

## Explorer of the Seas METADATA - 2005

Class of Data: Surface ocean carbon dioxide concentrations

Dataset Identifier: Explorer of the Seas

Two Files: Explorer\_2005\_East  
Explorer\_2005\_West

Statement of how to cite dataset:

Explorer website: [http://www.aoml.noaa.gov/ocd/gcc/explorer\\_cruisetracks.php](http://www.aoml.noaa.gov/ocd/gcc/explorer_cruisetracks.php)

These data are made freely available to the public and the scientific community in the belief that their wide dissemination will lead to greater understanding and new scientific insights. The availability of these data does not constitute publication of the data. We rely on the ethics and integrity of the user to assure that AOML receives fair credit for our work. Please send manuscripts using this data to AOML for review before they are submitted for publication so we can insure that the quality and limitations of the data are accurately represented.

Measurement platform identifier: Explorer of the Seas

Cruise Information:

Weekly cruises through the Caribbean departing from Miami, Florida.

Project Information:

This project 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: 7/11/07

Timestamp for the most recent update of dataset: 7/11/07

Timestamp period the dataset refers to: 1/02/2005 - 12/18/2005

Geographic area the dataset refers to:

16 N to 28 N  
62 W to 90 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)

Western Cruise Track:

Day 1 - Miami, Florida (25.8 N/80.7 W)  
Day 3 - Belize City, Belize (17.8 N/88.3 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)

Change in Western Cruise Track for EX0544W, EX0546W  
and EX0548W:

Day 1 - Miami, Florida (25.8 N/80.7 W)  
Day 3 - Belize City, Belize (17.8 N/88.3 W)  
Day 5 - Costa Maya, Mexico (18.7 N/87.7 W)  
Day 7 - George Town, Grand Cayman (19.3 N/81.4 W)  
Day 8 - Miami, Florida (25.8 N/80.7 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, EX0546W: EX = Explorer of the Seas, 05 = 2005, 46 = 46th 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:

```

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
fCO2W@SST_uatm
QCflag_water

```

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

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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

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Wind\_dir\_true\_degree  
Air\_Temp\_C  
Oxygen

Narrative description of system design:

#### CO2 ANALYTICAL SYSTEM:

The concentration of carbon dioxide (CO<sub>2</sub>) in surface ocean water is determined by measuring the concentration of CO<sub>2</sub> 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 CO<sub>2</sub>) partition between the water and the headspace. At equilibrium, the ratio of CO<sub>2</sub> in the water and in the headspace is influenced most by temperature, and that relationship is known. By measuring the concentration of CO<sub>2</sub> in the headspace and the temperature in the chamber, the partial pressure (or fugacity) of CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> molecule. The LI-COR detector passes IR radiation through two 6" cells. The reference cell is flushed with a gas of known CO<sub>2</sub> 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 CO<sub>2</sub> (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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> in surface seawater and water saturated air in order to determine the fCO<sub>2</sub>. For ambient air and equilibrator headspace, the fCO<sub>2a</sub> (or fCO<sub>2eq</sub>) is calculated assuming 100% water vapor content:

$$fCO_{2eq} = xCO_{2eq}(P - p_{H_2O}) \exp(B_{11} + 2d_{12})P/RT$$

where fCO<sub>2eq</sub> is the fugacity in the equilibrator, p<sub>H<sub>2</sub>O</sub> 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 cm<sup>3</sup>·atm·deg<sup>-1</sup>·mol<sup>-1</sup>). The exponential term is the fugacity correction where B<sub>11</sub> is the second virial coefficient of pure CO<sub>2</sub>

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

and d<sub>12</sub> = 57.7 - 0.118 T is the correction for an air-CO<sub>2</sub> mixture in units of cm<sup>3</sup>·mol<sup>-1</sup> (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the increase of fCO<sub>2</sub> 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 outlined in Weiss et al. (1982).

$$d\ln(fCO_2) = (T_{eq} - SST) (0.0317 - 2.7851E-4 T_{eq} - 1.839E-3 \ln(fCO_{2eq}))$$

where dln(fCO<sub>2</sub>) is the difference between the natural logarithm of the fugacity at T<sub>eq</sub> and SST, and T<sub>eq</sub> 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 xCO<sub>2</sub> value, pressure or temperature value is encountered, the fCO<sub>2</sub> 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. Any value outside the range of the standards (192 ppm, 426 ppm, and 514 ppm) should be considered approximate (5 ppm). While individual data points above 420 ppm or below 300 ppm 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 xCO<sub>2</sub>eq measurements are believed accurate to 1 ppm. The fCO<sub>2</sub>@SST measurements are believed to be precise to 2 ppm.

#### List of calibration gases used:

The standards used on the cruise are:

STANDARD	TANK #	CONCENTRATION	VENDOR
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STD1	CA4563	192.34	CMDL
STD2	CA3253	426.92	CMDL
STD3	CA3758	514.24	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 xCO<sub>2</sub> values are reported in parts per million (ppm) and fCO<sub>2</sub> values are reported in microatmospheres (uatm) assuming 100% humidity at the equilibrator temperature.

Bibliography:

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- 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 pCO<sub>2</sub> 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 fCO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> in seawater. *Nature* 300: 511-513.

Comments related to the individual legs:

Explorer of the Seas Naming Convention: EX05NNT where EX is the ship Abbreviation, 05 is the year, NN is the number of the cruise which will be a number between 1 and 52, and T is the cruise track which will be either W for the west track or E for the east track.



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.

EX0501W: Due to a leak in the system, data was removed on 1/3/05 from 20:47 to 22:57 and on 1/8/05 from 20:44 to 22:59.

EX0503W: Due to a leak in the system data was removed on 1/17/05 from 20:42 to 22:47 and on 1/22/05 from 20:47 to 22:59.

EX0504E: Due to a leak in the system, the following data was removed: 1/24/04 from 20:49 to 23:42. Problems with the gas flow during the water phase; removed the data from 1/27/05 (4:52) to 1/30/05 (9:47).

EX0506E: Water flow problems; removed data on 2/10/05.

EX0510E: Data collection was switched from VIDS2 to VIDS1 on 3/10/05 - no samples taken during the switch. Salinity data suspect from Julian Day 70 thru Julian Day 72.

EX0511W: Salinity data suspect from Julian Day 72 thru Julian Day 75.

EX0517W: Problems with the water flow and spray from the showerhead. The pressure regulator on the seawater flow was adjusted. The flow rate increased and the spray pattern got wider but still didn't touch the sides of the equilibrator.

EX0524E: No TSG data (SST and Salinity) on 6/14/05 from 4:05 to 11:47.

EX0525W: The IR was inadvertently turned off and the voltages for the three standards, reference gas, and water samples were zero from 6/23/05 (15:02) to 6/24/05 (16:49).

EX0527W: Change of cruise track due to tropical storm Emily:

- Day 1 - Miami, Florida (25.8 N/80.7 W)
- Day 3 - Belize City, Belize (17.8 N/88.3 W)
- Day 5 - Costa Maya, Mexico (18.7 N/87.7 W)
- Day 7 - Nassau, Bahamas (25.1 N/-77.3 W)
- Day 8 - Miami, Florida (25.8 N/80.7 W)

EX0528E: Change in cruise track due to tropical storm Emily:

- 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 6 - Nassau, Bahamas (25.1 N/77.3 W)
- Day 8 - Miami, Florida (25.8 N/80.7 W)

EX0530E: From Don Cucchiara (July 24) - the equilibrator headspace gas flow valve was opened all the way to get the gas flow to normal. Don noticed air coming out of the fridge drain line. He tightened the clamp on the tubing and the gas flow returned to normal. He reduced the flow on the valve and the gas flow remained at 80.

From Don Cucchiara (July 30) - Don adjusted the needle valve on the "Low Standard" gas to decrease the flow. After the calibration cycle was done, the gas flow decreased to 63. He adjusted the valve again, and after the next calibration cycle the flow was at 56.

EX0535W: Problems with the salinity sensor - removed the data on 8/30/05 from 9:08 to 10:52.

EX0536E: The system sprung a leak at the joint between the adjustable valve and the flow sensor. The leak was fixed.

EX0539E: After heavy rain events, the overflow holding tank fills up and the equilibrator drain backs up. Due to a tremendous amount of rain (10/07/05 at around 14:00), the water was coming up into the pCO2 system from the drain line. Chip closed the blue ball valve supply line (valve right below the equilibrator box) and then closed the discharge ball valve. Approximately two quarts of water backed up into the equilibrator box. He siphoned off this water using tubing, removed the door and dried up the rest of the remaining water. The door stayed off in port to allow everything to dry out and return the system to green status. After the pump came back on, it took a while for the water to flow through the supply line.

EX0540W: The system went down on October 10. The system was rebooted and data collection restarted. Data removed on 10/10/05 from 03:00 to 08:00.

EX0543E: On 10/31/05 (Monday morning), Chip noticed there was no flow thru the system even with the flow valve wide open. He connected the test hose to the faucet and flushed the system with fresh water. The spray pattern was good and the system returned to normal (flow was normal and registering) when the valve was returned to the seawater position.

EX0544W: Kevin Sullivan replaced the pressure regulator seawater flow valve, installed a float ball check valve (to prevent back wash of rainwater into the system) and fixed the leaks from the Ref gas cylinder line. The equilibrator was mounted higher so there is greater pressure on the drain line when the float ball check valve closes.

EX0545E: Due to a medical emergency, the ship did not stop in Puerto Rico but spent an extra day at sea with the next port stop, as usual, in St. Maarten. Due to rough seas (possibly related to tropical storm Gamma), the pump was going in and out of air bound so there is no data for 11/15/05 thru 11/16/05.

EX0546W: There was a problem with the gas flow thru the Ref and Sample lines. Chip adjusted the flow valve to see if the gas flow would stabilize which it did. Data was removed on 11/24/05 from 16:11 to 23:00 and on 11/25/05 from 4:49 to 8:00.

EX0547E: There were problems with the sample gas flow; the equilibrator headspace gas flow went below 1.0. Don adjusted the gas flow valve and the flow returned to normal (around 80). Data was removed on 11/28/05 (17:11) to 11/29/05 (2:00). On 11/29/05, there were problems with the water flow. Not much water was flowing thru the equilibrator. The system was flushed with fresh water for 2 to 3 minutes. The flow rate during the fresh water flush was 2.0 l/m. The system was returned to SW flow with a flow rate of about 1.0 l/m.

EX0548W: On 12/05/05, the Low Standard (STD1) flow was low. The gas flow knob was adjusted and the flow returned to normal.

EX0550W: Abbreviated cruise, no data was obtained.

EX0551W: Water pressure regulator broken, system down the entire leg.