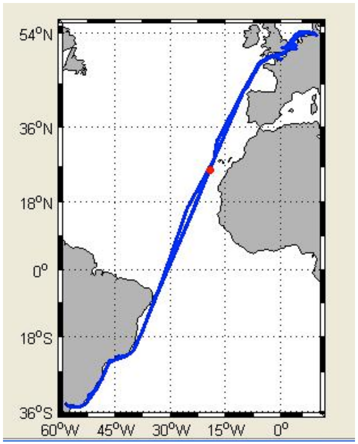
AX11 Cap San Lorenzo Readme File

Platform Information

In July 2014, IRD installed an instrument to measure CO_2 in surface water on the Cap San Lorenzo. The instrumentation was previously installed on Monte Olivia, Rio Blanco and Santa Cruz (same company, same line).
The vessel cruises from Europe to Argentina.



The CO_2 analyser was made by General Oceanics. It is fully automated. A Seabird SBE21 thermosalinograph is installed on the same sea water inlet piping. An air inlet is placed on the top of bridge. It allows atmospheric CO_2 measurements in conjunction with surface water CO_2 observations.

Cruise information
Survey type: VOS line
Vessel Name: Cap San Lorenzo
Country vessel: Germany
Call sign: LXSQ

Period: 28 February-12 March 2015

Geographical coverage: Atlantic Ocean
Bounds:
Westernmost longitude: 45°W
Easternmost longitude: 0°E
Northernmost latitude: 50°N
Southernmost latitude: 24°S

Class of Data: Surface ocean carbon dioxide concentrations

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CO_2 sensors (xCO2)
The accuracies of all components, when operating optimally, are such that the calculated seawater fCO2 has an accuracy of 2 uatm or better and the calculated mole fraction of CO2 (xCO2) in air has an accuracy of 0.1 uatm.

Infrared Analyzer
LI-COR model 7000
    ftp://ftp.licor.com/perm/env/LI-7000/Manual/LI-7000Manual.pdf
    CO2 resolution: 0.01 umol/m
    CO2 accuracy: ± 1% nominal
    Pressure resolution: 0.02 hPa
    Internal pressure transducer accuracy: ± 1.2 hPa
    (manufacturer specifications: ±0.1% FS, where FS = 0-1150 hPa)

The general principle of instrumental design can be found in Pierrot et al. (2009). The concentration of CO2 in the headspace gas was measured using the adsorption of infrared (IR) radiation by the CO2 molecule. The LI-COR analyzer passed IR radiation through two cells. The reference cell is constantly flushed with a reference gas CO2-free. The sample cell is flushed with the gas of interest (standard, outside atmosphere, or headspace gas from equilibration chamber). A vacuum-sealed, heated filament was the broadband IR source. The IR radiation alternated between the two cells via a chopping shutter disc spinning at 500 Hertz. An optical filter selected an adsorption band specific for CO2 (4.26 micron) to reach the detector. The solid state (lead selenide) detector was kept at -5 degrees C for excellent stability and low signal noise (less than 0.2 ppm).

The infrared analyzer is calibrated regularly using three standard gases (~250-~500 ppm) from Air Liquide - France, which were calibrated at LSCE against primary NOAA standards. The exact concentrations of the standards are:
    0 ppm (nitrogen gas)
    248.82 ± 0.01 ppm (July 2013)
    358.98 ± 0.02 ppm (February 2014)
    501.25 ± 0.11 ppm (January 2012)

CO_2 in marine air method (xCO2)
Outside air was constantly being pulled (~6 liters/min) from an inlet on the top of the bridge through ~80 m of tubing (3/8" OD Dekabon) to the analytical system. The flushing rate of the LI-COR analyzer during ATM analyses is ~70-150 ml/min.
Drying: The effects of water vapor on the sample analyses were kept to a minimum by removing as much water as possible. The water was first condensed out of the sample gas

stream by cooling to ~5° C using a thermoelectric device. The condenser has been moved outside of the wet box. Depending on local temperature, the condenser temperature varies from 4°C to 14°C.
Then water was further removed using Nafion® gas dryers before reaching the IR analyzer. The counterflow gas in the dryer is pre-dried outside air. Typical water content of the analyzed gas was less than 3 millimoles/mole with approximately 90% of the water being removed.

Sampling and equilibrator design
The seawater inlet is on the sea chest at an approximate depth of 3 meters. Seawater was pushed through a spray head into an equilibration chamber that was fabricated using a filter housing (ColeParmer, U-010509-00). The chamber had a ~0.5 L water reservoir and a ~0.8 L gaseous headspace. Water flow rate was ~2 - 3 L/min. The rate at which the headspace gas recirculated through the analyzer during EQU analyses was ~70 - 150 ml/min.
The equilibration chamber was vented to the surrounding space.
Drying: The effects of water vapor on the sample analyses were kept to a minimum by removing as much water as possible. The water was first condensed out of the sample gas stream by cooling to ~5° C using a thermoelectric device. The condenser has been moved outside of the wet box. Depending on local temperature, the condenser temperature varies from 4°C to 14°C.
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A typical sequence of the continuous analyses was:

STEP	TYPE	REPETITIONS
1	Standards (all)	1
2	ATM	8
3	EQU	90

Sea Surface Temperature (SST) and Salinity (SSS)
SeaBird model SBE-21

> http://www.seabird.com/pdf_documents/manuals/21_026.pdf
> Temperature resolution: 0.001°C
> Temperature accuracy: ± 0.01°C
> Salinity resolution: 0.002 ‰

Seawater samples are taken daily at the thermosalinograph outlet. Samples are analysed at SHOM-France in an OSIL Portasal, and compared to IAPSO Sea Water Standards.
The Salinity accuracy is expected to be ± 0.02 ‰

The thermosalinograph is calibrated every 18 months, either at Seabird-USA or at SHOM-France.
The seawater inlet of both CO2 analyser and TSG is located on the sea chest. The TSG is very close to the hull, the sea water flow rate is around 30 l/min. We consider that the temperature inside the TSG is the SST. The warming between the TSG and the CO2 analyser is 0.2°C ($T_{equ} – T_{TSG}$).

Equilibrator Temperature (Tequ)

Hart model 1521 with a 5610 thermistor probe

http://www.testequipmentdepot.com/hart/pdfs/1521_1522.pdf
Resolution: 0.001°C
Accuracy: ± 0.025°C

Atmospheric Pressure (Patm)
The barometric pressure was measured in the bridge, ~20 m above the equilibrator. The Druck barometer is placed in a box, which also contains the GPS and the Iridium transmitter.

Druck barometer RPT350

http://www.ge-mcs.com/en/pressure-and-level/transducerstransmitters/rtp350.html
Accuracy: ± 0.01 %

Equilibrator Pressure (Pequ)
The pressure in the equilibrator relative to the bow thruster compartment was measured with a Setra model 239 differential barometer. The LI-COR barometer measured the barometric pressure of the compartment.

Setra model 239, differential pressure

http://www.setra.com/ProductDetails/model_239.htm
Resolution: 0.01 hPa
Accuracy: ± 0.052 hPa
(manufacturer specifications: ± 0.14% FS, where FS = ± 7.5 inches WC)

The absolute pressure of the equilibrator headspace reported in data files is the sum of the infrared analyzer pressure and the differential pressure from the pressure transducer attached to the equilibrator.

Variables info

Column header	Explanation
dd	Day
mm	Month
yy	Year UTC date
hh	Hours UTC time
mn	Minutes
ss	Seconds
day	Decimal year day
Lon	Longitude in decimal degrees (negative values in west)
Lat	Latitude in decimal degrees (negative values in southern hemisphere)
sst	Temperature from the ship's thermosalinograph
sss	Salinity from the ship's thermosalinograph
Patm	Atmospheric pressure in millibar
Tequ	Equilibrator temperature
xCO2	Mole fraction of CO2 (dry) in air or equilibrated air (ppm)
H2Omm	Water content of Licor in mmol/mol
Pequ	Pressure in equilibrator
fCO2sw	Fugacity in CO_2 in seawater

CALCULATIONS

Mixing ratios of dried equilibrated headspace and air, corrected from the Licor drift, are converted to fugacity of CO_2 in surface seawater and water saturated air in order to determine the fCO_2.
For ambient air and equilibrator headspace the fCO_{2a}, or fCO_{2eq} is calculated assuming 100% water vapor content:

$$fCO2eq = xCO2eq\ (P - pH2O)\ \exp(B11 + 2\ \delta 12)\ P/RT$$

where fCO2eq is the fugacity in the equilibrator, pH2O 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 ($82.057\ cm^3 \cdot atm \cdot deg^{-1} \cdot mol^{-1}$). The exponential term is the fugacity correction where B11 is the second virial coefficient of pure CO2

$$B11 = -1636.75 + 12.0408\ T - 0.032795\ T^2 + 3.16528E\text{-}5\ T^3$$

and

$$\delta 12 = 57.7 - 0.118\ T$$

is the correction for an air-CO2 mixture in units of $cm^3 \cdot mol^{-1}$ (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the change of fCO2 due to changes in water temperature which when the water passes through the pump and through the rubber tubing within the ship. The water in the equilibrator is typically 0.2°C warmer than sea surface temperature.
The empirical temperature correction from equilibrator temperature to SST was:

$$fCO2(SST) = fCO2(eq)\ \exp(-0.0423\ (Teq - SST))$$

where SST is the sea surface temperature and Teq is the equilibrator temperature in ^oC.

METHOD REFERENCES:

Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Luger, T. Johannessen, A. Olsen, R. A. Feely, and C. E. Cosca (2009). Recommendations for autonomous underway pCO2 measuring systems and data-reduction routines. Deep Sea Research II, 56: 512-522.

Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar. Chem. 2: 203-215.