

This file describes the methods and data format for accompanying individual hydrocast chemistry files in CSV format. The hydrocasts conducted and samples collected on KM0804 by PI Joseph Resing.

## Methods

Hydrocasts were conducted using a Sea Bird 911 plus CTD (Conductivity, Temperature, Depth) augmented with a light scattering sensor (LSS, Seapoint Inc.) and an Oxidation Reduction Potential (ORP) sensor. Discrete water samples were collected using a rosette package with 21 Niskin-type bottles (18.5 L) with standard sampling spigots for gas collection and Teflon stopcocks for trace metal and trace particulate sample collection. The bottles were closed using Teflon coated springs and the endcaps were fitted with Viton O-rings. The CTD cable was a standard steel cable. No special effort was made to clean the niskin bottles. Hydrocasts were conducted as vertical casts with a single round trip between the ship and the depth of interest and as towed hydrocasts in which the CTD-rosette package was raised and lowered as the ship moved along a set course. Light scattering anomalies ( $\Delta$ NTU) are the difference between the light scatter value measured in a plume and that of the local background in nephelometric turbidity units (NTU). The ORP sensor and the Koichi Nakamura eH sensor measure the potential between a platinum electrode and a silver-silver chloride reference electrode. Laboratory experiments demonstrate that this sensor responds to  $\text{Fe}^{2+}$  and sulfide at nanomolar levels. Oxygen levels in seawater (80-200  $\mu\text{M}$ ) compared to the relatively small amounts of  $\text{H}_2\text{S}$  and  $\text{Fe}^{2+}$  (0.1-10  $\mu\text{M}$ ) in the plumes, indicate that this sensor doesn't measure the actual "oxidation reduction potential" of the seawater, but instead must respond to reduced species oxidizing at the surface of the Pt electrode, thereby producing a potential relative to the reference electrode.

Samples for total dissolvable Mn and Fe (TDMn and TDFe) were collected directly from the Teflon stopcocks into 125 mL I-Chem polyethylene bottles, while dissolved Mn and Fe (DMn and DFe) samples were collected as the filtrate from 0.4  $\mu\text{m}$  acid-washed poly-carbonate filters into 125 mL I-Chem polyethylene bottles after the passage of 2 L of water through the filters. The metals samples were then acidified with 0.5 mL of sub-boiling quartz distilled 6N HCl. Mn was determined with a precision of  $\pm 1$  nM by modifying the direct injection method of Resing and Mottl ([*Resing and Mottl*, 1992] by adding 4 g of nitrilo-triacetic acid to each liter of buffer. Fe was determined with a precision of  $\pm 2$  nM by modifying the method of [*Measures et al.*, 1995] for direct injection analysis. Total  $\text{CO}_2$  ( $\text{CO}_2$ ) was sampled and determined by standard methods [DOE, 1994]. pH samples were collected and analyzed as discussed previously [*Resing et al.*, 2004]. Changes in pH ( $\Delta\text{pH}$ ) and  $\text{CO}_2$  ( $\Delta\text{CO}_2$ ) were calculated by subtracting the regional background value of each. Hydrogen sulfide ( $\text{H}_2\text{S}$ ) was determined on samples spectrophotometrically [*Sakamoto-Arnold et al.*, 1986].

Elemental composition of particulate matter was determined by x-ray primary- and secondary-emission spectrometry with a Pd source and Mo, Ti, Ge, and Co secondary targets using a non-destructive thin-film technique [*Feely et al.*, 1991]. Precision averaged 2% for major elements, 7% for trace elements, and 11% for sulfur. Total particulate Sulfur (Total pS) is a combination of elemental sulfur and non-volatile sulfur (pS-NV). It is analyzed under an atmosphere of nitrogen. Elemental sulfur sublimes under a vacuum leaving pS-NV, thus Elemental sulfur is the difference between total pS and the sulfur concentration determined under a vacuum. Particulate compositions are designated by a "p" in front of the element of interest (e.g., particulate Al = pAl). The concentrations and isotopic ratios were determined on samples

sealed into copper tubing[*Young and Lupton, 1983*] followed by analysis on a 21-cm radius, dual-collector mass spectrometer with a precision of  $\pm 2 \times 10^{-17}$  mol kg<sup>-1</sup> in <sup>3</sup>He and  $\pm 0.2\%$  in  $\square^3$ He. Samples for methane concentration were drawn into 140 ml syringes and analyzed on board via a helium head-space technique by gas chromatography within hours of sampling e.g., [*Kelley et al., 1999*].

#### Table Abbreviations Designators

**Cast Type** T = Towed Hydrocast V= Vertical Hydrocast

**Cast Name** is constructed of Cast Type (T or V) Year (YY) Cruise designator (Alpha) number for of operations for a given cast type. So T08A01 is the first towed hydrocast on the A cruise in 2008.

Site Name indicates named seafloor sites

Cast # is the summation of all hydrocasts, Vertical and Towed,

Bottle Position is the position of the Niskin bottle on the Rosette

Niskin# is the Number of the individual Niskin

Date Month Day year

Time 24 hour clock

Press is pressure in Bars

Depth(m) is depth in m calculated from pressure

Temp(oC) is the water temperature

Cond(S/m) is conductivity

Sal(PSS) is Salinity

Theta is potential temperature

Sigma Theta is potential density

ORP is Oxidation Reduction Potential

dNTU (1791) is Nephelometry Turbidity units calculated from Light Scattering Sensor

Alt(m) is the height above bottom that a sample was collected

(V0) Altitude is altitude sensor output voltage

(V1) LSS-10721 is Light scatter sensor output voltage for LSS 10721

(V2) empty

(V3) empty

(V4) Koichi-Eh is Eh Sensor Voltage from Koichi Nokamuras's EH sensor

(V5) LSS-1791 is Light scatter sensor output voltage for LSS 1791

(V6) Ko-Ichi is Eh Sensor Voltage from Koichi Nokamuras's EH sensor

(V7) LSS-11542 is Light scatter sensor output voltage for LSS 11542

KoIchi-Eh (mv) is Oxidation Reduction Potential calculated from Koichi Nokamuras's EH sensor

pH is the pH of Seawater on individual samples on the NBS scale.

CH4(nM) is Methane

H2 is hydrogen

DIC # is the sample number of the Total CO2 sample

DIC Is total CO2

Change in CO2 is calculated from the difference between ambient CO2 and sample CO2

Alkalinity

TDM? \*\*\* indicates that a sample was collected for total Metals

DM? \*\*\* indicates that a sample was collected for dissolved Metals

T<sub>xx</sub> is the Total Dissolvable element where XX is the element (TMn = Total Manganese)  
D<sub>xx</sub> is the Dissolved element concentration where XX is the element (DMn = Dissolved Manganese)  
p<sub>xx</sub> is the particulate concentration for element XX (pMn = Particulate Manganese)  
H<sub>2</sub>S (uM) is Hydrogen sulphide content  
 $\delta(3\text{He})\%$  is the delta Helium isotopic value  
<sup>3</sup>He fMol kg<sup>-1</sup> is the concentration of <sup>3</sup>He in femtomoles/kg seawater  
<sup>4</sup>He  $\mu\text{Mol kg}^{-1}$  is the concentration of <sup>4</sup>He in micromoles/kg seawater  
SEM is the filter number of samples collected for SEM  
Filter# is the filter number for Total Suspended matter analysis by XRF  
Net (mg) is the weight of total suspended matter on the filters  
Vol is the volume of seawater passed through a filter  
 $\mu\text{g/l}$  is the mass concentration of particles on a filter  
Total pS is the concentration of Sulfur determined by XRF at atmospheric pressure  
pS – NV is the concentration of Sulfur determined by XRF under a vacuum  
Elemental pS is the difference in Sulfur concentrations between Total pS and pS –NV

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