PbSO_4° ions. In addition, it was shown that PbOH^+ is negligible compared to PbCO_3° at pH = 8.0.

The Pb seawater speciation model which can be constructed using the formation constant, $\beta_{\text{PbCO}_3^\circ}$, does not have the uncertainties associated with models based on determinations in simple media.

Based on our determinations the following inorganic Pb speciation model is constructed for that fraction of Pb in seawater which is chemically labile.

Inorganic Pb Speciation in Seawater

$\Sigma \text{CO}_2 = 2.05 \times 10^{-3} \text{ moles/kg SW}$
 pH = 8.0, 25°C, S = 34.7‰

<u>Species</u>	<u>Percentage of Total Inorganic Pb</u>
PbCO_3°	59
PbOH^+	< 1
Pb^{2+} , ΣPbCl_i , PbSO_4°	41

Figure 1-III

MOLAR ABSORPTIVITY VERSUS
WAVELENGTH AT 5 VALUES OF pH.
 7×10^{-6} MOLAR Pb IN SEAWATER
S = 34.7%

The methodology developed in this study allows facile determinations at other temperatures, pressures and salinities. In addition, it is expected that the results of this work will be particularly valuable as a guide in interpretation of anodic stripping voltammetry measurements made on untreated natural samples such as we are proposing to gather on the West Florida Shelf (Turner and Whitfield, 1979).

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APPENDIX IV

CLEAN TECHNIQUES AS APPLIED TO TRACE METAL DETERMINATIONS IN WATER, IN SUSPENDED MATTER, AND IN SEDIMENTS OF THE WEST FLORIDA SHELF

The pioneering work of Patterson on lead in seawater, that of Bruland, Martin and Knauer on cadmium, zinc and copper in the Pacific Ocean, that of Boyle and Edmond on copper, cadmium, nickel and iron during and after GEOSECS, and that of Windom in mercury and copper in shelf waters of the southeastern United States have all shown that extreme care in sampling is necessary if oceanographically consistent distributions of trace species are to be obtained. We are aware of the clean techniques these researchers have used to carry out their high quality research and we propose, with one marked exception, to use their techniques (cited earlier in proposal) during our sampling over the West Florida Shelf.

According to our cleaning protocol filter heads, teflon bottles, and Chelex columns will all be cleaned for several weeks prior to each cruise with Ultrex or better HCl in a class 100 clean room at the University of South Florida. To remove the wetting agent which has substantial quantities of iron, lead, and zinc, all Nuclepore membranes will be preleached with Ultrex, 1N HCl, rinsed several times with deionized-quartz redistilled water, dried and weighed on a microbalance housed in the class 100 clean room. It is also important to note that the clean room has controls for temperature and humidity so that the conditions under which the filter is tared prior to use can be duplicated when it is returned to the laboratory for processing.

Chemical leaches of sediments and suspended matter (using quartz redistilled acetic acid) will all take place in a vertical flow clean bench.

As a further insurance against contamination during the period when the acetic acid is reacting with these materials, a plastic cover will be in place over the samples. All solutions will be stored in conventional polyethylene bottles which have undergone a cleaning technique utilized by C. C. Patterson in his research with lead. In addition, all of the solutions from leaches of suspended matter or sediment will be acidified to a pH of 1.5 so that the trace metals are not adsorbed to walls.

The use of clean room technology and vertical flow clean benches is also an integral part of the approach that the aforementioned scientists have used in their study of trace metals in the ocean. However, many of these investigators have used large volume, Teflon-coated Niskin bottles as a means of collecting water samples. A recent discovery on a cruise of R/V RESEARCHER to the Sargasso Sea is that even these large volume, Teflon-coated bottles seriously contaminate collected surface waters with zinc, copper and lead (Spencer et al., 1980 Unpublished Data). What we consistently found was a 30- to 40-fold difference in zinc levels between water samples taken (by swimmer) with a 30-liter, Teflon-coated Niskin bottle and those taken (by swimmer) in a 1 liter Teflon (FEP) bottles. Although the analyses are not complete, there is no question that there is also a large difference in lead and copper levels between the Niskin bottle samples and those taken in 1 liter Teflon bottles. Despite the lack of quantification for the lead and copper concentrations, it is apparent that we cannot use a Teflon-coated Niskin bottle in our research on metals. Instead we will either have swimmers collect samples in 1-liter Teflon bottles or else use an all-Teflon sampler which is attached to polyethylene sheathed cable or Kevlar line. All trace metal samples will be taken from a plastic Boston whaler which is far removed from the surface vessel we

will be using as our main work platform.

For the soluble trace metal determinations we will utilize two techniques

- (1) separations onto Chelex columns followed by elution and quantification by atomic absorption spectrometry and (2) anodic stripping voltammetry.