

Data Compliance Plan for OCE-0327126, “Temporal Variations in Hydrothermal Fluid Chemistry at 9-10°N East Pacific Rise: Elucidating Ties to Crustal and Biological Processes,” Former PI: K. Von Damm (deceased August 2008); Current PI: J Bryce

The pronounced temporal variability in the 9-10°N East Pacific Rise (EPR) hydrothermal fluids observed by Von Damm since 1991 to 2003, coupled with the changes in the depth of the hydrothermal circulation inferred from the chemical data, led her to propose a time series study of the EPR hydrothermal field around 9°50'N. The purpose of the time series experiments, funded under this R2K grant, was to evaluate three specific hypotheses: (1) changes in the depth of phase separation reflect changes in depth to the heat source; (2) magma has migrated upward and will soon erupt and/or result in another diking event; and (3) changes in fluid compositions, reflecting changes in the pressure-temperature conditions of reaction and phase separation, are the causes of changes in the biological communities. The 2005-2006 eruption in the 9°50'N region clearly confirmed Von Damm's inference from the hydrothermal data that an eruption was imminent.

Of the work outlined in the OCE-037126 proposal and its supplement, four cruises have been completed, under Von Damm's direction, and over four hundred fluid samples were collected. These fluid samples consist of nearly ninety low-temperature (or diffuse-flow) fluids and approximately three hundred fifty high temperature fluids. Major ion chemical data for the 9-10°N fluids have been analyzed, and, accordingly, end member fluid compositions for the major ions have been calculated for each sampled vent.

The project was interrupted by Von Damm's ongoing health issues in 2007-2008, that culminated in a four-month battle with liver cancer that she lost on 15 August 2008. OCE-0327126 was transferred to PI Bryce in September 2008 to enable the completion of the follow-up analytical work. Bryce is also working with Von Damm's two last students (Floencia Prado and Jill McDermott) to complete their M.S. theses. Both McDermott and Prado defended their theses in April 2009, McDermott has filed her M.S. degree and Prado will file her degree this summer. McDermott, Prado and Bryce will present results of the time-series work in the Goldschmidt 2009 special session co-convened by Bryce to honor Von Damm's contributions to marine geoscience.

1.2 Study site and Sampling Strategies

The samples collected during this grant period comprise the last sampling of hydrothermal fluids from the eruption cycle that began in 1991, and the first samplings of the fluids following the 2005/6 eruption(s). This is the only site on the global mid-ocean ridge (MOR) where two eruptions have been observed (and sampled). The sample suite therefore comprises a unique sample set for constraining MOR hydrothermal processes. The 2004-2007 samples include those from the following vents: Biovent, M (through 2004), Q (through 2006), Tica, Bio9', Bio9" (through 2004), Bio9, P, Ty, Io, V, U, A and L (Figure 1).

1.3 Temperature, chloride and silica trends in hydrothermal fluids – 9°50'N

The current project has funded the last four years of effort of studying the temperature, chloride and silica compositions of approximately twenty vents. Extending earlier studies (Von Damm, 2004), the vent fluid chloride and silica time series extends for a full eruptive cycle. These data, when coupled with thermodynamic data (e.g., Von Damm et al., 1991; Foustoukous and Seyfried, 2007), can be used to place constraints on the T, P conditions of fluid circulation.

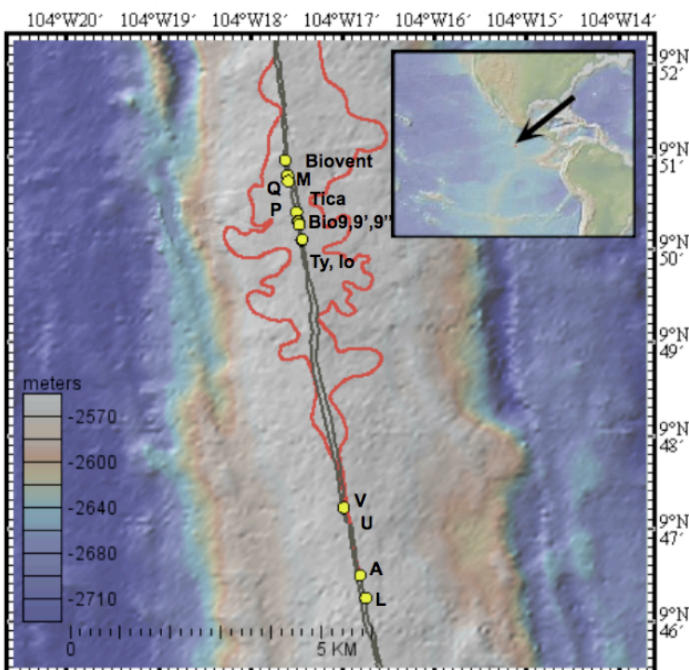


Figure 1. The hydrothermal vent field along the ~9°50'N segment of the East Pacific Rise (EPR). Vents are indicated with yellow symbols, and the red outline denotes the extent of the 2005-2006 magmatic event (cf. Soule et al., 2007). This figure is taken from Prado (2009) and is made using data from Carbotte et al. (2004) and Ryan et al. (2009).

The fluid time-series includes samples with chloride contents $> 1 \text{ mol kg}^{-1}$ and silica contents greater than 20 mmol kg^{-1} . Generally, Cl and SiO_2 contents in all vents evolve non-monotonically with time, emphasizing that every vent represents a unique rock/fluid exchange pathway. These geochemical proxies can contribute to improved high-resolution models of the spatially and temporally variable axial magma chamber dynamics (Carbotte et al., 2008). For example, in the case of M-vent, which had been active since at least 1991, the thermobarometric model indicates P, T conditions suggesting a gradual shoaling of the reaction zone with time until its extinction in 2006, post-eruption.

In addition to the point-measurement temperature data taken during each vent fluid sampling, self-recording temperature probes purchased and initially deployed during Von Damm's previous grant (OCE-0002458), had been deployed prior to the eruption. Several of these loggers were recovered with intact records that covered the eruption period – specifically the M-vent logger- during the post-eruption cruises that were funded by the current grant.

These time-series vent fluid temperature records are part of the integrated Cl, Si, and temperature time-series manuscript that we are currently working on and expect to submit for publication this summer (Von Damm et al., in prep). The data that will be presented in Von Damm et al., in prep, and the back-up fluid geochemical analyses as well as temperature time series records, will be sent to the R2K Data Management Office (DMO) and made available to the community this fall, 2009. These records will also be used to constrain the timing of the eruption(s), and the nature of the perturbations experienced by the hydrothermal system during a full eruptive episode (1991-2005/06).

1.4 Ongoing analyses

Nearly all of the fluid samples collected between 2004 and 2007 require additional metal analyses to decipher the relative significance of phase separation, degassing and water-rock interactions, as outlined in the original proposal. For full quantification for the metals, all three

fractions of each sample (dissolved + suspended + precipitate) must be run. Samples have been analyzed for their Mn, Fe, Cu and Zn contents via flame atomic absorption, but the abundances in many of the samples were too close to the detection limit for this method to provide proper quantification. Accordingly, nearly all of the samples will be re-run over the course of the next year using HR-ICP-MS to complete these elemental budgets. We currently have techniques in place for Cd, Mn, Fe, Cu and Zn and have analyzed a subset of fluids for these elements. Strontium and calcium isotopic analyses, in collaboration with Ian Ridley (USGS), are also planned for the 2004-2007 samples and a subset of earlier 9°50'N samples following the 1991 eruption. These isotopic analyses will be useful for constraining water-rock interactions as well as re-dissolution of anhydrite in the diffuse flow fluids. We expect these data to be available in early 2010.

Both McDermott and Prado used these data in their M.S. theses (timeline for subsequent manuscript submission is late 2009). In addition, we are preparing a manuscript that synthesizes sampled T, Cl and silica contents of EPR hiT vents with the time-series vent temperature measurements made with HOBO loggers provided by Dan Fornari and the WHOI-MISO Facility. The data to be included in this paper are an updated version of those provided by Von Damm (2004, AGU monograph) and will include geochemical analyses for 2004-2007 samples from the following vents: Biovent, M (through 2004), Q (through 2006), Tica, Bio9', Bio9" (through 2004), Bio9, P, Ty, Io, V, U, A and L. The paper in preparation title is: "Vent fluid temperature time-series data and correlative data pre- and post-eruption for high-temperature hydrothermal vents at the East Pacific Rise 9°50'N", authors - Von Damm, Prado, McDermott, Bryce, Lilley, Fornari, Shank. We expect that the data (end-members and back-up geochemical analyses) will be made available digitally through the R2K DMO Data Portal no later than 11/2009. Further questions regarding these data should be directed to Julie Bryce at julie.bryce@unh.edu.

2. THE VON DAMM FLUID COLLECTION

The nearly 2500 hydrothermal fluids in the Von Damm collection include high temperature ("black smoker") fluids as well as low temperature ("diffuse flow") fluids and ambient seawater from a variety of ridge segments (Figure 2). Samples were collected from cruises to hydrothermal systems in the EPR (9-10°N, 21°N), Southern EPR (17° - 22°S), Gorda Ridge, Mid Atlantic Ridge (Lucky Strike and Logatchev), and the Central Indian Ridge (CIR). These ridge segments represent a range of spreading rates, host systems (bare rock vs. ultramafic vs. sediment), and several of the ridge segments (Gorda, EPR and the Southern EPR) were sampled multiple times. The best-developed time series, capturing a full eruptive cycle, are from the 9°50' N region. Table 1 summarizes the cruises for which there are vent fluid samples in Von Damm's former laboratory at UNH, and Table 2 presents the key chemical data from these important specimen. With additional funding, we also hope to make these samples available to the community as well as provide tables of fluid chemical analyses from past Von Damm publications that have used these samples.

In nearly all cases, high-T fluids in the Von Damm collection were sampled using 760mL titanium syringe bottle ('Major') pairs on the *ROV Jason*, *Tiburon* or *DSV Alvin*, depending on the cruise (cf. Table 1). The samples were acquired following methods described in Von Damm et al. (1985, an approach that enables collection of uncontaminated samples for all metals except for titanium). In the case of *Alvin* samples, *in situ* sampling temperatures were recorded using

Alvin's high-temperature probe as well as an inductively coupled link (ICL) temperature device on each pair of sampling bottles after that device was routinely available for cruises post ~2000.

Once on board, samples were acidified with 0.5-1.0 mL of concentrated triple-distilled hydrochloric acid and subsequently stored in high-density polyethylene (HDPE) bottles on the day of sampling. Prior to acidification, splits for shipboard chemical analysis were collected. A challenge in trace metal analysis is the potential for entrainment of precipitating particles within the sampling bottles, and thus the precipitates were rinsed out of the bottles during the sample draw, termed the “dregs” fraction, and saved in HDPE bottles for digestion in the onshore laboratory.

Ambient local (e.g., bottom) seawater samples were also collected utilizing the fluid sampling procedure. Many “major” samples were accompanied with sampling into evacuated “gas tight” vessels. “Gas tight” samples are collected primarily for on-board gas extraction, but major element characterization is also carried out in order to provide a means to calculate end-member gas compositions.

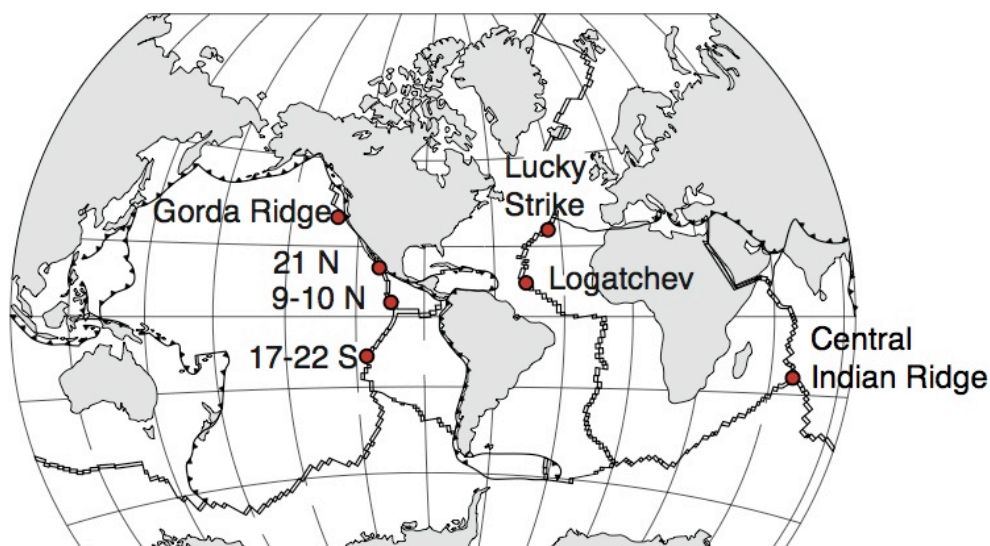


Figure 2. Sites represented in the Von Damm Hydrothermal Fluid Legacy Collection.

Table 1. Scientific cruises upon which vent fluids were collected by Von Damm.

<i>Cruise Name</i>	<i>Year</i>	<i>Cruise ID</i>	<i>Month</i>	<i>Location</i>	<i>Total Samples</i>	<i>Majors</i>	<i>Gas- tights</i>
J. Edmond's 21N	1992	125-39	Mar	21N EPR	17	17	
Adventure1	1991	125-24	Mar-Apr	9 - 10N	169	124	45
Adventure2	1992	125-38	Feb-Mar	9 - 10N	66	43	23
LuckyStrike1993	1993	129-06	Jun	Lucky Strike- MAR	34	17	17
Adventure3	1993	131-08	Dec	9 - 10N	38	27	11
Adventure4	1994	131-11	Mar-Apr	9 - 10N	241	160	81
Adventure5	1994	131-24	Oct	9 - 10N	92	59	33
Adventure6	1995	132-18	Nov	9 - 10N	101	61	40
Legacy	1996	132-25	Apr	9 - 10N	59	56	3
LuckyStrike1996	1996	J176-183	Jul	Lucky Strike- MAR	29	26	3
LuckyStrike1997	1997	AT03-02	Jun-Jul	Lucky Strike- MAR	20	11	9
Adventure7	1997	AT03-10	Oct-Nov	9 - 10N	141	99	42
SOUEPR	1998	AT03-28	Oct-Nov	SEPR	347	243	104
Extreme	1999	AT03-34	May	9 - 10N	24	16	8
9N_Dec1999	1999	AT03-44	Dec	9 - 10N	19	0	19
Guaymas	2000	AT03-46	Jan	9 - 10N	11	0	11
Adventure8	2000	AT03-50	Apr	9 - 10N	68	45	23
Gorda-Seacliff	2000	T186-192	Aug	Gorda Ridge	16	8	8
Gorda-Escanaba	2000	T195-197	Aug	Gorda Ridge	10	5	5
Indian Ocean	2001	kn162-13	Apr	Kairei Field	15	10	5
Indian Ocean	2001	kn162-13	Apr	Edmond Field	12	7	5
Adventure9	2002	AT07-06	Jan	21 N EPR	58	36	22
Adventure9	2002	AT07-06	Jan-Feb	9 - 10N	218	140	78
Gorda2002	2002	T449-456	Aug	Gorda Ridge	24	12	12
STAG	2003	AT07-36	Jun-Jul	TAG-Mid Atlantic	12	12	0
Field-03	2003	AT11-03	Nov	Ridge	70	60	10
PIRATES-1	2004	AT11-09	Mar-Apr	9 - 10N	139	99	40
AT11-20	2004	AT11-20	Nov	9 - 10N	68	50	18
RESET06	2006	AT15-06	Jun-Jul	9 - 10N	48	33	15
AT15-13	2006	AT15-13	Nov-Dec	9 - 10N	146	98	48
AT15-17	2007	AT15-17	Apr	9° 03' OSC	8	8	0
AT15-27	2007	AT15-27	Dec	9 - 10N	175	115	60
<i>Total # of Samples</i>					<i>2495</i>	<i>1680</i>	<i>798</i>

Note: This table represents individual fluid samples. Since 1994, each "Major" sample included three components – the dissolved + suspended + precipitated fractions. Totaling all of these fractions, the Von Damm legacy fluid collection has more than 5000 specimens.

<i>Vent Field/System</i>	<i>Site</i>	<i>Year(s) sampled</i>	<i>Range Max Exit T (°C)</i>	<i>Minimum Mg (mmolkg⁻¹)</i>	<i>EM Cl range (mmolkg⁻¹)</i>	<i>Data Source</i>
Lucky Strike	MAR	1993, 1996	202-333	1.9 – 11.4	436 - 546	Langmuir et al. (1997); Von Damm et al. (1998)
Brandon	SouEPR	1998	376-405	1.0-24.8	317-558	Von Damm et al. (2003)
Escanaba Trough	Gorda	2000, 2002	207 - 218	18.7 - 49.4	632 - 653	Von Damm et al. (2005b)
Sea Cliff	Gorda	2000, 2002, 2004	292 - ≥ 308	1.3-32.2	450-464	Von Damm et al. (2006b)
Karei	CIR	2001	315-365	1.1-9.3	571-620	Gallant & Von Damm (2006)
Edmond	CIR	2001	273-382	1.7-19.1	926-933	Gallant & Von Damm (2006)
Medusa	EPR	2007	335	2.1-19.8	355	Von Damm et al. (in prep)

Table 2. Summary of sample characteristics from selections from the Von Damm Hydrothermal Fluids collection