

Explorer of the Seas METADATA - 2007

Class of Data: Surface ocean carbon dioxide concentrations

Dataset Identifier: AOML_Explorer

Two Files: Explorer_2007_NS
Explorer_2007_EW

Statement of how to cite dataset:

Explorer website: http://www.aoml.noaa.gov/ocd/gcc/explorer_introduction.php

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Measurement platform identifier: Explorer of the Seas

Cruise Information:

Weekly cruises to Bermuda, Canada or through the Caribbean departing from Miami, Florida or Bayonne, New Jersey.

Project Information:

This project was sponsored by the underway pCO₂ on ships project of the NOAA Climate Program and represents a collaboration between Royal Caribbean International, the University of Miami's Rosenstiel School of Marine and Atmospheric Science, the National Oceanic and Atmospheric Administration, the National Science Foundation, the Office of Naval Research, and the National Aeronautics and Space Administration.

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Timestamp for initial submission of dataset: 8/01/08

Timestamp for the most recent update of dataset: 8/01/08

Timestamp period the dataset refers to: 1/07/2007 - 12/01/2007

Geographic area the dataset refers to:

13 N to 46 N
88 W to 60 W

Eastern Cruise Track:

Day 1 - Miami, Florida (25.8 N/80.7 W)
Day 3 - San Juan, Puerto Rico (18.5 N/66.1 W)
Day 4 - Philipsburg, St. Maarten (18.0 N/63.0 W)
Day 5 - Charlotte Amalie, St. Thomas (18.3 N/64.9 W)
Day 7 - Nassau, Bahamas (25.1 N/77.3 W)
Day 8 - Miami, Florida (25.8 N/80.7 W)

Change in Eastern Cruise Track for EX0718E and EX0719E:

Day 1 - Miami, Florida (25.8 N/80.2 W)
Day 3 - Labadee, Haiti (19.8 N/72.3 W)
Day 4 - Ocho Rios, Jamaica (18.4 N/77.1 W)
Day 6 - Miami, Florida (25.8 N/80.2 W)

Western Cruise Track:

Day 1 - Miami, Florida (25.8 N/80.7 W)
Day 3 - Belize City, Belize (17.4 N/88.1 W)
Day 4 - Costa Maya, Mexico (18.7 N/87.7 W)
Day 5 - Cozumel, Mexico (20.5 N/87.0 W)
Day 6 - George Town, Grand Cayman (19.3 N/81.4 W)
Day 8 - Miami, Florida (25.8 N/80.7 W)

Northern Cruise Track:

Day 1 - Bayonne, New Jersey (40.7 N/74.1 W)
Day 3 - Kings Wharf, Bermuda (32.3 N/64.8 W)
Day 6 - Bayonne, New Jersey (40.7 N/74.1 W)

B Cruise Track:

Day 1 - Bayonne, New Jersey (40.7 N/74.1 W)
Day 3 - Kings Wharf, Bermuda (32.3 N/64.8 W)
Day 5 - Philipsburg, St. Maarten (18.0 N/63.0 W)
Day 6 - Charlotte Amalie, St. Thomas (18.3 N/64.9 W)
Day 7 - San Juan, Puerto Rico (18.5 N/66.1 W)
Day 10 - Bayonne, New Jersey (40.7 N/74.1 W)

E9 Cruise Track:

Day 1 - Bayonne, New Jersey (40.7 N/74.1 W)
Day 4 - Labadee, Haiti (19.8 N/72.3 W)
Day 5 - Casa de Campo, Dominican Republic (18.4 N/69.0 W)
Day 6 - Charlotte Amalie, St. Thomas (18.3 N/64.9 W)

Day 7 - San Juan, Puerto Rico (18.5 N/66.1 W)
Day 10 - Bayonne, New Jersey (40.7 N/74.1 W)

Change in E9 Cruise Track for EX0744E9:

Day 1 - Bayonne, New Jersey (40.7 N/74.1 W)
Day 5 - Philisburg, St. Maarten (18.0 N/63.0 W)
Day 6 - Charlotte Amalie, St. Thomas (18.3 N/64.9 W)
Day 7 - San Juan, Puerto Rico (18.5 N/66.1 W)
Day 10 - Bayonne, New Jersey (40.7 N/74.1 W)

NE Cruise Track:

Day 1 - Bayonne, New Jersey (40.7 N/74.1 W)
Day 2 - New London, Connecticut (41.4 N/72.1 W)
Day 4 - Halifax, Nova Scotia (44.6 N/63.6 W)
Day 5 - Saint John, New Brunswick (45.3 N/66.1 W)
Day 6 - Bar Harbor, Maine (44.4 N/68.2 W)
Day 7 - Portland, Maine (43.7 N/70.2 W)
Day 8 - Boston, Massachusetts (42.3 N/71.0 W)
Day 9 - Bayonne, New Jersey (40.7 N/74.1 W)

BB Cruise Track:

Day 1 - Bayonne, New Jersey (40.7 N/74.1 W)
Day 3 - Kings Wharf, Bermuda (32.3 N/64.8 W)
Day 6 - Boston, Massachusetts (43.3 N/71.0 W)
Day 7 - Bayonne, New Jersey (40.7 N/74.1 W)

C9 Cruise Track:

Day 1 - Bayonne, New Jersey (40.7 N/74.1 W)
Day 4 - Labadee, Haiti (19.8 N/72.3 W)
Day 5 - Casa De Campo, Dominican Republic (18.4 N/69.0 W)
Day 6 - Charlotte Amalie, St. Thomas (18.3 N/64.9 W)
Day 7 - San Juan, Puerto Rico (18.5 N/66.1 W)
Day 9 - Bayonne, New Jersey (40.7 N/74.1 W)

C12 Cruise Track:

Day 1 - Bayonne, New Jersey (40.7 N/74.1 W)
Day 4 - Philisburg, St. Maarten (18.0 N/63.0 W)
Day 5 - St. Johns, Antigua (17.1 N/61.8 W)
Day 6 - Roseau, Dominica (15.3 N/61.4 W)
Day 7 - Bridgetown, Barbados (13.1 N/59.6 W)
Day 8 - Basseterre, St. Kitts (17.3 N/62.7 W)
Day 9 - Charlotte Amalie, St. Thomas (18.3 N/64.9 W)
Day 10 - San Juan, Puerto Rico (18.5 N/66.1 W)
Day 13 - Bayonne, New Jersey (40.7 N/74.1 W)

List of variables included in this dataset:

COLUMN	HEADER	EXPLANATION
1.	Group_Ship:	AOML_Explorer for all Explorer of the Seas data.
2.	Cruise:	Cruise Name (For example, EX0715W: EX = Explorer

of the Seas, 07 = 2007, 15 = 15th weekly cruise, and
W = western track).

3. JD_GMT: Decimal year day.
4. Date_DDMMYYYY: The date format has been changed to comply with the IOCCP recommendations.
5. TIME_HH:MM:SS: GMT time.
NOTE: local time = GMT - 4 hr or GMT - 5 hr.
6. Lat_dec_degree: Latitude in decimal degrees (negative values are in the southern hemisphere).
7. Long_dec_degree: Longitude in decimal degrees (negative values are in the western latitudes).
8. xCO2eq_ppm: Mole fraction of CO2 (dry) in the headspace equilibrator at equilibrator temperature (Teq) in parts per million.
9. xCO2a_ppm: Mole fraction of CO2 in air in parts per million.
This field is not measured on the Explorer of the Seas - all data initialized to -9.
10. Pres_Equil_hPa: Barometric pressure in the lab in hectopascals (1 hectopascal = 1 millibar).
11. Pres_sealevel_hPa: Barometric pressure from ship's barometer, corrected to sea level in hectopascals (1 hectopascal = 1 millibar).
12. EqTemp_C: Temperature in equilibrator water in degrees centigade. Temperature in equilibrator measured with a calibrated thermistor.
13. SST(TSG)_C: Temperature from the ship's thermosalinograph in degrees centigrade.
14. Sal(TSG)_Permil: Salinity from the ship's thermosalinograph on the Practical Salinity Scale.
15. Water_flow_l/min: Water flow through equilibrator in liters per minute.
16. Gasflow_IR_ml/min: Gas flow through the Licor infrared analyzer before the flow is stopped in milliliters per minute.
17. Temp_IR_C: Temperature of the Licor infrared analyzer sample cell in degrees centigrade.
18. Pres_IR_hPa: Pressure in the Licor infrared analyzer in hectopascals.
NOTE: There is no pressure sensor in the Licor but since it is vented to atmosphere prior to measurement, this value is the same as the pressure in the lab (number 10 above). (1 hectopascal = 1 millibar).
19. Ship_heading_true_degree: Ship's heading from ship's navigation system in degrees with 0 = North and 90 = East.

20. Ship_speed_knot: Ship's speed from ship's navigation system in knots.
21. Wind_dir_rel_degree: Wind direction relative to the ship from ship's navigation system in degrees with 0 = from the bow and 90 = from starboard.
22. Wind_speed_rel_m/s: Wind speed relative to the ship from ship's navigation system in meters per second.
23. fCO2W@SST_uatm: Fugacity of CO2 in sea water in microatmospheres calculated as outlined below.
24. Qcflag_water: Quality control flag for sea water xCO2 and fCO2 values with 2 = good value, 3 = questionable value, 4 = bad value, and 9 = no measurement taken.
25. fCO2a_uatm: Fugacity of CO2 in air in microatmospheres. This field is not measured on the Explorer of the Seas - all data initialized to -9.
26. Qcflag_air: Quality control flag for air xCO2 and fCO2. Since no air values were taken, all values are initialized to 9.
27. dfCO2_uatm: Sea water fCO2 - air fCO2 in microatmospheres. This uses the average air value for the current hour. This field is not measured on the Explorer of the Seas - all data initialized to -9.
28. Fluoro_ug/l: Reading from the fluorometer in micrograms per liter.
29. Wind_speed_true_m/s: True wind speed in meters per second.
30. Wind_dir_true_degree: True wind direction in degrees were 0 = North and 90 = East.
31. Air_Temp_C: Outside air temperature from ship's computer system in degrees centigrade.
32. Oxygen: Units not known at this time.

The following fields have been QC'ed by the CO2 group:

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Group_Ship
Cruise
JD_GMT
DATE_DDMMYYYY
TIME_HH:MM:SS
Lat_dec_degree
Long_dec_degree
xCO2eq_ppm
Pres_Equil_hPa
EqTemp_C
Water_flow_l/min
Gasflow_IR_ml/min
Temp_IR_C
Pres_IR_hPa

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fCO2W@SST_uatm
QCflag_water

The following fields are from the ship's onboard systems and the quality of this data cannot be verified:

Pres_sealevel_hPa
SST(TSG)_C
Sal(TSG)_Permil
Ship_heading_true_degree
Ship_speed_knot
Wind_dir_rel_degree
Wind_speed_rel_m/s
Fluoro_ug/l
Wind_speed_true_m/s
Wind_dir_true_degree
Air_Temp_C
Oxygen

Narrative description of system design:

CO2 ANALYTICAL SYSTEM:

The concentration of carbon dioxide (CO₂) in surface ocean water is determined by measuring the concentration of CO₂ in gas that is in contact with the water. Surface water is pumped over 200 m through 7/8" Teflon tubing from an inlet in the ship's bow to the equilibration chamber. Water comes from the bow intake 2 m below the water line and the TSG is located close to the inlet. Since the sea surface temperature is high and the ship is well air-conditioned, the Teq is on average about 0.4 °C lower than SST. The equilibration chamber has an enclosed volume of gas, or headspace, and a pool of seawater that continuously overflows to a drain. As the water flows through the chamber, the dissolved gases (like CO₂) partition between the water and the headspace. At equilibrium, the ratio of CO₂ in the water and in the headspace is influenced most by temperature, and that relationship is known. By measuring the concentration of CO₂ in the headspace and the temperature in the chamber, the partial pressure (or fugacity) of CO₂ in the surface water can be calculated.

INSTRUMENT DESCRIPTION

The general principle of instrumental design can be found in Wanninkhof and Thoning (1993), Ho et al. (1995), and Feely et al. (1998). The concentration of CO₂ in the headspace gas is measured using the adsorption of infrared (IR) radiation, which results from changes in the rotational and vibrational energy state of the CO₂ molecule. The LI-COR detector passes IR radiation through two 6" cells. The reference cell is flushed with a gas of known CO₂ concentration. The sample cell is flushed with the headspace gas. A vacuum-sealed, heated filament is the broadband IR source. The IR radiation alternates between the two cells via a chopping shutter disc. An optical filter selects an adsorption band specific for CO₂ (4.26 micron) to reach the detector. The solid state (lead selenide) detector is kept at -12 degrees °C for excellent stability and low signal noise (less than 0.2 ppm).

Several steps are taken to reduce interferences and to increase the accuracy of the measurements. After the equilibration chamber, the headspace travels through a drying trap to remove water vapor. During each analysis, the headspace gas is compared to a reference gas of known concentration. To

improve the accuracy of the measurements, three different gaseous standards for CO₂ are analyzed once an hour instead of the headspace gas.

Analyzer: LI-COR 6252 (analog output) infrared (IR) analyzer.

Method of Analysis: Differential analyses relative to a reference gas which is close to the CO₂ concentration of the middle standard. Measures dried equilibrator headspace gas. Gas flow is stopped prior to IR readings.

Drying Method: The equilibrator headspace sample gas first goes through an air filter and a thermoelectric refrigerator (~6-10 °C). The sample and standard gases pass through a Perma Pure (Nafion) dryer and a short column of magnesium perchlorate before reaching the analyzer. The counter flow in the Perma Pure tube is the reference gas.

Equilibrator (setup, size, flows): The equilibrator was fabricated using a filter housing (ColeParmer, U-010509-00) with ~0.5 L water reservoir and ~0.8 L gaseous headspace. Water flow rate is ~1.5 L/min. Headspace recirculation rate is ~80 ml/min.

Narrative statement identifying measurement method for each required parameter:

CALCULATIONS:

The mixing ratios of ambient air and equilibrated headspace air are calculated by fitting a second-order polynomial through the hourly averaged millivolt response of the detector versus mixing ratios of the standards. Mixing ratios of dried equilibrated headspace and air are converted to fugacity of CO₂ in surface seawater and water saturated air in order to determine the fCO₂. For ambient air and equilibrator headspace, the fCO_{2a} (or fCO_{2eq}) is calculated assuming 100% water vapor content:

$$fCO_{2eq} = xCO_{2eq}(P-pH_2O) \exp(B_{11}+2d_{12})P/RT$$

where fCO_{2eq} is the fugacity in the equilibrator, pH_{2O} is the water vapor pressure at the sea surface temperature, P is the atmospheric pressure (in atm), T is the SST or equilibrator temperature (in K) and R is the ideal gas constant (82.057 cm³·atm·deg⁻¹·mol⁻¹). The exponential term is the fugacity correction where B₁₁ is the second virial coefficient of pure CO₂

$$B_{11} = -1636.75 + 12.0408T - 0.032795T^2 + 3.16528E-5 T^3$$

and d₁₂ = 57.7 - 0.118 T is the correction for an air-CO₂ mixture in units of cm³·mol⁻¹ (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the increase of fCO₂ due to heating of the water from passing through the pump and through 5 cm ID PVC tubing within the ship. The water in the equilibrator is typically 0.4 °C cooler than sea surface temperature. The empirical temperature correction from equilibrator temperature to SST is:

$$fCO_2(SST) = fCO_2(eq) \exp(-0.0423 (T_{eq}-SST))$$

where SST is sea surface temperature and T_{eq} is the equilibrator temperature in degrees °C.

Sampling Cycle:

The system runs on an hourly cycle during which 3 standard gases, a reference gas and 20 surface water samples (from the equilibrator head space) are analyzed on the following schedule:

Mins. after hour	Sample
=====	=====
0:00	Low Standard
2:10	Mid Standard
4:25	High Standard
6:40	Reference
8:55	Water
11:28	Water
14:01	Water
16:34	Water
19:07	Water
21:40	Water
24:13	Water
26:46	Water
29:19	Water
31:52	Water
34:25	Water
36:58	Water
39:31	Water
42:04	Water
44:37	Water
47:10	Water
49:43	Water
52:16	Water
54:49	Water
57:22	Water

NOTES ON DATA:

Columns have a default value of -9 in case of instrument malfunction, erroneous readings or missing data. Furthermore, if a suspicious xCO2 value, pressure or temperature value is encountered, the fCO2 is not calculated.

Analytical Instrument Manufacturer/Model:

The Explorer of the Seas system was built by Dave Chipman in 2000. The analyzer is a LI-COR 6252 (analog output) infrared analyzer.

Standard Gases and Reference Gas: The three standard gases come from CMDL in Boulder and are directly traceable to the WMO scale. The reference gas is a non-calibrated gas from a commercial company. While individual data points above 420 or below 300 may not be accurate, the general trends should be indicative of the seawater chemistry.

Description of any additional environmental control:

The system is located in the ocean laboratory of the Explorer of the Seas. The room is air-conditioned with little temperature fluctuation.

Resolution of measurement:

The resolution of the instrument is better than 0.1 ppm.

Estimated overall uncertainty of measurement:

The xCO₂eq measurements are believed accurate to 0.1 ppm. The fCO₂@SST measurements are believed to be precise to 0.2 ppm.

List of calibration gases used:

The standards used on the cruise are:

STANDARD	TANK #	CONCENTRATION	VENDOR
STD1	CA02040	319.82	CMDL
STD2	CA02030	377.14	CMDL
STD3	CA02020	458.04	CMDL

Traceability to an internationally recognized scale (including date/place of last calibration made):

All standards are obtained from NOAA/CMDL, now called the Global Monitoring Division of the Earth Research Laboratory and are directly traceable to WHO scale.

Uncertainty of assigned value of each calibration gas:

The uncertainty based on pre and post cruise calibrations is less than 0.05 ppm.

Pressure/Temperature/Salinity:

Thermosalinograph information can be found at <http://www.rsmas.miami.edu/rccl/facilities.html>.

Units:

All xCO₂ values are reported in parts per million (ppm) and fCO₂ values are reported in microatmospheres (uatm) assuming 100% humidity at the equilibrator temperature.

Bibliography:

- DOE (1994). Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. DOE.
- Feely, R. A., R. Wanninkhof, H. B. Milburn, C. E. Cosca, M. Stapp and P. P. Murphy (1998). A new automated underway system for making high precision pCO₂ measurements onboard research ships. *Analytica Chim. Acta* 377: 185-191.
- Ho, D. T., R. Wanninkhof, J. Masters, R. A. Feely and C. E. Cosca (1997). Measurement of underway fCO₂ in the Eastern Equatorial Pacific on NOAA ships BALDRIGE and DISCOVERER, NOAA data report ERL AOML-30, 52 pp., NTIS Springfield.
- Wanninkhof, R. and K. Thoning (1993). Measurement of fugacity of CO₂ in surface water using continuous and discrete sampling methods. *Mar. Chem.* 44(2-4): 189-205.
- Weiss, R. F. (1970). The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Research* 17: 721-735.
- Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2: 203-215.

Weiss, R. F., R. A. Jahnke and C. D. Keeling (1982). Seasonal effects of temperature and salinity on the partial pressure of CO₂ in seawater. Nature 300: 511-513.

Comments related to the individual legs:

Explorer of the Seas Naming Convention: EX06NNT where EX is the ship abbreviation, 07 is the year, NN is the number of the cruise which will be a number between 1 and 47, and T is the cruise track which will be either W for the western cruise track leaving from Miami, Florida, E for the eastern cruise track leaving from Miami, Florida, N for the northern cruise track leaving from Bayonne, New Jersey, B for a variation of the southern cruise track leaving from Bayonne, New Jersey with an initial port stop in Bermuda, E9 for a variation of the southern cruise track leaving from Bayonne, New Jersey without a port stop in Bermuda, and NE for a northern cruise track leaving Bayonne, New Jersey with port stops in New England and Canada. During the later part of 2007, there were various nine and twelve day cruises added with cruise names that did not follow the standard naming convention.

For all legs, due to the slow response time of the system, the first 10 minutes of data for each hour for the entire leg was removed. This slow response time is not fully understood. On certain legs the response time was worse and up to 40 minutes of data was removed.

For all legs, the first hour of data after leaving port is removed.

EX0701: Removed the following questionable data - JD 6.864 to JD 6.95.

EX0702: Some data removed due to fluctuating water flow.

EX0704: Removed the following questionable data - JD 24.187 - JD 24.208.

EX0706: Removed the following questionable data - JD 38.140 - JD 38.208.

Ex0712E, Ex0713W: The gas flow meter sensor is broken - gas flow is not being logged.

Ex0714W: April 2 - Shailer Cummings replaced the broken gas flow meter.

Ex0715W: April 11 - The system was down from JD 101.625 to JD 101.834.

Ex0716E: Removed the following questionable data - JD 109.057 to JD 109.123 and JD 109.939 to JD 110.066.

Ex0717W: April 11 - The system was down from JD 101.625 to JD 101.834.

Ex0718E: System down on April 30 from 01:26 to 21:34 and on May 1 from 6:59 to 23:57. Liz restarted the system. Change in Eastern cruise track - five nights at sea instead of seven with port stops in Labadee, Haiti and Ocho Rios, Jamaica only.

Ex0719E: Change in Eastern cruise track - five nights at sea instead of seven with port stops in Labadee, Haiti and Ocho Rios, Jamaica only.

Ex0720B: The ship will be permanently repositioning to Bayonne,

New Jersey (Cape Liberty Cruise Port).

Ex0722B: Removed the following questionable data - JD 150.975 to JD 151.022. May 31 - due to low water flow, the entire seawater system (including the pCO₂ system) was flushed with fresh water. The water flow in the pCO₂ system was still low after the flush.

Ex724B: Removed the following questionable data - JD 164.975 to JD 165.000. June 5 - due to low water flow, the entire seawater system (including the pCO₂ system) was flushed with fresh water. Don then hooked up the fresh water line directly to the pCO₂ system and flushed the pCO₂ system for 10 minutes. After the flush, the flow rate was 1.75 lpm. On June 9, the pCO₂ system was flushed again with fresh water for 15 to 20 minutes. After the system was flushed, the flow rate was 1.8 lpm. On June 10, Don cleaned both the housing and the metal filter in the pCO₂ system. On June 13, the pCO₂ system was down from 9:11 to 17:02 for a ship-wide blackout test. On Sunday, June 17, Kevin Sullivan checked and cleaned the system.

Ex0728B: Intermittent low sample gas flow from July 10 thru July 14. Questionable data was removed.

Ex0729: Due to a buildup of salt in the return line from the dry box to the equilibrator there was low gas flow in the water phase throughout most of the cruise.

Ex0730B: Low sample gas flow throughout the cruise - Dennis Pierrot found there was a salt buildup in the return line from the dry box to the equilibrator. He cleaned the line and the sample gas flow returned to normal.

Ex0732N: Removed the following questionable data - JD 224.216 to JD 224.375.

Ex0733N: Very low sample gas flow throughout the first half of the cruise - water was trapped in the tubing between the headspace pump and the dry box (J-box). Don ran air thru the line (tube) for 3 hours to remove the water blocking the tube.

Ex0734B: Removed the following questionable data - JD 224.216 to JD 224.375.

Ex0744E9: Due to the rough seas from Hurricane Noel, there is no data for November 3 and November 4. Change in E9 cruise track - 10 days at sea with port stops in St. Maarten, St. Thomas, and Puerto Rico.

Ex0745BB: This cruise is a variation of the Northern cruise track with a port stop in Boston, Massachusetts.

Ex0746C12: Chip replaced the reference flow meter on 11/17/07. Low water flow from 11/21/07 (22:11) to 11/22/07 (21:24). This cruise is a variation of the Eastern cruise track with 12 days at sea and port stops in St. Maarten, Antigua, Dominica, Barbados, St. Kitts, St. Thomas, and Puerto Rico.

Ex0747C9: This cruise is a variation of the Eastern cruise track with 10 days at sea and port stops in Haiti, Dominican Republic, St. Thomas and Puerto Rico.

