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STUDIES OF TRACE METALS AND ACTIVE HYDROTHERMAL VENTING ON THE GORDA RIDGE

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NOTICE

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TABLE OF CONTENTS

-

i.

| | <u>Page</u> |
|-------------------------|-------------|
| Abstract | iii |
| Intoduction | 1 |
| Background | 1 |
| Methods | 3 |
| Results | 4 |
| A. NOAA Ship SURVEYOR | 4 |
| B. R/V WECOMA (W8508AA) | 12 |
| Conclusions | 24 |
| Acknowledgements | 24 |
| References | 27 |
| Appendix | 29 |

LIST OF TABLES

| Table | <u>Page</u> |
|---|-------------|
| Table 1. Station summary for samples collected during "VENTS Gorda Survey on NOAA Ship SURVEYOR. | 6 |
| Table 2. W8508AA Post-Cruise Station Summary. | 18 |

LIST OF FIGURES

| Fig | ire | Ī | <u>Page</u> |
|-----|---------------------------|-----------------|-------------|
| 1. | Map of NOAA Ship SURVEYOR | Cruise. | 5 |
| 2. | Near-bottom Mn profiles, | stations GR1-6 | 8 |
| 3. | Near-bottom Mn profiles, | stations GR9-15 | 9 |

i

-

LIST OF FIGURES (continued)

| Figu | ure | Page |
|------|--|------|
| 4. | Near-bottom Mn profiles - overlays of all data. | 10 |
| 5. | Near-bottom profile for all metals at GR6. | 11 |
| 6. | Full water column profiles for all metals | 13 |
| 7. | Near-bottom profiles of metals in hydrothermal plume - GR14 | 14 |
| 8. | Near-bottom profiles of metals in hydrothermal plume - GR15 | 15 |
| 9. | Northern Gorda Ridge hydrothermal sites defined by SURVEYOR | 16 |
| 10. | Bathymetric map and stations from WECOMA W8508AA | 17 |
| 11. | Bathymetric cross section of ridge axis at GR14 | 20 |
| 12. | CTD and transmission data from CTD10 . | 21 |
| 13. | CTD and transmission data from hydrothermal anomaly at CTD11 | 22 |
| 14. | Manganese and CTD data from CTD12 (at GR14). | 23 |
| 15. | Near-bottom metal concentrations from hydrothermal plume CTD12 | 25 |
| 16. | Manganese profiles from radon hydrocasts. | 26 |

ii

ABSTRACT

The largest single source of dissolved manganese to the oceans is seafloor hydrothermal circulation. "Fingerprints" from the inputs of Mn and other elements to the deep ocean can be used to find the origin of the vent water. Active seafloor hydrothermal vents can be associated with significant deposits of massive metal sulfide minerals. The Gorda Ridge, located approximately 130 miles off Southern Oregon and Northern California and within the US EEZ, has become a focus of studies on hydrothermal systems. The research reported here presents concentration data for Mn (determined at sea) and for Fe, Cu, Ni, Cd and Zn. These data include background environments and major hydrothermal "signals". Supporting data on thermal and suspended particle anomalies associated with active venting are also discussed. Together, the data sets <u>demonstrate</u> the presence of active hydrothermal venting along the Northern Gorda Ridge.

STUDIES OF TRACE METALS AND ACTIVE HYDROTHERMAL VENTING ON THE GORDA RIDGE.

I. <u>INTRODUCTION.</u> In this report, we will discuss the results of two research projects which investigated trace metal distributions in the water column at sites along the Gorda Ridge spreading center. The ridge is located approximately 130 miles off the Oregon and Northern California coasts and was the target of two research expeditions during 1985. The first cruise was on the NOAA Ship SURVEYOR (Edward Baker, Chief Scientist) as part of the NOAA VENTS program. The second cruise, funded by the Minerals Management Service through the Oregon Department of Geology and Mineral Industries (DOGAMI), was carried out on the R/V WECOMA (Robert Collier, Chief Scientist) and focused on specific sites at the northern Gorda Ridge where evidence of active hydrothermal venting was demonstrated on the SURVEYOR cruise.

This research had two specific goals:

- 1) To help identify regions of active hydrothermal venting using towed instruments to detect thermal and particle anomalies coupled with ship-board analyses of manganese in seawater samples;
- 2) To determine the distributions of manganese and other trace metals throughout the water column to assess the background concentrations and regional variability of these elements.

All phases of this work were supported by the cooperative research efforts of scientists from Oregon State University (also supported by DOGAMI) and from NOAA, the USGS and the Univ. of Washington. These efforts were coordinated through the Gorda Ridge Technical Task Force.

II. <u>BACKGROUND.</u> Over the past decade, studies of the chemistry and distribution of trace elements in seawater have become an important part of marine geochemical research. This has been possible through the development of non-contaminating materials and techniques for sampling, handling and analysis of seawater samples and through steady improvements in analytical techniques and sensitivities. The trace metals are sensitive tracers of

many important biological and geochemical processes. Their distributions are also the focus of environmental concerns because anthropogenic activity is capable of altering the natural cycles of many of these potentially-toxic materials. An excellent compilation of the "state of the art" can be found in the book edited by Wong et al. (1983).

Seafloor hydrothermal circulation is one of the major processes which affects the geochemical cycle of elements (especially metals) in seawater. A compilation of papers discussing a wide variety of hydrothermal processes at seafloor spreading centers can be found in the book edited by Rona et al. (1983). The major and minor element chemistries of these vent systems are discussed elsewhere (see Von Damm et al., 1985).

The major input of manganese to the oceans is from hydrothermal fluids (Bender et al., 1977, Edmond et al. 1982) and the study of the geochemical cycle of Mn has been closely linked to that of hydrothermal circulation. However, Mn is also one of the more useful tracers of active hydrothermal venting and has been used as a "prospecting" tool since the first successful discoveries of seafloor hot springs (e.g. Klinkhammer et al., 1977). Detection of Mn "plumes" was a critical step in the search for the most recently discovered hydrothermal vents on the Mid-Atlantic Ridge (Klinkhammer et al. 1985). The unique properties of Mn that make it a powerful tracer are: 1) it is enriched in the primary vent fluids by a factor of $\sim 10^5$ times that in deep ocean water; 2) its residence time in seawater is long enough to allow it to be detected a significant distance away from its injection point (unlike Fe or ²²²Rn) yet it is removed rapidly enough to prevent an accumulation of dissolved Mn in the deep ocean which would mask the local inputs (e.g. like Si); 3) its analysis is "relatively" simple, sensitive, and it is not as prone to environmental contamination during sampling as some other metals.

A variety of other physical and chemical tracers of hydrothermal activity exist which have been applied at nearly all spatial and temporal scales in the oceans. One of the most obvious and sensitive tools is the detection of the thermal anomalies associated with the injection of these buoyant fluids near the seafloor (Weiss et al., 1977; Lupton et al., 1985). These anomalies have to be carefully interpreted in terms of the ambient temperature-salinity relationship which is often nearly linear near the depths of typical ridge crest inputs. These data are collected by a

remotely towed device ("CTD") which carries sensors for conductivity (salinity), temperature and pressure (depth). Our research on the Gorda Ridge made extensive use of this tool.

Another hydrothermal anomaly which can be detected in these plumes is fine suspended particulate material. This is injected directly by the vent or it precipitates from solution as the water cools and mixes with ambient seawater. The deep ocean contains low concentrations of suspended particulate matter - on the order of 10-20 μ g/liter - and the chemical composition of this material largely reflects its biogenic or crustal origin. Hydrothermal "plumes" contain significant increases in particle concentration and their composition is extremely enriched in metals (especially Fe and Mn). A common instrument added to the "CTD" is a transmissometer or nephelometer to measure the absorbance or scattering of light by these suspended particles (Massoth et al, 1984). Preliminary survey work on the Gorda Ridge using the above mentioned techniques was previously reported by Massoth et al. (1982).

III. METHODS. All phases of the collection, handling, storage and analysis of these samples for trace metal concentrations were carried out using demonstrated methods designed to eliminate contamination. Water samples were collected with acid-cleaned Niskin water samplers - including standard 5 and 30 liter samplers fitted with all-silicone internal parts and 30 liter Niskin GOFLO-type bottles belonging to J. Trefrey (FIT). These samplers were usually deployed on the CTD-rossette and but in a few cases they were mounted directly on the stainless hydrowire. Numerous opportunities occurred to compare the consistency of samples collected in parallel with these different samplers. In no case, for the metals analyzed in this work, were there any contaminations that could be traced to a specific sampler type. On the W8508AA, a standard Neil Brown Instrument Systems CTD (Mark III)/ rosette was used to collect all hydrographic data and most of the water samples. Samples for metal analyses were carefully and rapidly drawn from the Niskin bottles after they arrived on deck. All further handling of the samples was carried out in laminar flow clean hoods.

Metal analyses included two general preconcentration techniques - one for Mn and one for the other metals (Cu, Ni, Cd, Fe and Zn). All elemental concentrations were determined by atomic absorption spectrophotometry using

a graphite platform furnace atomizer and appropriate background correction. Manganese was preconcentrated from 15 ml of seawater using an 8-hydroxyquinoline/chloroform liquid-liquid extraction system (Klinkhammer, 1980). Back extraction from the solvent with 3N nitric acid resulted in a concentration factor of 30. Our detection limit was approximately 0.1 nmol Mn/liter seawater. Manganese samples were run at sea in support of the "prospecting" effort using a laboratory van which included our spectrophotometer. Other samples were run in the shore lab. All shipboard samples were analyzed within 3 hours of collection without acidification. Klinkhammer et al.(1985) have shown that this fraction (termed "total reactive Mn" or TRM) essentially corresponds to the dissolved Mn. Samples stored for later analysis were acidified to pH 2 to prevent loss of Mn to the container. These values are referred to as "total dissolvable Mn"(TDM).

The other trace metals were preconcentrated using the method of Boyle et al.(1981). The metals were co-precipitated from seawater with a cobalt-APDC complex. After centrifugation and removal of the seawater, the precipitate was digested/dissolved into a small volume of nitric acid to achieve a concentration factor of 30.

IV. <u>RESULTS</u>. The results of these studies will be presented here in two sections. The first will cover samples collected from the NOAA Ship SURVEYOR and the second section will cover all CTD surveys and samples collected from the R/V WECOMA cruise (W8508AA).

A. SURVEYOR Cruise (VENTS - Gorda Survey, RP-15-SU-85A).

The SURVEYOR conducted leg I of the NOAA VENTS program with an 18 day cruise to the Gorda Ridge (May 6-23, 1985). A variety of techniques were used to determine the existence and distribution of active hydrothermal vents along the ridge axis (Fig. 1). A summary of the stations occupied is given in Table 1. Measurements made at sea by various co-investigators included hydrography; particulate matter loading (nephelometry); methane; dissolved Mn and ²²²Rn; particulate Fe, P, As, Mn, Zn, and Cu concentrations. We participated in the cruise to carry out Mn analyses and to collect samples for subsequent trace metal determinations in the lab at OSU.



Fig. 1. Map outlining the stations occupied during the NOAA Ship SURVEYOR cruise (VENTS - GORDA SURVEY, RP-15-SU-85A) in May, 1985. Stations numbered are referred to with a "GR#" prefix in the text. (map prepared by P. Rona for a news item submitted to EOS [Baker et al., 1985]).

TABLE 1. STATION SUMMARY FOR SAMPLES COLLECTED DURING "VENTS - GORDA
SURVEY" ON NOAA SHIP SURVEYOR, CHIEF SCIENTIST - DR. E. T. BAKER

Dr. Robert W. Collier, P.I.

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| STN# | DATE | SITE DESCRIPTION | LATITUDE | LONGITUDE | DEPTH (meters) |
|------|---------|------------------------|-----------|------------|-------------------|
| GR1 | 5/09/85 | CASCADIA DEPRESSION | 43°44.1'N | 128°41.3'W | 3510m |
| GR2 | 5/10/85 | OFF-AXIS WEST | 42°22.9′ | 127°23.3′ | 2693 |
| GR3 | 5/11/85 | AXIAL, OFFSET BASIN | 42°23.5′ | 127°04.4′ | 3201 |
| GR4 | 5/12/85 | AXIAL, N. OFFSET BASIN | 42°25.0′ | 126°56.7′ | 3204 |
| GR5 | 5/13/85 | AXIAL, S. OFFSET BASIN | 42°03.6′ | 127°08.3′ | 3485 |
| GR5A | 5/19/85 | (reoccupation of GR5) | 42°03.4′ | 127°09.1 | 3666 |
| GR6 | 5/18/85 | OFF-AXIS EAST | 41°57.7′ | 126°35.9′ | 3497 |
| GR9 | 5/16/85 | AXIAL, ESCANABA OFFSET | 41°30.7′ | 127°26.7′ | 3438 |
| GR10 | 5/15/85 | N. ESCANABA | 41°00.6′ | 127°31.2′ | 3322 |
| GR13 | 5/19/85 | S. NARROWGATE | 42°12.7′ | 127°05.4′ | 3037 |
| GR14 | 5/20/85 | N. NARROWGATE | 42°44.7′ | 126°43.7′ | 3007 |
| GR15 | 5/20/85 | N. AXIAL | 42°57.1′ | 126°35.0′ | 3373 |

A variety of the hydrothermal tracers previously discussed demonstrated the presence of active hydrothermal venting along the Gorda Ridge. The "strength" of the signals was generally weak at the southern end of the ridge system, intermediate in the central region, and relatively high near the northern end of the ridge axis. The major hydrothermal signals were found at the sites GR14 and GR15 and included T-S anomalies, strong light scattering layers, very high concentrations of Mn, ²²²Rn and particulate metals. These two sites became the object of the follow-up cruise with the WECOMA.

Manganese. The concentrations of Mn determined at sea are presented in Figs. 2 and 3. Figure 4 presents overlays of these profiles to aid in their interpretation. The stations GR2, 5A, 6, and 9 (Fig. 4A) represent the background concentrations of Mn in the region. Stations 2 and 6 were collected off-axis with this intent; stations 5A and 9 were located on-axis but showed no evidence of hydrothermal Mn. These are "typical" pelagic profiles for the deep Pacific (Klinkhammer and Bender, 1980) and show very low mid-water concentrations (<1.0 nmol Mn/liter) with a steady increase near the bottom associated with benthic inputs and suspended nepheloid layers.

Station GR10 (Fig. 4B) was the only station occupied in the Escanaba Trough. There is some evidence of elevated Mn concentrations indicating hydrothermal inputs. Station GR5 was located in the axial valley and GR5A was a reoccupation of the station several days later (Fig. 4C). There were significant hydrothermal signals present at GR5 which was located near the east axial wall. GR5A was located in the center of the axial valley and showed no evidence of hydrothermal Mn. <u>These results demonstrate that the hydrothermal signals are spatially heterogeneous and that the absence of a signal in a vertical profile does not eliminate the possibility of near-by hydrothermal circulation.</u>

Stations GR13, 3, 14 and 15 (Fig. 4C) were located in the northern axial valley. The two northern stations, GR14 and GR15 show remarkable Mn maxima which are equivalent to those found associated with "black smoker" vent fields (Lupton et al. 1980). The vertical structure seen in the hydrothermal Mn at GR14 was directly matched by thermal and suspended particle "spikes".

<u>Other Metals.</u> GR6 was chosen as a background station off-axis (to the east). The concentrations of trace metals for the deep-waters at this site are presented in Fig. 5. All of these values represent the commonly ex-



Fig. 2. Near-bottom manganese profiles (concentrations reported in nanomol Mn/liter) for stations GRL-GR6 (see Fig. 1). Detailed station locations are given in Table 1. Data are tabulated in Appendix I.



Fig. 3. Near-bottom manganese profiles for stations GR9-GR15 (see Fig. 1).



Fig. 4. Line-drawings overlaying manganese profiles from specific stations. Group A (GR2,5A,6,9) represent the best estimate of "background" concentration and variability. Group B (GR9,10) are from the northern Escanaba Trough. Group C (GR5,5A) are from the axial valley, southern offset basin. Station 5A is a reoccupation of 5 taken 6 days later and is positioned in the center of the valley (5 was taken on the east wall). Group D (GR3,13,14,15) are from the northern axial valley and include the major water column anomalies.



Fig. 5. Near-bottom profiles of total dissolvable trace metals from GR6. This was an off-axis station (east) and represents good "back-ground" profiles.

pected concentrations of these metals in the North Pacific (e.g. Bruland 1980; Gordon et al. 1982). The concentration data for Fe and Zn represent some of the few analyses of these metals available for the Pacific Ocean. We also analyzed water samples from the complete water column at station GR13 and these results are shown in Fig. 6. The vertical distribution of Mn shows a broad maximum centered at 2000 meters depth. This is too shallow to be associated with any local inputs from the Gorda Ridge but it is at the same depth as the major hydrothermal plume on the Juan de Fuca Ridge, located over 300 miles to the north (Massoth et al, 1982, Lupton et al, 1985). It is possible that Mn is transported along isopycnals and this would be similar to the broad helium concentration maximum seen in the region.

The concentrations of other metals in the two hydrothermal plumes are shown in Figs. 7 and 8. Large hydrothermal inputs of Mn and Fe are apparent at both stations although the ratio of Fe/Mn is lower at GR14. The upcast collected at GR15 showed that the CTD had moved out of the plume after drifting 2 km to the southwest. This variability is similar to that demonstrated at GR5. No other strong hydrothermal inputs of metals were observed. There is some indication of the removal of Cu, Ni and Cd from the water column <u>under</u> the hydrothermal plume at GR15 (Fig. 8) which might reflect scavenging of these metals by the hydrothermal iron amd manganese oxides.

B. WECOMA Cruise (W8508AA).

In an attempt to locate the origin of the hydrothermal signals discovered during the SURVEYOR cruise, the Gorda Ridge Technical Task Force recommended another cruise to the northern sites GR14 and GR15 (Fig. 9). This cruise (August 1-7, 1985) was schedule to conclude before the USGS cruise to the area on the R/V LEE in hopes of providing better targets for camera and dredge sampling. The samples collected on the WECOMA cruise included extensive CTD work with rossette samples; hydrocasts; and gravity cores. In order to maximize areal coverage with the CTD, we raised and lowered the instrument through the bottom 400 meters of the water column while making headway with the ship (~1 kt). This "harrowing" yet very successful procedure (which gives most CTD owners nightmares) has been named "tow-yoing". The station positions for this cruise are outlined in Figure 10 and the specific activities are given in Table 2.



Fig. 6. Full water column profiles of total dissolvable trace metals from GR13. This station was also a good "background" station. The concentration are consistent with other Pacific data (e.g. see summaries within Wong et al., 1983).



Fig. 7. Near-bottom profiles of total dissolvable metals at GR14. This was the station with the first major hydrothermal anomaly discovered. Note the order-of-magnitude increase in manganese concentrations (compared to background stations).



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Fig. 8. Near-bottom profiles of total dissolvable metals at GR15. This station also shows strong hydrothermal anomalies (metals and nephels).



Fig. 9. Reproduction from Seabeam data of the northern Gorda Ridge hydrothermal sites identified during the SURVEYOR cruise and reoccupied during the WECOMA cruise (W8508AA).



Northern Gorda Ridge Hydrothermal Survey R/V WECOMA (W8508AA) 8/1-7/1985

Fig. 10. Bathymetric map (reproduced from Fig. 9) including stations occupied during W8508AA in August, 1985. Solid lines are the tracks of "two-yo'd" CTD casts, hydrocasts are noted as HC#, SURVEYOR stations GR14 and GR15 are noted in circles, a bathymetric transect (12 kHz) was run (Fig. 11) and is shown with a wavey line marked "A" - "B".

| STATION | DATE | TIME (GMT |) LAT | LONG | COMMENTS |
|-----------|--------|-----------|-----------|------------|----------------------|
| GC1 | 8/2/85 | 1145 | 42°43.6′ | 126°43.8′ | no core |
| CTD1 | | 1458 | 44.42 | 40.60 | 10 casts, 12 samples |
| CTD2 | | 2245 | 46.0 | 38.9 | 10 casts, 12 samples |
| HYDRO1 | 8/3/85 | 0535 | 44.9 | 42.3 | 8 samples |
| GC2 | | 0820 | 44.6 | 42.9 | no core |
| GC3 | | 0959 | 43.2 | 43.7 | no core |
| CTD3 | | 1422 | 47.16 | 38.61 | 10 casts, 12 samples |
| CTD4 | | 2057 | 49.4 | 36.9 | 13 casts, 12 samples |
| GC4 | 8/4/85 | 0830 | 42°56.6′ | 126°32.1′ | 119 cm from 3109m |
| GC5 | | 1113 | 56.5 | 32.1 | 155cm from 3109m |
| CTD5 | | 1448 | 57.46 | 29.45 | 23 casts, 12 samples |
| HYDRO2 | 8/5/85 | 0338 | 42°46.2′ | 126°39.12′ | 8 samples |
| GC6 | | 0555 | 57.3 | 34.2 | 107cm from 3412m |
| CTD6 | | 0745 | 58.9 | 34.6 | 10 casts, 12 samples |
| HYDRO3 | | 1514 | 56.88 | 34.59 | 8 samples |
| GC7 | | 1758 | 55.9 | 36.2 | no core |
| CTD7 | | 2118 | 56.30 | 31.87 | 12 casts, 12 samples |
| (CTD8 abo | cted) | | | | |
| CTD9 | 8/6/85 | 0504 | 42°56.94′ | 126°32.42′ | 8 casts, 12 samples |
| GC8 | | 1025 | 43°01.1′ | 126°36.4′ | 184cm from 3162m |
| GC9 | | 1244 | 43°01.8′ | 126°34.7 | 227cm from 3096m |
| HYDRO4 | | 1505 | 42°56.58′ | 126°33.14′ | 8 samples |
| CTD10 | | 1845 | 53.92 | 38.29 | 8 casts, 12 samples |
| CTD11 | 8/7/85 | 0145 | 42°45.00′ | 126°41.65′ | 9 casts, 12 samples |
| HYDRO5 | | 0644 | 46.27 | 42.39 | 8 samples |
| CTD12 | | 0912 | 45.80 | 41.80 | 2 casts, 12 samples |

TABLE 2. W8508AA POST-CRUISE STATION SUMMARY

1. (A 10.)

Thermal Anomalies. Over 111 "tow-yoed" casts were made with the CTD at stations GR14 and GR15. Numerous small temperature anomalies were detected as well as several large anomalies. The strongest thermal anomalies were sampled on CTD casts near station GR14. These included CTD2, CTD11, and CTD12 near the bathymetric section shown in Figure 11. Notice that these signals are clearly lifted well off the bottom (>200 meters) which may suggest they are expressions of a hydrothermal input which carries considerable buoyancy flux (Lupton et al, 1985). Figure 12 shows temperature, salinity, and light transmission data for a typical "background" station. The full water column potential temperature and salinity data are shown on the left hand side of the figure. These are typical data for the the North East Pacific. The right hand side of Figure 12 shows the same properties over an expanded (near-bottom) depth range. Potential temperature (θ) and salinity are linearly related over these depth ranges (Fig 10, bottom right). Any significant input of hydrothermal fluids to the deep ocean will dramatically alter these simple relationships. In order to remove " θ -S" variations from the potential temperature signal and to amplify the hydrothermal signal, it is now common practice to subtract the "anticipated" temperature (calculated from the measured salinity) from the the measured temperature. The result is an estimate of the "temperature anomaly" present due to hydrothermal inputs. Figure 13 is a cast from CTD11 which shows the strongest anomaly sampled (~30 millidegrees). Figure 13A and B are examples of the real-time data available on the ship as the tow proceeds. The linear θ -S relationship is dramatically altered (Fig. 13C). High particle concentrations are also associated with this hydrothermal layer as evidenced by a drop in light transmission. Even though this plume appears to be rising in in the water column as seen in progressive casts, it is dynamically stable (no density inversions) which suggests it has probably reached its equilibrium isopycnal depth. Notice that the anomaly in Fig. 13D is made up of both higher temperature and higher salinity water. Salinity normally increases with depth in this environment. As the warm, buoyant water rises, it mixes with this water resulting in a dynamically stable mixture of saline, warm water.

<u>Manganese.</u> Samples were collected from these plumes for dissolved Mn and other metal analyses. All Mn deteminations were performed on acidified samples within 36 hours of returning into Newport, Oregon on the WECOMA. Fig. 14 shows a vertical profile of Mn concentrations taken during CTD12 at



Fig. 11. Bathymetrtic transect (12 kHz record) running normal to the ridge axis (west to east) through GR14. Region of hydrothermal anomalies detected on CTD11 and 12 is shown. Point A on the line is located at $42^{\circ}46.06'$ N and $126^{\circ}43.85'$ W. Point B is at $42^{\circ}44.61$ "N and $126^{\circ}37.49'$ W. See Fig. 10.



Fig. 12. General temperature, salinity and transmissometry data from CTD10 in the central axis of the north basin (Fig. 10). This station represents a good "background" data set. See text for discussion of parameters.



Fig. 13. Potential temperature, salinity and light transmission data from station GR14 (Collected 8/6/85 from R/V WECOMA). Parts A and B are copies of the video output available on board during the actual CTD cast and C and D are plots of the complete digitized data set for one cast. "T-ANOM" represents the deviation of the water mass from the ambient T-S systematics expressed in temperature units (see text). It can be seen from the data in D that this anomaly is dynamically stable and contains warm, high salinity water entrained as the plume rises from its source. 22



Fig. 14. Reactive Mn concentrations in samples collected during CTD12 (cast 2, up). The right side of the figure is data similar to Fig. 13 (top). Note that the strong thermal anomaly detected on the down cast was significantly weaker (and somewhat higher in the water column) during the upcast when the samples were collected. The "dots" running horizon-tally across this record are due to CTD noise generated when tripping sample bottles.

station GR14. Also shown are the temperature anomalies and transmissometer data in the plume. The deep water around the site shows ubiquitous high concentrations of Mn with higher concentrations within the major temperature anomalies.

Other Metals. The concentrations of the other trace metals sampled during CTD12 are shown in Figure 15. Again, significant inputs of Mn and Fe are seen with little or no enrichment of other metals.

Several wire hydrocasts were collected for ²²²Rn analysis (D. Kadko, OSU) and the concentrations of Mn in these profiles are presented in Fig. 16. Very high Mn was detected in hydrocast #4 (east of GR15) and this was associated with with the highest radon counted during the cruise. Since ²²²Rn has a half-life of only 3.6 days, these samples must have been collected close to an active or very strong source (see open file report by D. Kadko). Although the strongest temperature anomalies were sampled at GR14, the GR15 site was surveyed much less extensively and signals such as this radon data suggest that it may have similar or greater hydrothermal inputs. A tabulated summary of all metal concentrations is given in the Appendix.

V. <u>CONCLUSIONS</u> A large set of seawater samples were collected at the Gorda Ridge spreading center and analyzed for dissolved and total Mn, Fe, Cu, Ni, Cd and Zn. Conclusive evidence of active hydrothermal venting was demonstrated by numerous concentration anomalies for Mn and Fe. There were no detectable inputs of other trace metals. The background concentrations and regional variability was established for all of these metals in the Gorda Ridge survey area. These metal data are supported by a large amount of other physical and chemical measurements, all of which show significant hydrothermal effects.

VI. <u>ACKNOWLEDGEMENTS</u>. This research (DOGAMI contract # 63-630-8506) was funded by the U.S. Minerals Management Service in a cooperative agreement with the Oregon Department of Geology and Mineral Industries. The grant was awarded through the Gorda Ridge Technical Task Force. The NOAA VENTS program scientists contributed significant shiptime, technical support, and data on their SURVEYOR cruise to accomplish the initial survey on the ridge.



Fig. 15. Total dissolvable metal concentrations from the lower water column samples collected during CTD12 (see Fig. 14). These could be compared to Fig. 7 from the SURVEYOR occupation of GR14.



Fig. 16. Manganese profiles from the Radon-222 hydrocasts (D. Kadko,OSU) collected during W8508AA.

D. Caldwell and J. Huyer made the OSU CTD available in spite of the relatively high risk of our operations in this environment. We would like to thank the officers and crew of the NOAA Ship SURVEYOR and the OSU R/V WECOMA for their skilled and friendly support.

VII. <u>REFERENCES.</u>

- Bender, M.L., G.P. Klinkhammer, and D.W. Spencer. 1977. Manganese in seawater and the marine manganese balance. Deep-Sea Res. 24:799-812.
- Boyle, E., S.S. Huested, and S. Jones. 1981. On the distribution of Cu, Ni, and Cd in the surface waters of the North Atlantic and North Pacific Oceans. J. Geophys. Res. 86:9844-9858.
- Bruland, K.W. 1980. Oceanographic distributions of Cd, Zn, Ni, and Cuin the North Pacific. Earth Planet. Sci. Lett. 47:177-198.
- Edmond, J.M., K.L. Von Damm, R.E. McDuff, and C.L. Measures. 1982. Chemistry of hot springs on the East Pacific Rise and their effluent dispersal. Nature 297:187-191.
- Gordon, R.M., J.M. Martin, and G.A. Knauer. 1982. Iron in Northeast Pacific waters. Nature 299:611-612.
- Klinkhammer, G.P. 1980. Determination of manganese in seawater by flameless atomic absorption spectrometry after preconcentration with 8-hydoxyquinone in chloroform. Anal. Chem. 52:117-120.

______ and M.P. Bender. 1980. The distribution of manganese in the Pacific Ocean. Earth. Planet. Sci. Lett. 46:361-384.

_______, M.P. Bender, and R.F. Weiss. 1977. Hydrothermal manganese in the Galapagos Rift. Nature 269:319-320.

, P. Rona, M. Greaves, and H. Elderfield. 1985. Hydrothermal manganese plumes in the Mid-Atlantic Ridge rift valley. Nature 324:727-731.

- Lupton, J.E., G.P. Klinkhammer, W.R. Normark, R. Haymon, K.C. MacDonald, R.F. Weiss and H. Craig. 1980. Helium-3 and manganese at the 21°N East Pacific Rise hydrothermal site.
- Lupton, J.E., J.R. Delaney, H.P. Johnson, and M.K. Tivey. 1985. Entrainment and vertical transport of deep-ocean water by buoyant hydrothermal plumes. Nature 316:621-623.
- Massoth, G.J., R.A. Feely, and H.C. Curl. 1982. Hydrothermal manganese over the Juan de Fuca and Gorda Ridges. EOS 63:999 (abstract).
- Massoth, G.J., E.T. Baker, R.A. Feely and H.C. Curl. 1984. Hydrothermal signals away from the Southern Juan de Fuca Ridge. EOS 65:1112 (abstract)

- Rona, P.A., K. Bostrom, L. Laubier, and K.L. Smith (eds.) 1983. <u>Hydrothermal Processes at Seafloor Spreading Centers.</u> NATO conf. Ser. 4: Mar. Sci. V.12. Plenum.
- Von Damm, K.L., J.M. Edmond, B. Grant, C.I. Measures, B. Walden, and R.F. Weiss. 1985. Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. Geochim. Cosmochim. Acta 49:2197-2220.
- Weiss, R.F., P. Lonsdale, J.E. Lupton, A.E. Bainbridge, and H. Craig. 1977. Hydrothermal plumes in the Galapagos Rift. Nature 267:600-603.
- Wong, C.S., E. Boyle, K.W. Bruland, J.D. Burton, and E.D. Goldberg (eds.). 1983. <u>Trace Metals in Seawater.</u> NATO Conf. Ser. 4: Mar. Sci. V.9. Plenum.

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APPENDIX I

This Appendix lists pertinent data from both the Surveyor (NOAA) and Wecoma (OSU) Gorda Ridge cruises. Stations listed are Surveyor-GR1,2,3,5,5A,6,9,10,13,14,15 and Wecoma-CTD6,11,12 - Hydrocasts 1,2,4,5. Depths, in meters, below the ocean surface are listed as negative

numbers. Metal concentrations are nM (nmol metal/liter seawater). Wecoma Station 11 (CTD11) contains metal analysis of filtered and unfiltered samples. Dissolved iron concentrations are generally 25% less than particulate iron levels. Other metals show no significant variation between dissolved and particulate metal concentrations.

Radon data given in Wecoma hydrocasts are from Dr. D. Kadko, College of Oceanography, OSU.

| DEDELL | N TO KT N# | | MANCANECE |
|----------|------------|---------|-----------|
| -DEPTH | NISKIN# | SAMPLE# | MANGANESE |
| 1 -2620 | 10 | 1.19 | 0.9 |
| 2 -2631 | 19 | 1.04 | 0.6 |
| 3 -2732 | 9 | 1.14 | 0.8 |
| 4 -2834 | 8 | 1.17 | 0.6 |
| 5 -2845 | 20 | 1.09 | |
| 6 -3047 | 28 | 1.05 | 0.6 |
| 7 -3054 | 5 | 1.06 | 3.1 |
| 8 -3139 | 26 | 1.16 | 2.2 |
| 9 -3241 | 6 | 1.07 | 2.1 |
| 10 -3251 | 22 | 1.01 | 2.4 |
| 11 -3342 | 3 | 1.13 | 1.0 |
| 12 -3355 | 34 | 1.11 | 1.2 |
| 13 -3395 | 23 | 1.08 | 0.9 |
| 14 -3423 | · 2 | 1.02 | 1.1 |
| 15 -3500 | 1 | 1.18 | 4.6 |
| 16 -3500 | 25 | 1.10 | 4.9 |

GR2

GR1

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| | -DEPTH | NISKIN# | SAMPLE# | MANGANESE |
|---|--------|---------|---------|-----------|
| 1 | -1775 | 25 | 2.07 | 1.1 |
| 2 | -1975 | 9 | 2.08 | 0.7 |
| 3 | -2088 | 7 | 2.02 | 1.0 |
| 4 | -2175 | 6 | 2.12 | 1.0 |
| 5 | -2290 | 5 | 2.11 | 0.7 |
| 6 | -2494 | 3 | 2.06 | 0.7 |
| 7 | -2597 | 2 | 2.01 | 1.1 |

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GR3

| | -DEPTH | NISKIN# | SAMPLE# | MANGANESE |
|----|--------|---------|---------|-----------|
| 1 | -2301 | 34 | 3.16 | 3.3 |
| 2 | -2429 | 1 | 3.17 | 3.9 |
| 3 | -2529 | 20 | 3.12 | 3.5 |
| 4 | -2579 | 6 | 3.11 | 2.7 |
| 5 | -2679 | 28 | 3.21 | 2.5 |
| 6 | -2778 | 22 | 3.18 | 3.4 |
| 7 | -2779 | 5 | 3.07 | 2.2 |
| 8 | -2879 | 18 | 3.10 | 2.3 |
| 9 | -2980 | 23 | 3.01 | 2.3 |
| 10 | -3009 | 2 | 3.06 | 1.6 |
| 11 | -3113 | 26 | 3.04 | 1.9 |
| 12 | -3191 | 1 | 3.02 | 1.7 |
| 13 | -3191 | 19 | 3.22 | 1.6 |
| | | | | |

| DEPTH | NISKIN | SMPL | Mn |
|----------|--------|------|-----|
| | | 5.08 | 1.2 |
| 1 -2075 | 23 | | |
| 2 -2228 | 34 | 5.18 | 2.1 |
| 3 -2331 | 10 | 5.17 | 2.2 |
| 4 -2485 | 20 | 5.06 | 2.2 |
| 5 -2627 | 28 | 5.04 | 2.2 |
| 6 -2637 | 8 | 5.12 | 1.9 |
| 7 -2785 | 7 | 5.13 | 1.9 |
| 8 -2791 | 22 | 5.01 | 2.3 |
| 9 -2891 | 6 | 5.16 | 1.5 |
| 10 -2945 | 18 | 5.05 | 1.9 |
| 11 -2990 | 5 | 5.11 | 2.2 |
| 12 -3090 | 4 | 5.07 | 1.8 |
| 13 -3098 | 31 | 5.03 | 3.8 |
| 14 -3190 | 3 | 5.14 | 5.4 |
| 15 -3252 | 19 | 5.09 | 1.1 |
| 16 -3313 | 26 | 5.02 | 4.7 |
| 17 -3343 | 2 | 5.10 | 4.3 |
| 18 -3475 | - 1 | 5.15 | 4.3 |
| 19 -2990 | 5 | 5.11 | 1.3 |
| 20 -3090 | 4 | 5.07 | 1.5 |
| 21 -3190 | 3 | 5.14 | 3.4 |
| 22 -3343 | 2 | 5.10 | 3.5 |
| | 1 | 5.15 | 4.3 |
| 23 -3475 | 1 | 2.12 | د |

| GR5A | | | |
|----------|---------|---------|-----------|
| -DEPTH | NISKIN# | SAMPLE# | MANGANESE |
| 1 -223 | 4 | 51.10 | 0.5 |
| 2 -2412 | 5 | 51.06 | 0.4 |
| 3 -2880 | 34 | 51.01 | 0.7 |
| 4 -3009 | 3 | 51.07 | 0.2 |
| 5 -3012 | 23 | 51.02 | 0.4 |
| 6 -3111 | 28 | 51.17 | 0.3 |
| 7 -3172 | 6 | 51.14 | 0.7 |
| 8 -3255 | 22 | 51.08 | 1.3 |
| 9 -3362 | 31 | 51.09 | 1.0 |
| 10 -3374 | 2 | 51.05 | 1.2 |
| 11 -3469 | 20 | 51.03 | 1.2 |
| 12 -3476 | 2 | 51.12 | 1.5 |
| 13 -3569 | 19 | 51.16 | 1.6 |
| 14 -3656 | 26 | 51.15 | 2.0 |

GR5

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| -DEPTH | SAMPLE# | MAN GA NESE | IRON | COPPER | NICKEL | CADMIUM | ZINC |
|---------|---------|-------------|------|---------------------------|--------|---------|------|
| 1 -2131 | 6.09 | 0.6 | 8.3 | 5 . 1 ⁻ | 10.8 | 0.84 | 8.0 |
| 2 -2318 | 6.08 | 0.6 | 10.1 | 3.7 | 8.7 | 0.89 | |
| 3 -2473 | 6.07 | 0.5 | 14.1 | 3.8 | 10.0 | 0.89 | 7.8 |
| 4 -2677 | 6.06 | 0.4 | 20.8 | | 9.7 | 0.89 | 8.4 |
| 5 -2880 | 6.05 | 0.2 | 17.4 | 3.9 | 9.6 | 0.90 | 8.1 |
| 6 -3083 | 6.04 | 0.3 | 21.0 | 4.0 | 9.2 | 0.89 | 6.8 |
| 7 -3288 | 6.03 | 0.8 | 37.6 | 4.2 | 9.8 | 0.90 | 7.4 |
| 8 -3487 | 6.02 | 2.0 | 29.5 | 4.6 | 9.2 | 0.85 | 8.7 |

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GR9

32

GR10

| i i | | -DEPTH | NISKIN# | SAMPLE# | MAN GANESE | -DEPTH | NISKIN# | SAMPLE# | MANGANESE |
|-----|----|--------|---------|---------|------------|----------|---------|---------|-----------|
| | 1 | -2341 | 34 | 9.05 | 0.9 | 1 -2076 | 10 | 10.13 | 1.7 |
| | 2 | -2486 | 10 | 9.16 | 0.5 | 2 -2224 | 34 | 10.06 | 2.2 |
| | 3 | -2496 | 23 | 9.06 | 0.6 | 3 -2274 | 9 | 10.08 | 1.1 |
| | 4 | -2651 | 28 | 9.03 | 0.6 | 4 -2372 | 20 | 10.07 | 2.2 |
| | 5 | -2718 | 7 | 9.15 | 0.5 | 5 -2471 | 8 | 10.11 | 1.3 |
| | 6 | -2806 | 22 | 9.04 | 0.6 | 6 -2521 | 28 | 10.02 | 1.0 |
| | 7 | -2815 | 6 | 9.14 | 0.4 | 7 -2660 | 7 | 10.10 | 1.0 |
| | 8 | -2961 | 31 | 9.02 | 0.6 | 8 -2669 | 22 | 10.03 | 1.0 |
| | 9 | -3025 | 5 | 9.13 | 0.7 | 9 -2761 | 6 | 10.18 | 1.9 |
| | 10 | -3116 | 18 | 9.08 | 1.6 | 10 -2835 | 31 | 10.05 | 1.8 |
| | 11 | -3125 | 4 | 9.12 | 1.4 | 11 -2854 | 5 | 10.12 | 1.7 |
| | 12 | -3220 | 3 | 9.11 | 1.6 | 12 -2935 | 18 | 10.04 | 2.6 |
| | 13 | -3271 | 19 | 9.07 | 2.1 | 13 -3004 | 4 | 10.16 | 1.9 |
| | 14 | -3321 | 2 | 9.10 | 2.6 | 14 -3085 | 19 | 10.15 | 2.2 |
| | 15 | -3428 | 26 | 9.01 | 3.0 | 15 -3119 | 3 | 10.17 | 2.7 |
| | 16 | -3428 | 1 | 9.09 | 2.6 | 16 -3212 | 2 | 10.09 | 1.9 |
| | 17 | -2651 | 28 | 9.03 | 0.3 | 17 -3312 | 26 | 10.01 | 1.9 |
| | 18 | -2806 | 22 | 9.04 | 0.5 | | | | |
| | 19 | -2961 | 31 | 9.02 | 0.6 | | | | |
| | 20 | -3428 | 26 | 9.01 | 3.0 | | | | |

GR6

| L. | -11J | | | | | | | |
|----|--------|---------|-----------|------|--------|--------|---------|------|
| | -DEPTH | SAMPLE# | MANGANESE | IRON | COPPER | NICKEL | CADMIUM | ZINC |
| 1 | -62 | 13.10 | 0.9 | 23.3 | 2.5 | 5.8 | 0.68 | 3.9 |
| 2 | -315 | 13.07 | 0.7 | 11.7 | 2.2 | 6.6 | 0.80 | 4.9 |
| 3 | -618 | 13.06 | 0.9 | 12.6 | 2.1 | 7.8 | 0.88 | 5.8 |
| 4 | -921 | 13.03 | 0.6 | 9.0 | 2.4 | 8.8 | 0.91 | 7.6 |
| 5 | -1225 | 13.01 | 0.5 | 9.1 | 3.1 | 9.2 | 1.00 | 7.9 |
| 6 | -1528 | 13.19 | 0.7 | 8.1 | 3.0 | 9.8 | 0.91 | 7.6 |
| 7 | -1981 | 13.15 | 1.3 | 9.0 | 3.8 | 9.4 | 0.91 | 9.5 |
| | -2234 | 13.05 | 1.2 | 16.7 | 4.4 | 9.6 | 0.85 | 10.2 |
| | -2437 | 13.12 | 1.0 | 17.9 | 4.3 | 11.0 | 0.90 | |
| | -2532 | 13.09 | 1.2 | 23.6 | 4.2 | 9.1 | 0.80 | 7.5 |
| | -2634 | 13.16 | 0.9 | 21.9 | 4.2 | 9.4 | 0.88 | 11.7 |
| | -2735 | 13.18 | 0.8 | 21.6 | 4.4 | 9.7 | 0.89 | 8.5 |
| | -2840 | 13.11 | 0.6 | 21.6 | 4.3 | 10.1 | 0.84 | 11.7 |
| - | -2941 | 13.13 | 0.100E+00 | 19.8 | 4.2 | 9.3 | 0.90 | 9.2 |
| | -2941 | 13.02 | 0.3 | 22.9 | 4.2 | 9.8 | 1.00 | 8.2 |
| - | -3027 | 13.04 | 0.7 | 24.9 | 4.4 | 8.9 | 0.80 | 9.8 |

GR14

| -DEPTH | NISKIN# | SAMPLE# | MANGANESE | IRON | COPPER | NICKEL | CADMIUM |
|-----------------|---------|---------|-----------|-------|--------|--------|---------|
| 1 -2466 | 2 | 14.14 | 4.1 | 29.8 | 4.3 | 8.9 | 0.75 |
| 2 -2568 | 31 | 14.10 | 5.5 | 32.4 | 5.3 | 9.0 | 0.68 |
| 3 -2720 | 20 | 14.12 | 6.5 | 34.6 | 3.7 | 10.0 | 0.71 |
| 4 -2761 | 7 | 14.06 | 9.9 | | • | | |
| 5 -2762 | 2 | 14.05 | 10.2 | 70.9 | 4.2 | 9.2 | |
| 6 -2787 | 5 | 14.03 | 8.1 | 63.7 | 3.7 | 10.1 | 0.70 |
| 7 -2837 | 4 | 14.15 | 10.1 | 65.2 | 3.7 | 9.2 | 0.69 |
| 8 - 2868 | 10 | 14.11 | 7.6 | 138.3 | 3.7 | 9.1 | 0.72 |
| 9 - 2888 | 2 | 14.07 | 9.4 | 56.7 | | 11.0 | 1.06 |
| 10 -2997 | 1 | 14.16 | 7.2 | | | | |
| 11 -2997 | 1 | 14.01 | 7.1 | 41.4 | 3.7 | 9.0 | 0.7179 |

GR15

| -DEPTH | SAMPLE# | MANGANESE | IRON | COPPER | NICKEL | CADMIUM | ZINC |
|-----------|---------|-----------|------|--------|--------|---------|------|
| 1 -2832 | 15.06 | 10.2 | 48.9 | 4.4 | 9.8 | 0.84 | 7.3 |
| 2 -2999 | 15.02 | 9.1 | 39.5 | 5.6 | 9.4 | 0.99 | 10.9 |
| 3 -3082 | 15.04 | 7.4 | 40.4 | 4.3 | 9.1 | 0.85 | 13.2 |
| 4 -3165 | 15.10 | 4.0 | 36.7 | 3.9 | 8.7 | 0.85 | 8.7 |
| 5 -3264 | 15.08 | 3.7 | 27.3 | 4.0 | 8.9 | 0.80 | 10.8 |
| 6 -3363 | 15.05 | 3.5 | 24.4 | 4.5 | 10.2 | 0.86 | 7.8 |
| 7 -2953 · | 15.07 | 0.2 | | | | | |
| 8 -3286 | 15.01 | 5.3 | | | | | |

| -DEPTH | CAST# | SAMPLE# | MANGANESE |
|-----------------|-------|---------|-----------|
| 1 -3049 | 3.2 | 6.1 | 3.7 |
| 2 -2857 | 3.2 | 6.2 | 12.3 |
| 3 -2759 | 3.2 | 6.3 | 13.5 |
| 4 -2759 | 6.1 | 6.4 | 10.0 |
| 5 -2857 | 6.1 | 6.5 | 11.9 |
| 6 -3053 | 6.1 | 6.6 | 5.0 |
| 7 -3072 | 8.2 | 6.7 | 5.5 |
| 8 -2867 | 8.2 | 6.8 | 11.3 |
| 9 -266 2 | 8.2 | 6.9 | 11.4 |
| 10 -3053 | 10.2 | 6.10 | 8.9 |
| 11 -2867 | 10.2 | 6.11 | 7.8 |
| 12 -2662 | 10.2 | 6.12 | |
| | | | |

CTD12

| -DEPTH | SAMPLE# | MANGANESE | IRON | COPPER | NICKEL | CADMIUM |
|----------|---------|-----------|------|--------|--------|---------|
| 1 -2220 | 1.11 | 2.3 | 9.7 | 3.9 | 9.5 | 0.86 |
| 2 -2269 | 1.10 | 3.9 | 12.2 | 4.2 | 9.6 | 0.85 |
| 3 -2321 | 1.9 | 8.4 | | | | |
| 4 -2367 | 1.8 | 9.3 | 20.7 | 4.2 | 9.3 | 0.84 |
| 5 -2416 | 1.7 | 14.2 | 22.1 | 4.4 | 9.9 | 0.89 |
| 6 -2466 | 1.6 | 10.6 | 26.0 | | 11.0 | 0.89 |
| 7 -2515 | 1.5 | 11.5 | | | | |
| 8 -2564 | 1.4 | 12.4 | 30.4 | 4.6 | 10.4 | 0.95 |
| 9 -2613 | -1.3 | 13.0 | 26.2 | 4.4 | 9.8 | 0.85 |
| 10 -2662 | 1.2 | 10.5 | 29.2 | 4.8 | 10.5 | 0.94 |
| 11 -2704 | 1.1 | 10.1 | 26.9 | 4.4 | 10.2 | 0.86 |

| CTD11 | L | | | | | | | | |
|----------|-----|-------|---------|------------|------|--------|--------|---------|------|
| -DEP | РТН | CAST# | SAMPLE# | MAN GANESE | IRON | COPPER | NICKEL | CADMIUM | ZINC |
| 1 -260 |)3 | 1.2 | 11.1 | 11.6 | | | | | |
| 2 -249 | 96 | 2.2 | 11.2 | 11.9 | | | | | |
| 3 -236 | 68 | 2.2 | 11.3 | 7.8 | | | | | |
| 4 -259 | 95 | 3.2 | 11.4 | 12.8 | 25.1 | 3.9 | 9.3 | 0.85 | 10.6 |
| 5 -248 | 86 | 3.2 | 11.5 | 14.9 | 24.9 | 3.9 | 8.8 | 0.82 | 13.0 |
| 6 -247 | 77 | 4.2 | 11.6 | 16.9 | 28.3 | 3.9 | 8.9 | 0.89 | 9.4 |
| 7 -243 | 32 | 4.2 | 11.7 | 17.0 | 25.1 | 4.0 | 8.8 | 0.81 | 8.7 |
| 8 -253 | 35 | 7.2 | 11.8 | 8.4 | | | | | |
| 9 -239 | 90 | 7.2 | 11.9 | 7.1 | | | | | |
| 10 -240 | 30 | 8.1 | 11.10 | 6.1 | | | | | |
| 11 -246 | 62 | 9.2 | 11.11 | 3.0 | | | | | |
| 12 -236 | 63 | 9.2 | 11.12 | 3.8 | | | | | |
| 13 | | | | | | | | | |
| *14 -259 | 95 | 3.2 | 11.4 | | 8.4 | 3.8 | 8.8 | 0.80 | 10.4 |
| *15 -248 | 86 | 3.2 | 11.5 | | 4.8 | 3.3 | 8.2 | 0.83 | 10.7 |
| *16 -247 | 77 | 4.2 | 11.6 | | 6.8 | 3.5 | 8.9 | 0.89 | 10.2 |
| *17 -243 | 32 | 4.2 | 11.7 | | 4.5 | 3.2 | 7.7 | 0.78 | 9.0 |

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*filtered sample

HYDRO1

| -DEPTH | NISKIN# | SAMPLE# | MANGANESE | EXCESS.RN |
|---------|---------|---------|-----------|-----------|
| 1 -2100 | 5 | 1.1 | 6.9 | 0.0 |
| 2 -2175 | 11 | 1.2 | 8.8 | 0.0 |
| 3 -2250 | 12 | 1.3 | 8.9 | 0.3 |
| 4 -2325 | 6 | 1.4 | 3.0 | 3.5 |
| 5 -2400 | 1 | 1.5 | 2.4 | 0.7 |
| 6 -2475 | 4 | 1.6 | 2.2 | 0.0 |
| 7 -2575 | 21 | 1.7 | 1.2 | 11.3 |
| 8 -2625 | 19 | 1.8 | 1.3 | 23.1 |

HYDRO2

| -DEPTH | NISKIN# | SAMPLE# | MANGANESE | EXCESS.RN |
|---------|---------|---------|-----------|-----------|
| 1 -2125 | 1 | 2.1000 | 1.7 | 0.0 |
| 2 -2185 | 4 | 2.2000 | 2.6 | 0.0 |
| 3 -2245 | 21 | 2.3000 | 2.1 | 0.3 |
| 4 -2305 | 11 | 2.4000 | 3.0 | 3.5 |
| 5 -2365 | 5 | 2.5000 | 2.8 | 0.7 |
| 6 -2425 | 12 | 2.6000 | 3.7 | 0.0 |
| 7 -2485 | 6 | 2.7000 | 5.1 | 11.3 |
| 8 -2565 | 19 | 2.8000 | 5.3 | 23.1 |
| | | | | |

HYDRO4

| -DEPTH 1 -2615 2 -2665 3 -2715 4 -2765 5 -2815 6 -2865 7 -2915 8 -2965 | NISKIN# 1 21 11 5 12 6 19 | SAMPLE# 4.1 4.2 4.3 4.4 4.5 4.6 4.7 4.8 | MANGANESE 10.7 11.5 13.1 10.8 11.5 11.2 11.2 12.3 | EXCESS.RN 0.0 2.4 3.3 21.1 8.8 13.0 12.7 |
|--|--|---|---|---|
| 8 -2965 | 19 | 4.8 | 12.3 | 12.7 |

HYDRO5

| -DEPTH | NISKIN# | SAMPLE# | MANGANESE | EXCESS.RN |
|---------|---------|---------|-----------|-----------|
| 1 -2160 | 1 | 5.1 | 2.1 | 0.0 |
| 2 -2260 | 4 | 5.2 | 2.9 | 0.0 |
| 3 -2310 | 21 | 5.3 | 2.7 | 1.4 |
| 4 -2360 | 11 | 5.4 | 1.6 | 0.0 |
| 5 -2410 | 5 | 5.5 | 3.3 | 4.1 |
| 6 -2460 | 12 | 5.6 | 2.9 | 5.9 |
| 7 -2510 | • 6 | 5.7 | 3.6 | 7.4 |
| 8 -2610 | 19 | 5.8 | 5.5 | 7.6 |
| | | 24 | | |

36

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