

# The “GOLLUM” O<sub>2</sub> intercomparison programme: Latest results and next steps

A. C. Manning, R. F. Keeling, A. J. Etchells, **M. Hewitt**, M. L. Bender, K. Bracchi, G. W. Brailsford, W. A. Brand, N. Cassar, A. C. Cox, M. Leuenberger, H. A. J. Meijer, S. Morimoto, T. Nakazawa, R. E. M. Neubert, W. J. Paplawsky, J. M. Richter, B. B. Stephens, Y. Tohjima, S. van der Laan, I. T. van der Laan-Luijkx, A. Watt and P. A. Wilson

23 authors listed – if anyone else should be included, please let me know.



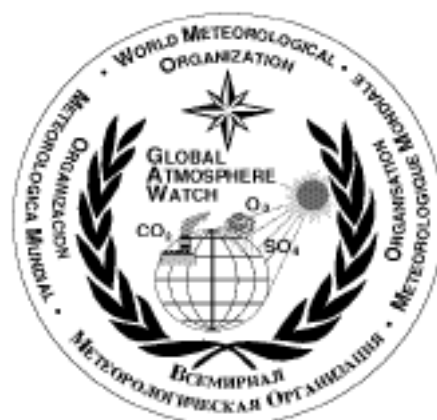
**UEA** University of  
East Anglia

School of Environmental Sciences  
*Carbon Related Atmospheric Measurement Lab*

# Talk outline

- Historical background and GOLLUM beginnings.
- Details of the GOLLUM programme.
- Some data and results.
- Some suggestions for what next – for open discussion.

# WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH



No. 148

## Report of the Eleventh WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques

(Tokyo, Japan, 25 – 28 September 2001)

### 3) O<sub>2</sub>/N<sub>2</sub> CALIBRATION

Intercalibration activities be undertaken to improve the usefulness of O<sub>2</sub>/N<sub>2</sub> measurements, which are now being conducted by a growing number of laboratories world-wide. At present, there are no absolute standards for atmospheric O<sub>2</sub>/N<sub>2</sub> ratio, and each laboratory has reported results relative to individual laboratory reference gases. The scientific value of O<sub>2</sub>/N<sub>2</sub> measurements would be largely enhanced if measures were taken to bring the observations onto a common scale, with a precision of a few per meg, and if this scale could be tied to absolute standards, with an absolute accuracy of 5 per meg or better. Both tasks are very challenging, however, and it is not clear how best to implement such measures at this time. What is needed at present are creative efforts on the part of individual laboratories or among groups of laboratories to test strategies for intercalibration and to test approaches to standards development. At the Scripps Institution of Oceanography, for example, a program is underway to develop air standards for O<sub>2</sub>/N<sub>2</sub> ratio analysis based on gravimetry. Another identifiable need is having several stations worldwide where samples can be collected in parallel for several laboratories, as this will aid in establishing the offsets between the individual laboratory scales in the absence of a common scale. Two such stations already exist: (1) Cape Grim station, where samples are currently being collected for laboratories at Princeton, Scripps, and CSIRO, and (2) the Scripps Pier in La Jolla, California, where samples are being collected for Princeton and Scripps.

# **WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH**



**No. 161**

## **12<sup>th</sup> WMO/IAEA MEETING OF EXPERTS ON CARBON DIOXIDE CONCENTRATION AND RELATED TRACERS MEASUREMENT TECHNIQUES**

**(Toronto, Canada, 15-18 September 2003)**



In considering an ideal calibration and intercomparison programme, the following points were considered:

- a) Ultimately there is a need for a globally standardised calibration scale which all labs/field sites are linked to.
- b) One or more mechanisms are needed which provide quality assurance that data derived from flask measurements from one lab are comparable to data derived from flask measurements from a second lab.
- c) One or more mechanisms are needed which provide quality assurance that data derived from continuous measurements from one lab/field site are comparable to data derived from continuous measurements from a second lab/field site.
- d) Any calibration or intercomparison programme must take into account the fact that many different analyser techniques are currently used within the community to achieve high-precision O<sub>2</sub>/N<sub>2</sub> measurements (e.g. interferometric, mass spectrometric, paramagnetic, VUV absorption, gas chromatographic, and electrochemical fuel cell).

Ten of the twelve O<sub>2</sub>/N<sub>2</sub> labs (of Annex 1) were represented at this meeting, and the following recommendations were agreed upon by all participants:

- a) A “Round-Robin Cylinder” intercomparison programme will be initiated. This will consist of two sets of three high pressure cylinders to be analysed by all participating labs, with the two sets to rotate in opposite direction. At this stage we do not recommend that this programme should result in a common calibration scale, instead it should be used to establish and maintain a link between existing calibration scales. This decision should be reassessed at the 13th WMO/IAEA Experts Meeting in 2005.
- b) For those laboratories which make flask measurements, we will initiate a “Sausage Flasks Matrix” intercomparison programme. This will involve a primary laboratory simultaneously filling a pair of flasks from each participating laboratory from a high pressure cylinder and distributing to all labs for analysis.

- c) Although we did not formalise a programme, we strongly encourage all flask measurement laboratories to initiate or continue “Shared Flasks” intercomparison programmes. That is, programmes whereby two (or more) laboratories analyse sample air from a station site, either from exactly the same flasks, or from flasks filled simultaneously at a given site. The wider community at this meeting discussed the possibility of a “Super-Site”, where a single field station is used to link all flask analysis laboratories in such intercomparison programmes. If such a Super-Site is adopted, it would be wise for the O<sub>2</sub>/N<sub>2</sub> community to adopt the same site.
- d) Ralph Keeling (SIO) agreed to be the “Primary Lab”, supplying all high pressure gas cylinders for the round-robin cylinder programme, and filling all flasks for the sausage flasks matrix programme.
- e) Andrew Manning (MPI-BGC) agreed to collate all data resulting from the two programmes.

# Naming the programme

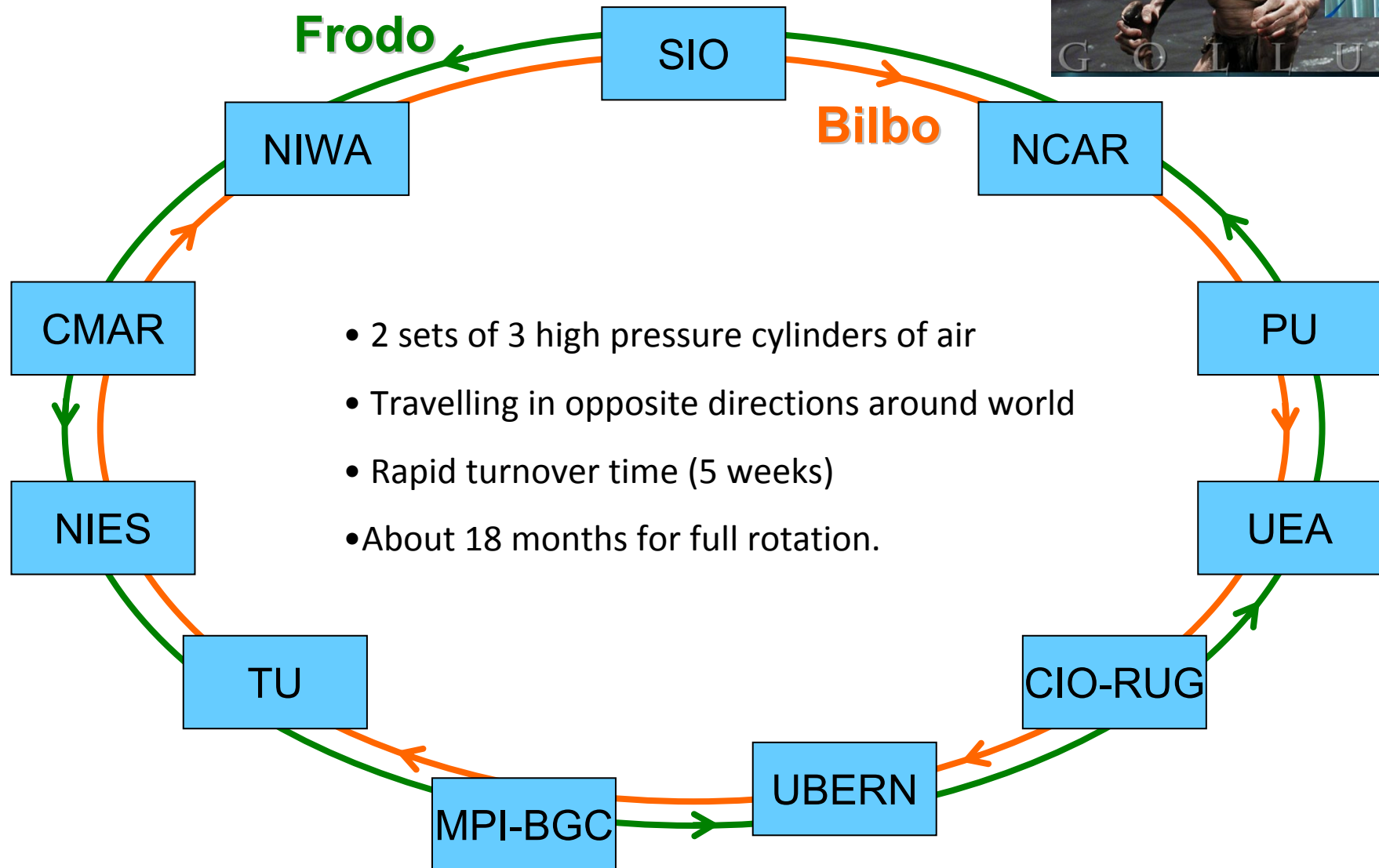
- **ATOMIC**
  - **AT**mospheric **O**xygen **M**easurement **I**nter**C**omparison programme
  
- **GOLLUM**
  - **G**lobal **O**xygen **L**aboratories **L**ink **U**ltra-precise **M**easurements



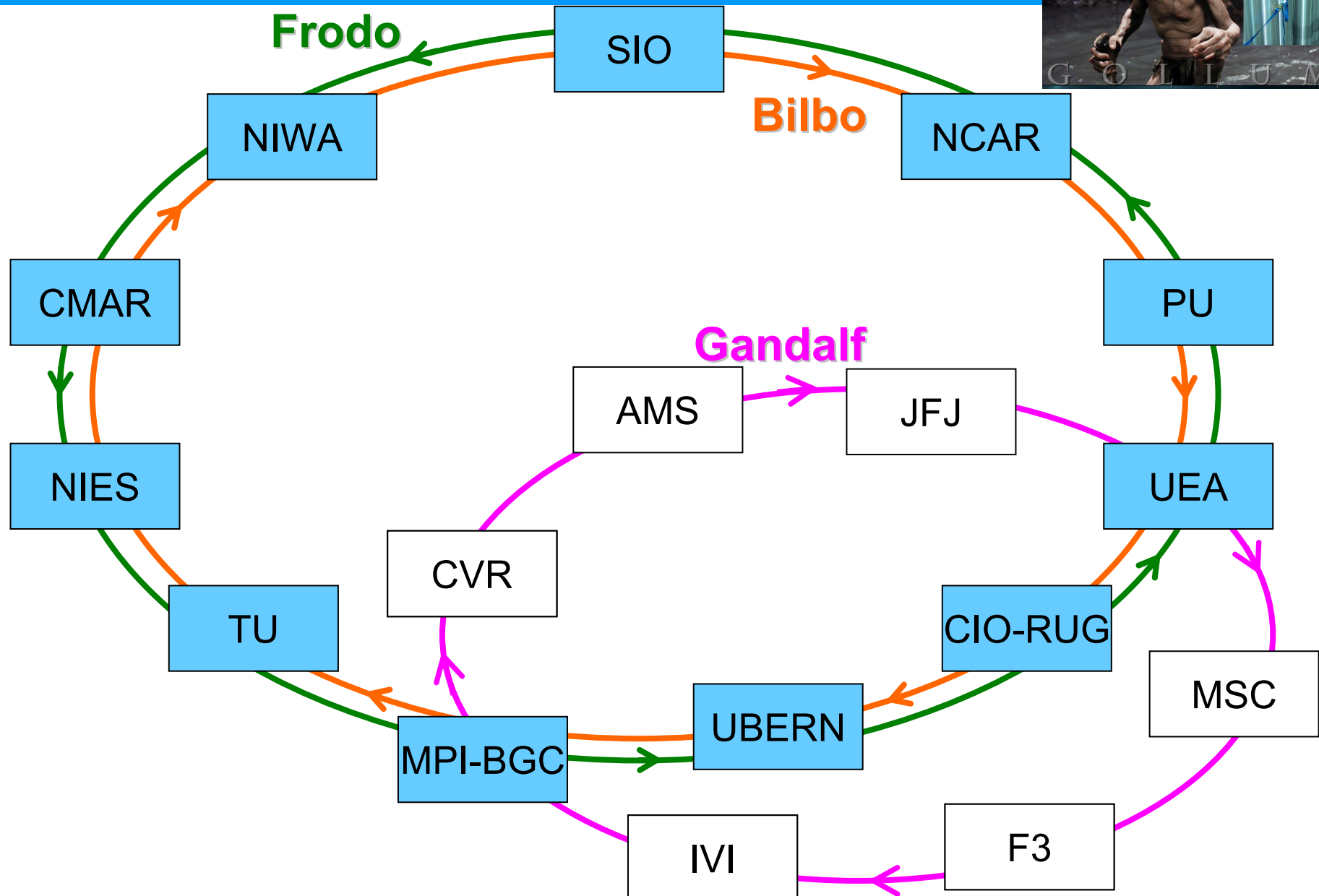
# Scale of the “GOLLUM” programme

- **23** authors.
- **10** measurement laboratories.
- **7** countries.
- **3** atmospheric species' compatibility assessed ( $O_2/N_2$ ;  $Ar/N_2$ ;  $CO_2$ ).
- **11+** years of intercomparison measurements.
- **6** high pressure cylinders in 2 loops of 3 cylinders each.
- **29** graphs on the website.
  
- **11+ year programme has been entirely unfunded!!!**

# GOLLUM rotations



# GOLLUM rotations





## Background on Atmospheric oxygen measurement

Atmospheric oxygen ( $O_2$ ) measurements are used to provide insight and quantitative understanding of the global carbon cycle [*Bender et al.*, 1996; *Bender et al.*, 1998; *Keeling and Shertz*, 1992]. More recently they have been used in other applications such as understanding air-sea gas exchange [*Keeling et al.*, 1998] and critiquing ocean biogeochemical and atmospheric transport models [*Battle et al.*, 2006; *Stephens et al.*, 1998].

Atmospheric  $O_2$  measurements were first established in 1988 by Professor Ralph Keeling at Scripps Institution of Oceanography [*Keeling*, 1988], and are now made at ~12 laboratories around the world and at ~25 field stations. The

## Disclaimer:

1. All results here are preliminary and provisional
2. These data must NOT be used to adjust any laboratory's calibration scales.
3. If you wish to use or present these data for

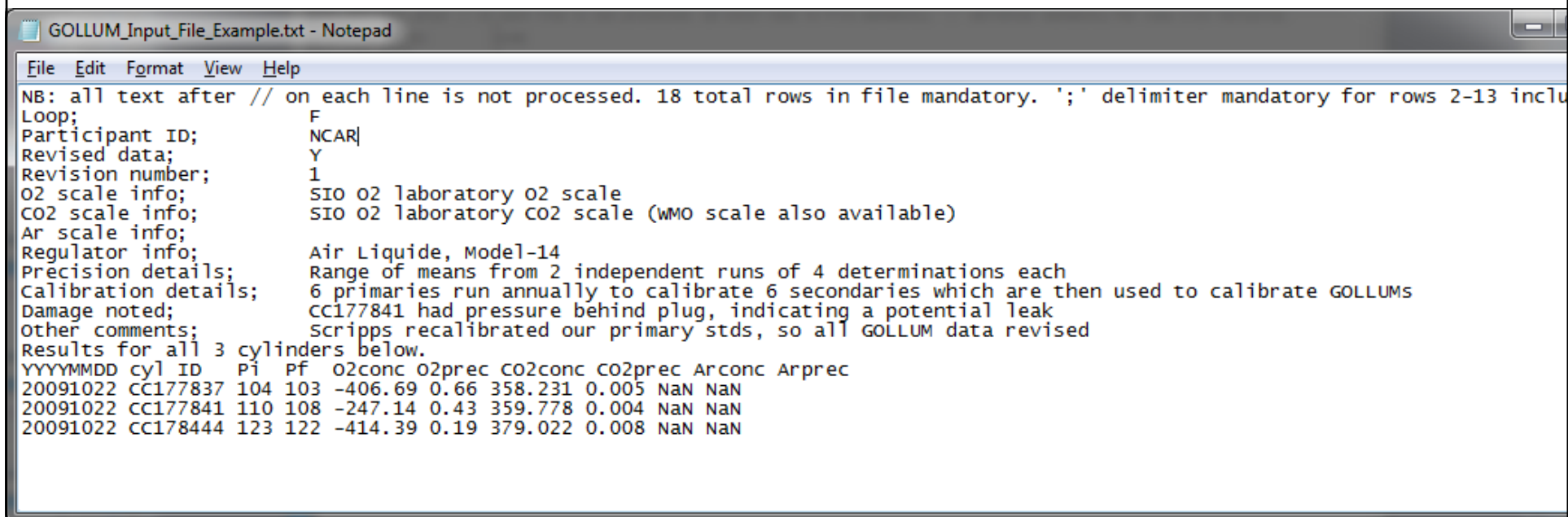
# Excel logsheet for submitting data

	A	B	C	D	E	F	G	H	I
1	<b><u>GOLLUM Logsheets</u></b>								
2									
3	Email a copy of this logsheet to Andrew Manning (a.manning@uea.ac.uk)								
4	within <b>4 weeks</b> of making your analyses.								
5	Are you submitting revised data? (Y/N):							<b>N</b>	
6	Revision Number (0 if original, unrevised data):							<b>0</b>	
7									
8	<b>Participant Name:</b>		<b>Frodo</b>			<b>Bilbo</b>		<b>Calibration scale info</b> (for	
9	<b>SIO</b>	<b>Analysis date</b>	<b>CC177837</b>	<b>CC177841</b>	<b>CC178444</b>	<b>CC177811</b>	<b>CC178269</b>	<b>CC180655</b>	who?; name of scale?; range of scale
10	<b>received pressure (bar)</b>								
11	<b>final pressure (bar)</b>								
12	<b>O2/N2 conc (per meg)</b>								
13	<b>O2/N2 precision (per meg)</b>								
14	<b>CO2 conc (ppm)</b>								
15	<b>CO2 precision (ppm)</b>								
16	<b>Ar/N2 conc (per meg)</b>								
17	<b>Ar/N2 precision (per meg)</b>								
18									
19	<b>Please state the make and model of regulators used:</b>								
20									
21									
22	<b>If you have given numbers in the "precision" rows, please describe here how you calculate these:</b>								
23									
24									
25	<b>Are these "final" or provisional concentration numbers? Please describe:</b>								
26									
27									
28	<b>Describe the on-site calibration you performed before analysing these cylinders:</b>								
29									
30									
31	<b>Please describe any damage you have observed to the cylinders or boxes:</b>								
32									



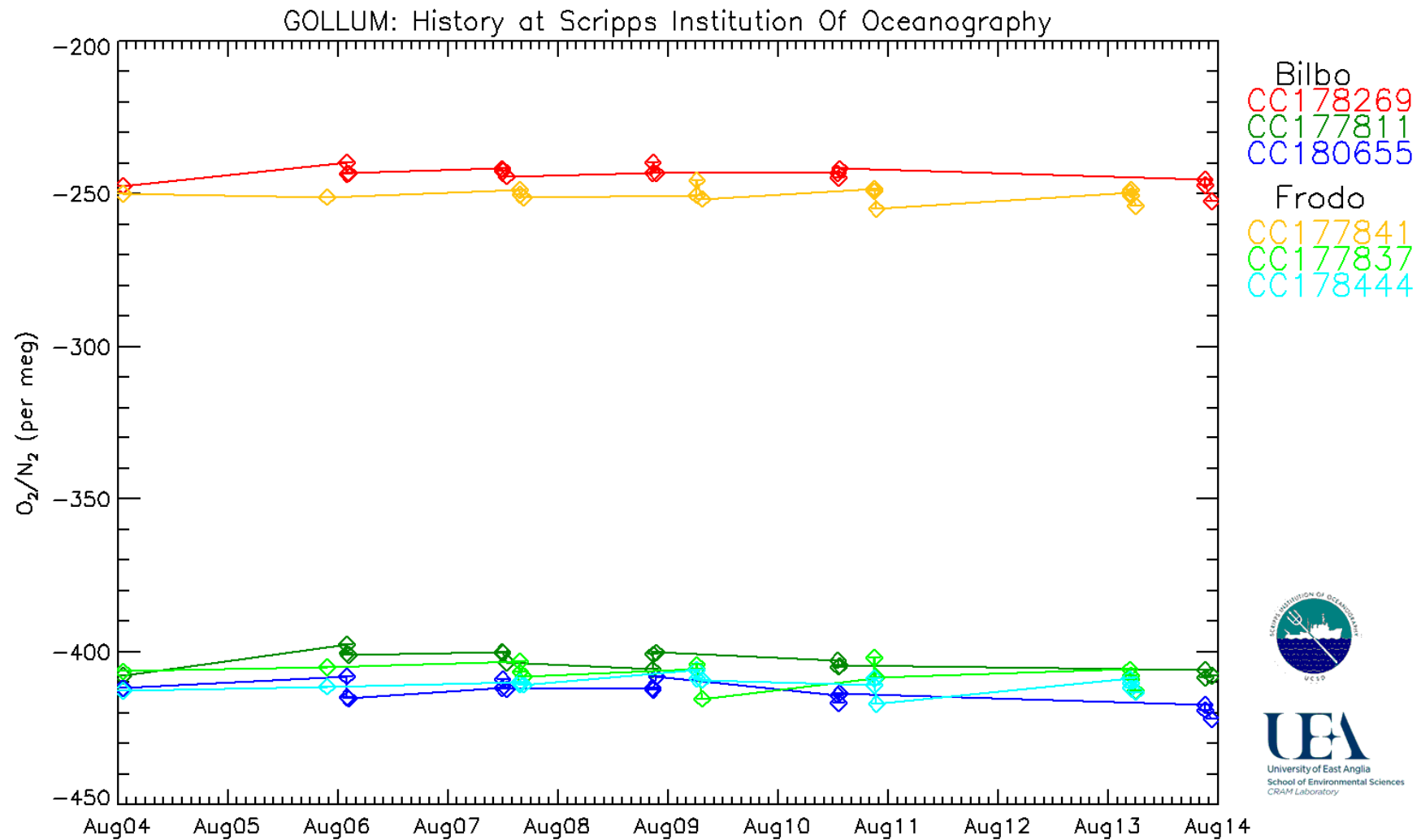
# New ASCII text file for submitting data

- Allows automated generation of files for submission by participants.
- Should result in less errors and mistakes.
- And big reduction in manual labour requirements.



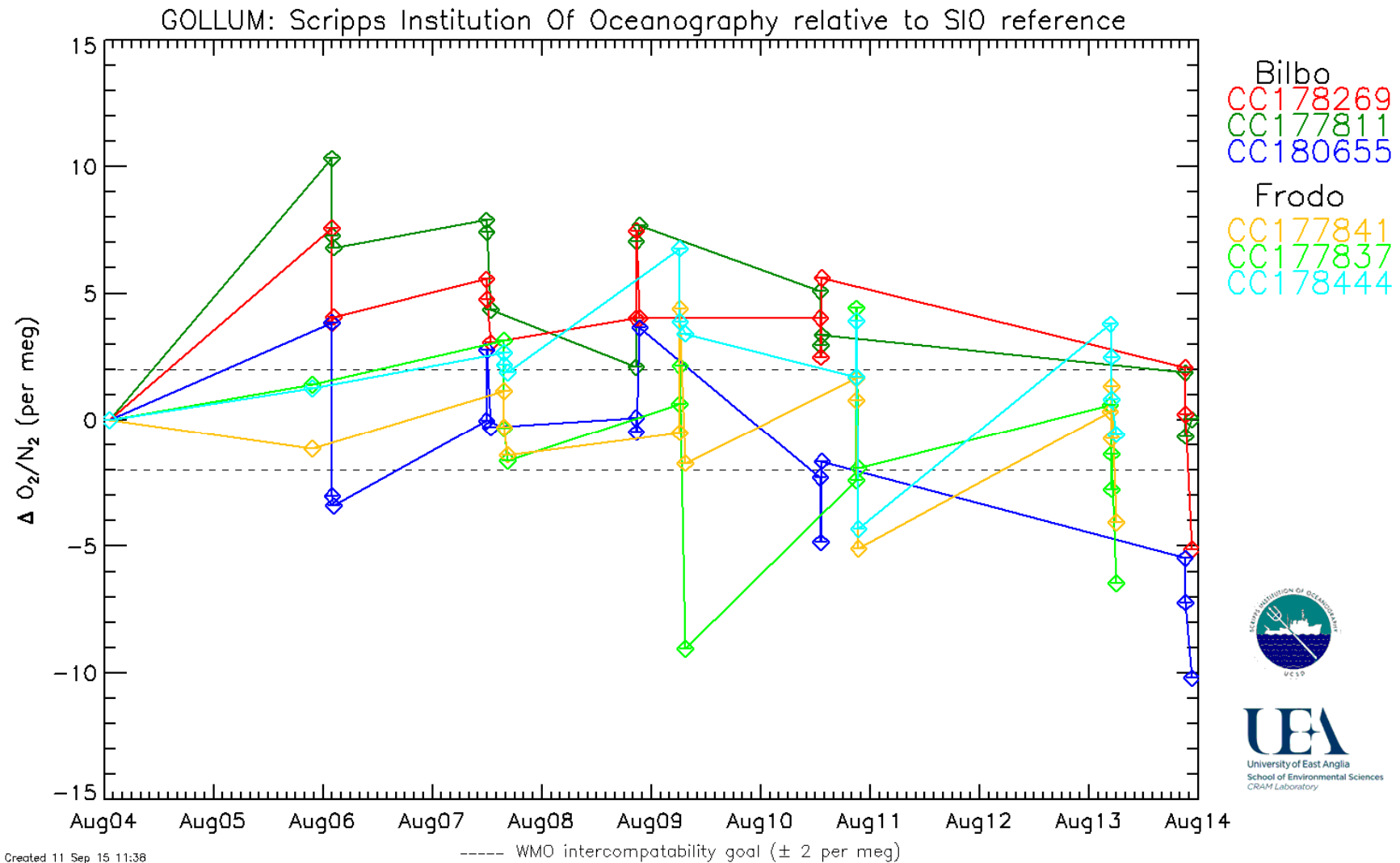
```
GOLLUM_Input_File_Example.txt - Notepad
File Edit Format View Help
NB: all text after // on each line is not processed. 18 total rows in file mandatory. ';' delimiter mandatory for rows 2-13 inclu
Loop; F
Participant ID; NCAR|
Revised data; Y
Revision number; 1
O2 scale info; SIO O2 laboratory O2 scale
CO2 scale info; SIO O2 laboratory CO2 scale (WMO scale also available)
Ar scale info;
Regulator info; Air Liquide, Model-14
Precision details; Range of means from 2 independent runs of 4 determinations each
Calibration details; 6 primaries run annually to calibrate 6 secondaries which are then used to calibrate GOLLUMs
Damage noted; CC177841 had pressure behind plug, indicating a potential leak
Other comments; Scripps recalibrated our primary stds, so all GOLLUM data revised
Results for all 3 cylinders below.
YYYYMMDD cyl ID Pi Pf O2conc O2prec CO2conc CO2prec Arconc Arprec
20091022 CC177837 104 103 -406.69 0.66 358.231 0.005 NaN NaN
20091022 CC177841 110 108 -247.14 0.43 359.778 0.004 NaN NaN
20091022 CC178444 123 122 -414.39 0.19 379.022 0.008 NaN NaN
```

# Results: Scripps: O<sub>2</sub>

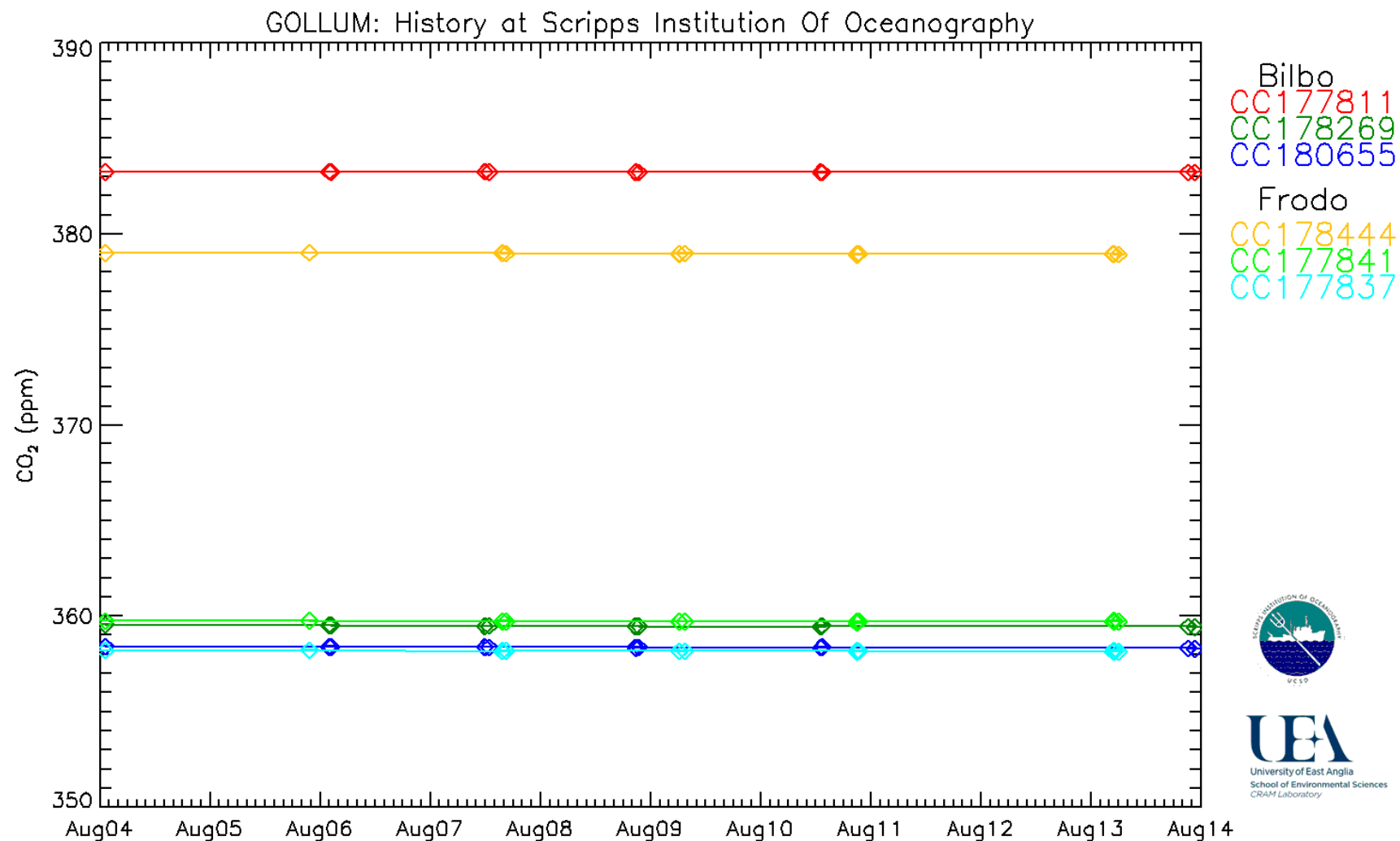


Created 11 Sep 15 11:38

# Results: Scripps: Relative O<sub>2</sub>

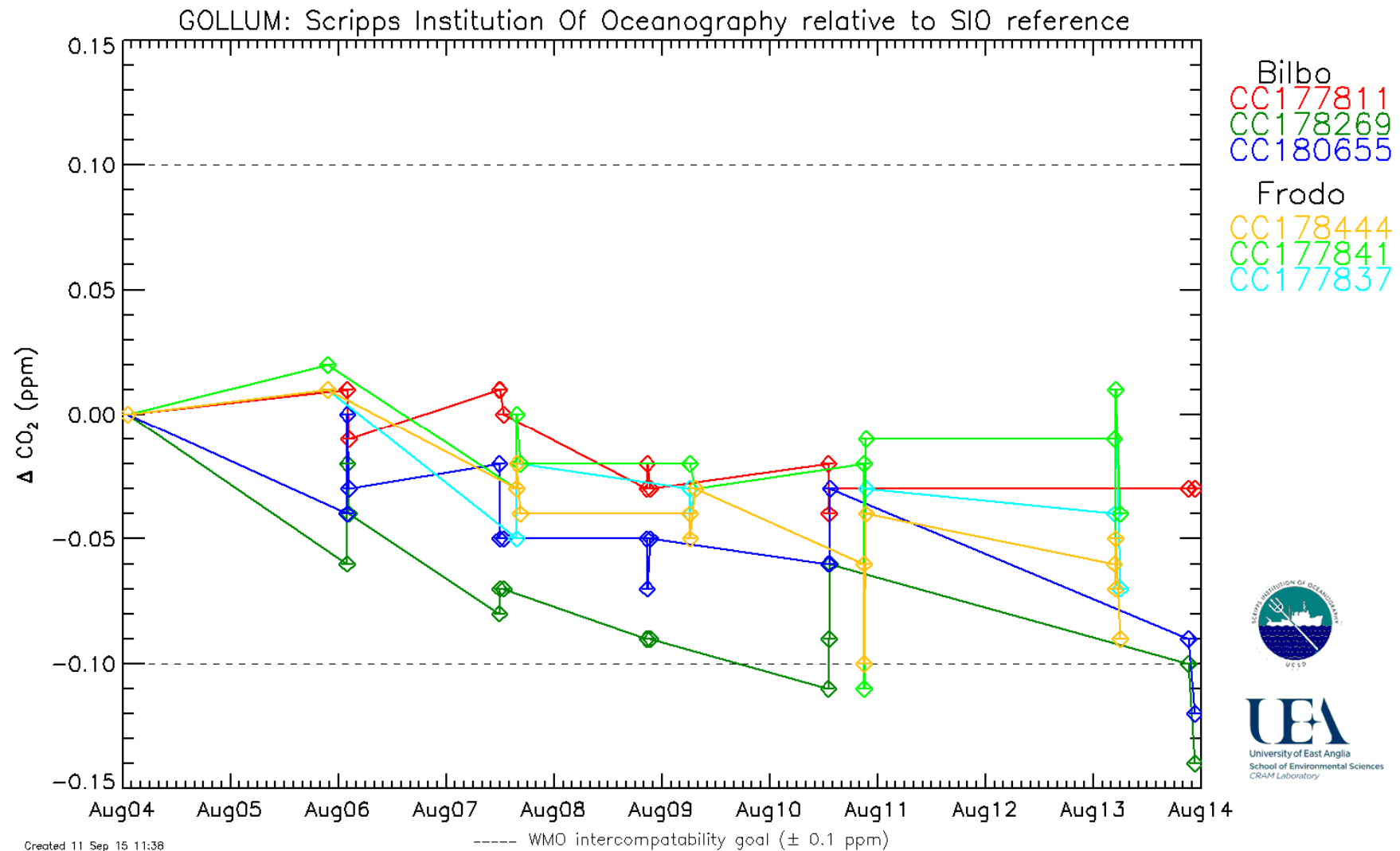


# Results: Scripps: CO<sub>2</sub>



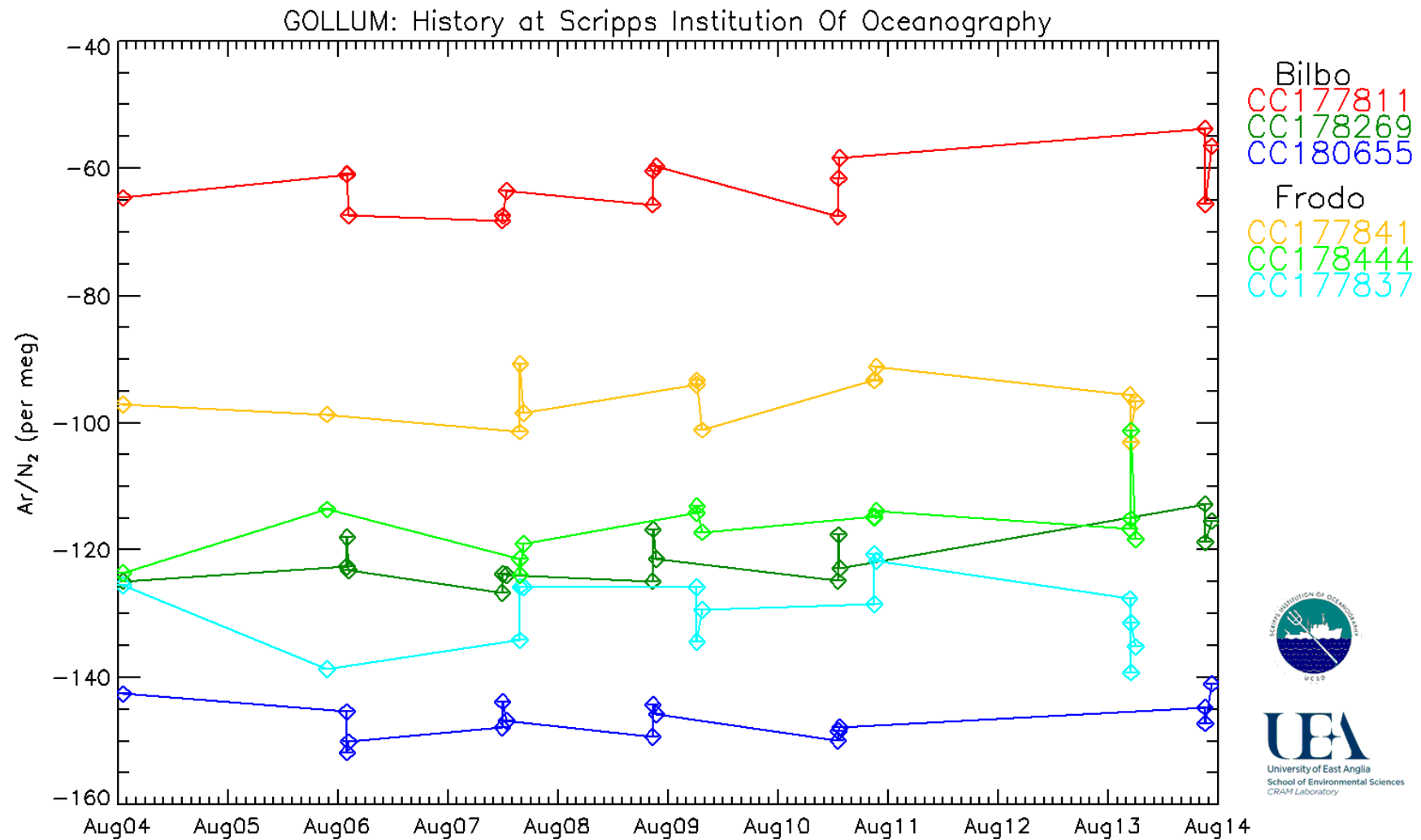
Created 11 Sep 15 11:38

# Results: Scripps: Relative CO<sub>2</sub>



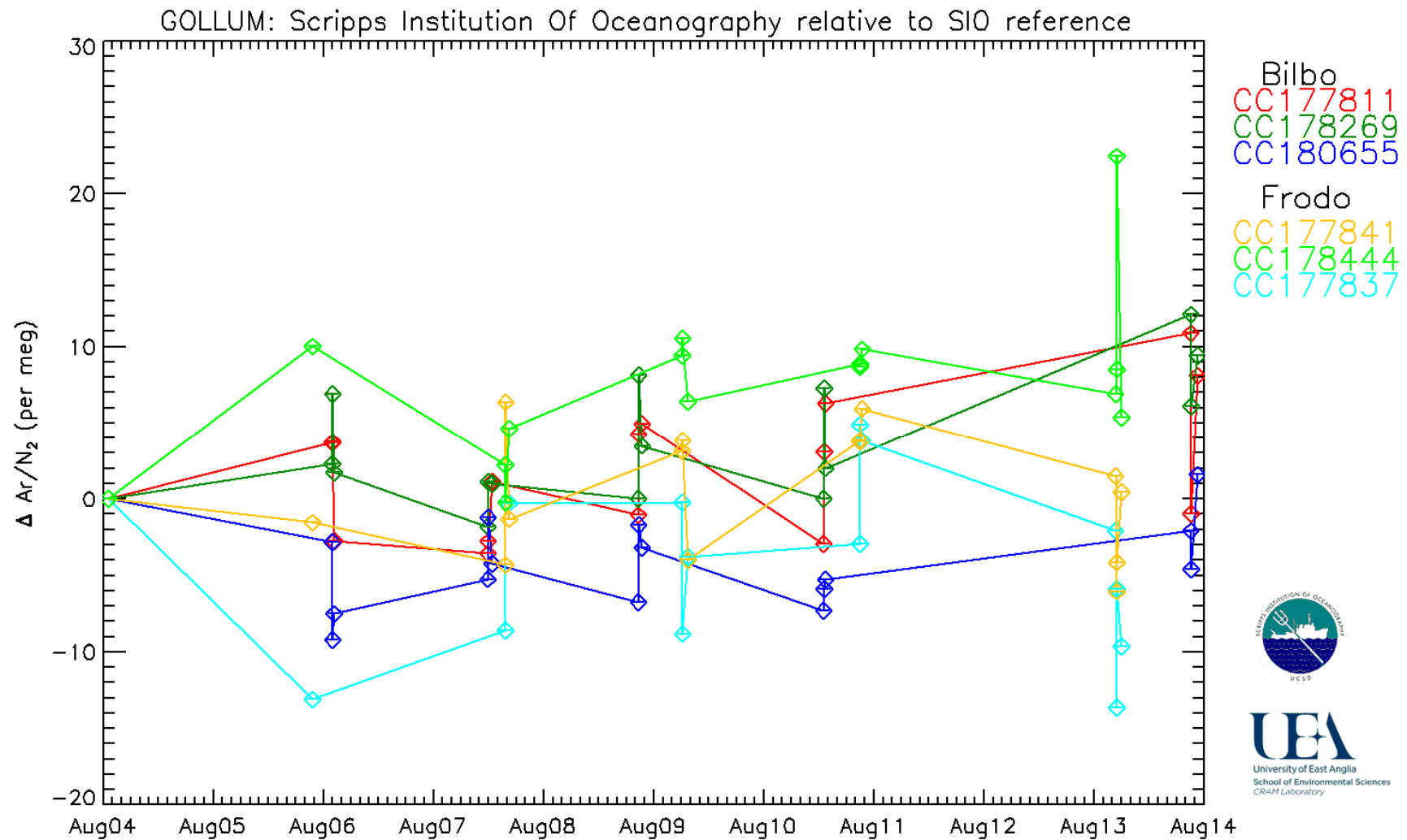


# Results: Scripps: Ar



Created 11 Sep 15 11:38

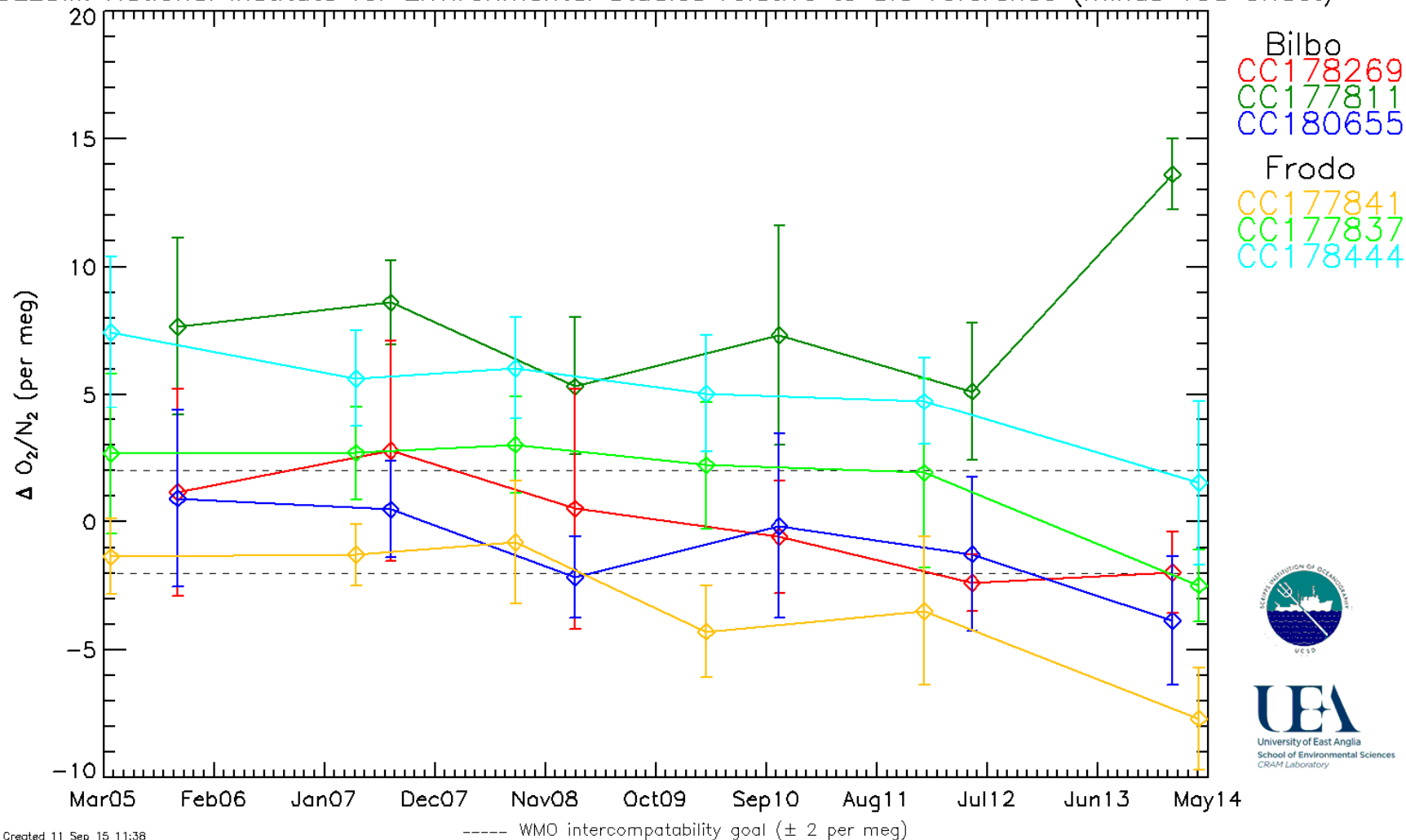
# Results: Scripps: Relative Ar



# Results: NIES: Relative O<sub>2</sub>

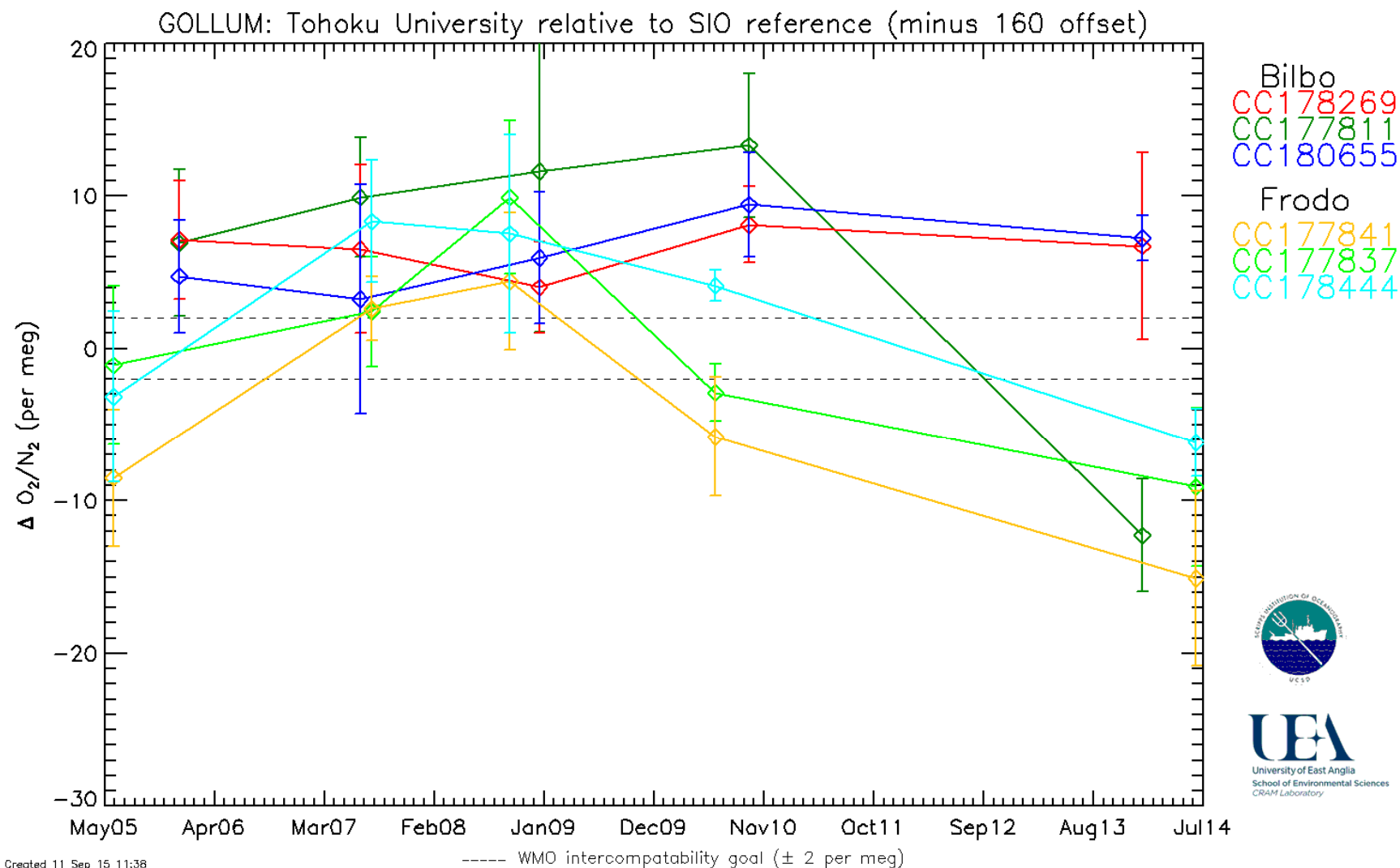
- Note: y-axis scale of next few graphs is not constant; but WMO goal gives some indication.

Source: National Institute for Environmental Studies relative to SIO reference (minus 195 offset)

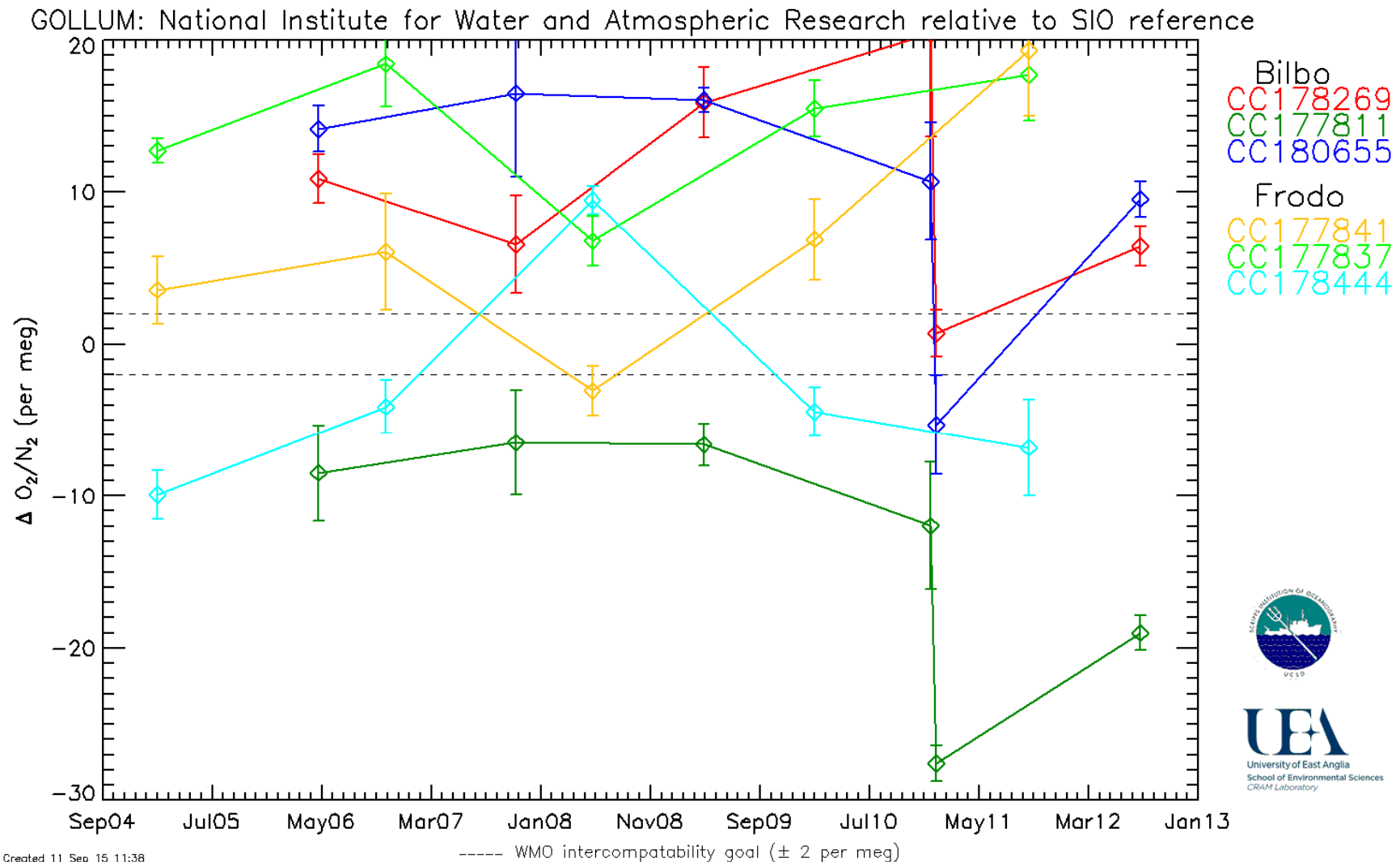


**UEA**  
University of East Anglia  
School of Environmental Sciences  
CRAM Laboratory

# Results: Tohoku University: Relative O<sub>2</sub>

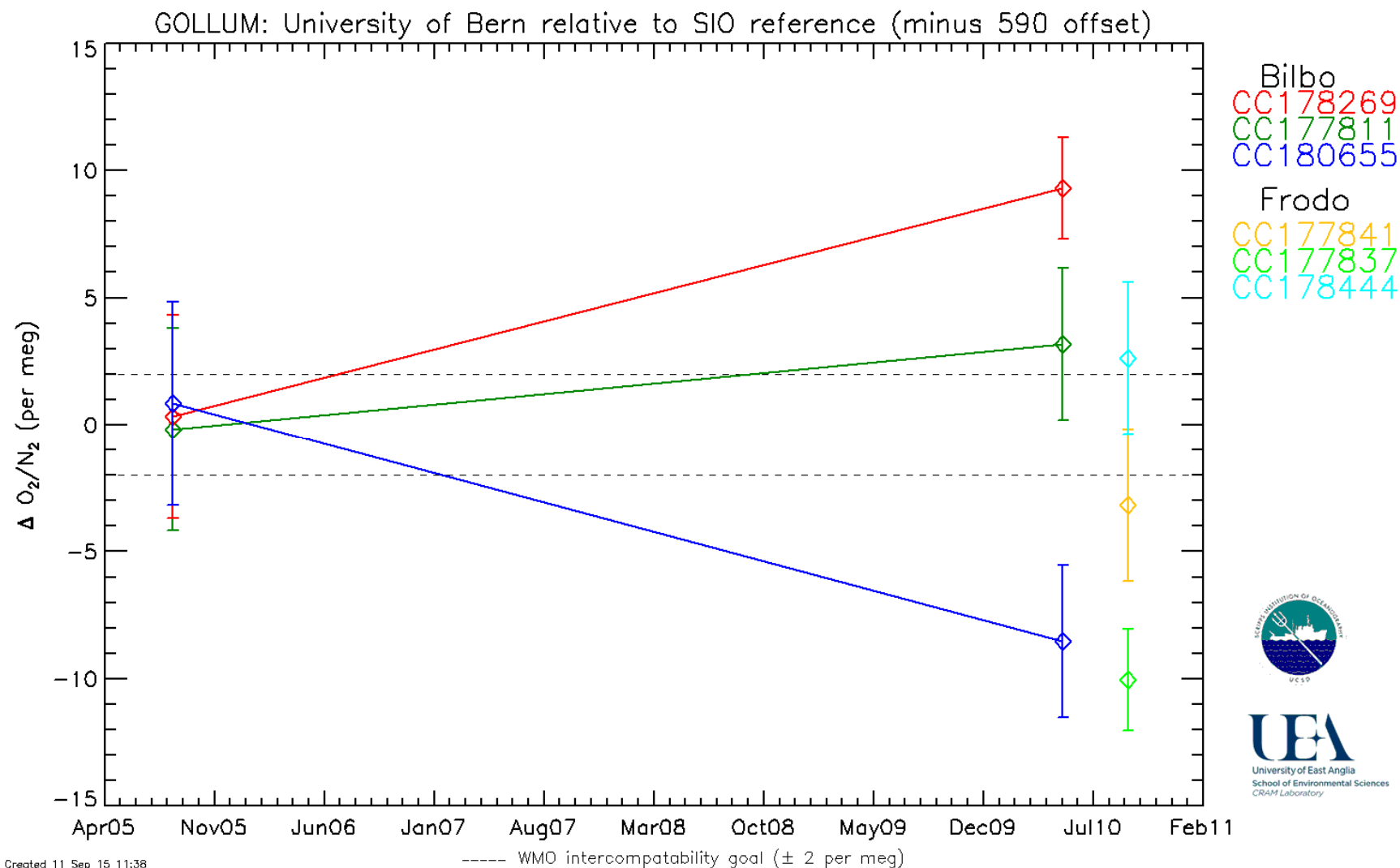


# Results: NIWA: Relative O<sub>2</sub>

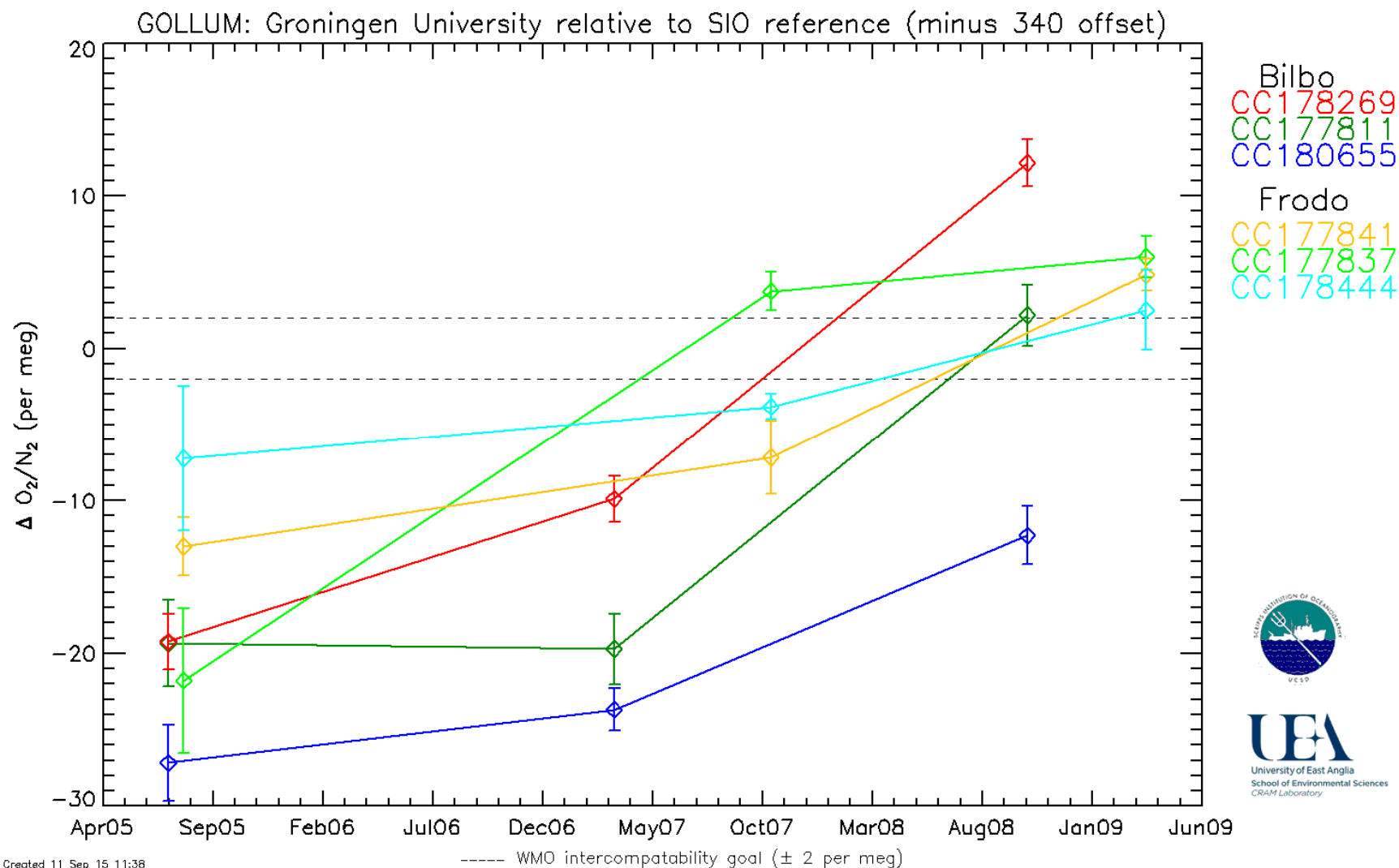




# Results: University of Bern: Relative O<sub>2</sub>

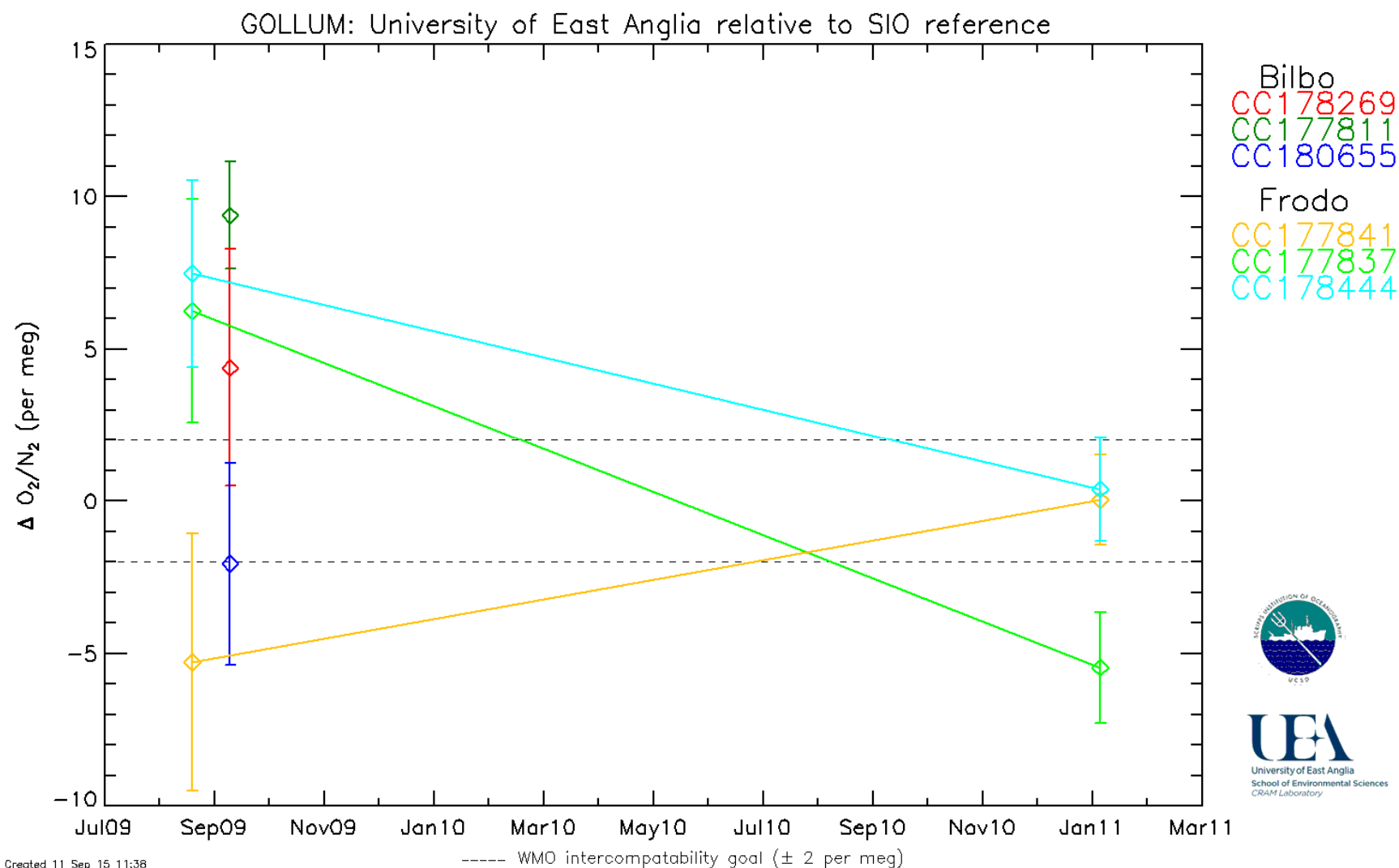


# Results: Groningen University: Relative O<sub>2</sub>

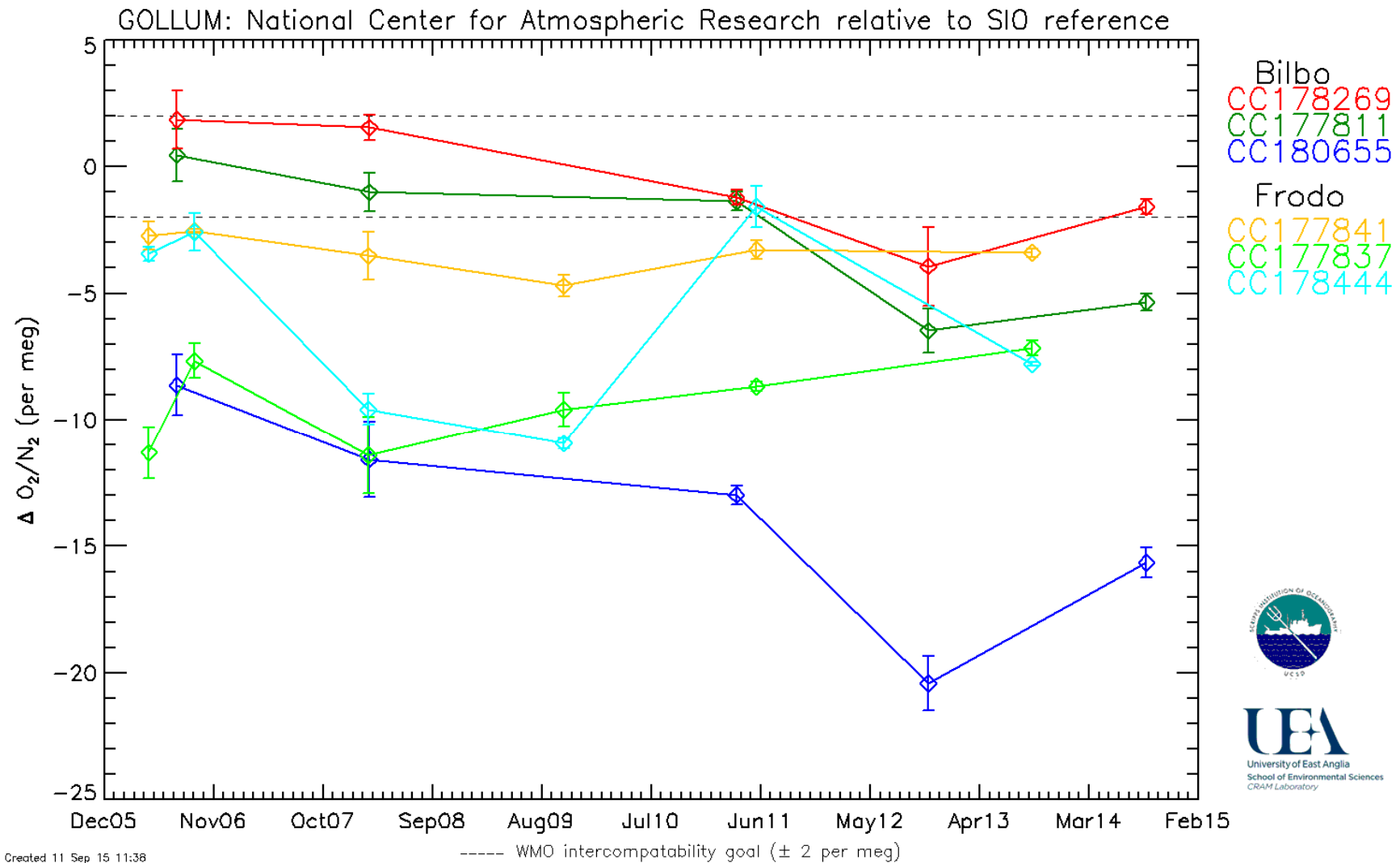


**UEA**  
University of East Anglia  
School of Environmental Sciences  
CRAM Laboratory

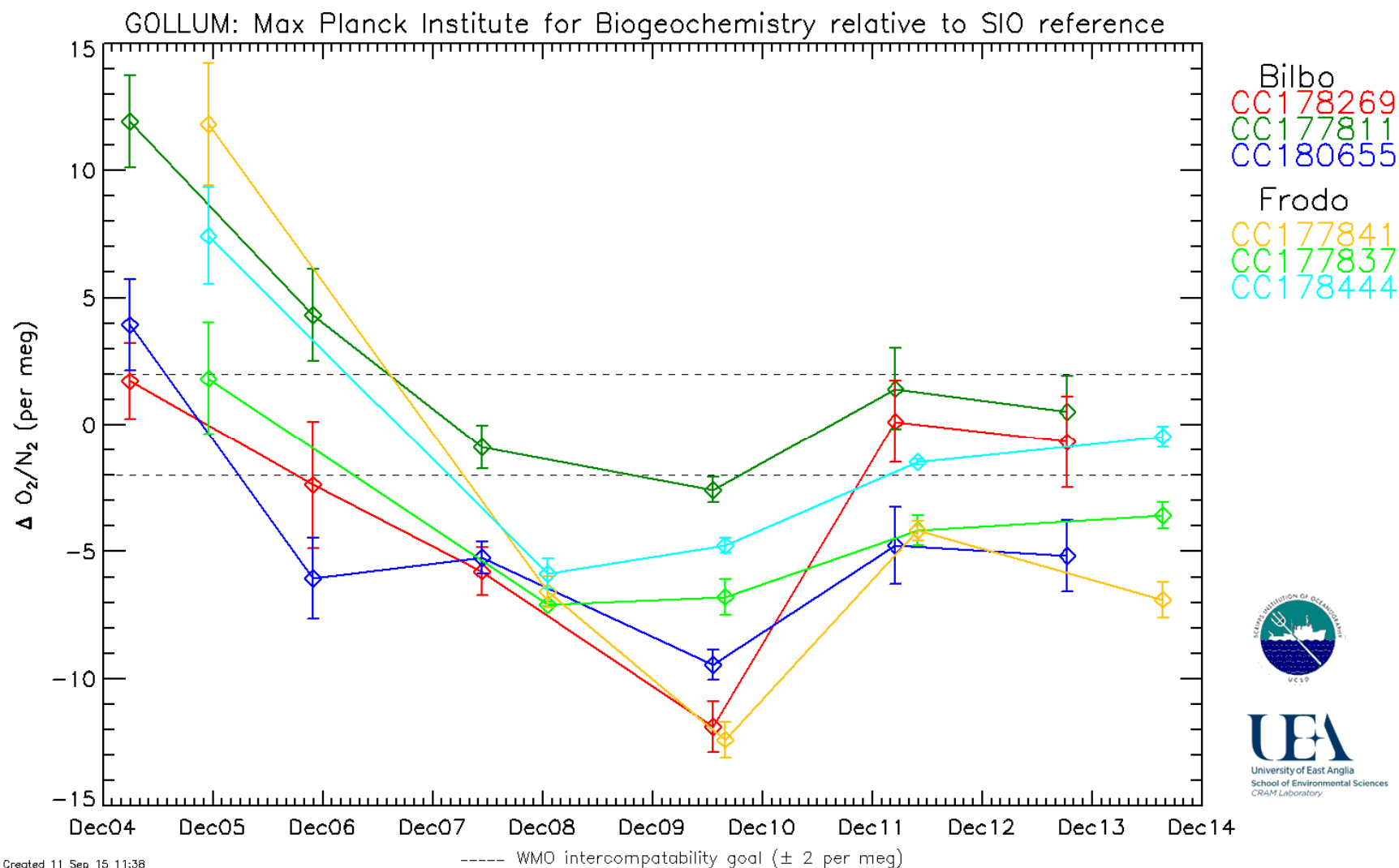
# Results: University of East Anglia: Relative O<sub>2</sub>



# Results: NCAR: Relative O<sub>2</sub>



# Results: Max Planck: Relative O<sub>2</sub>

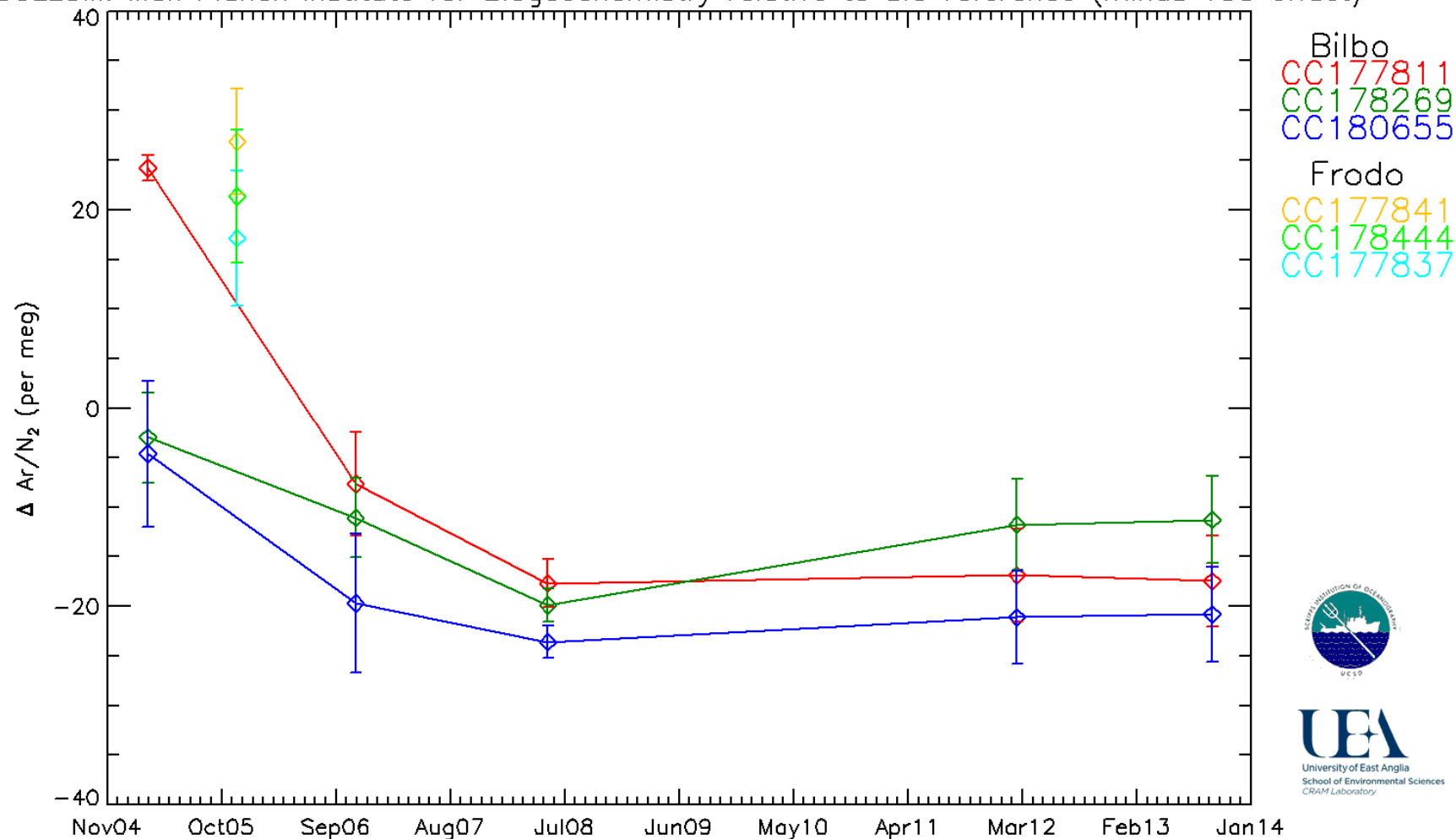


**UEA**  
University of East Anglia  
School of Environmental Sciences  
CRAM Laboratory



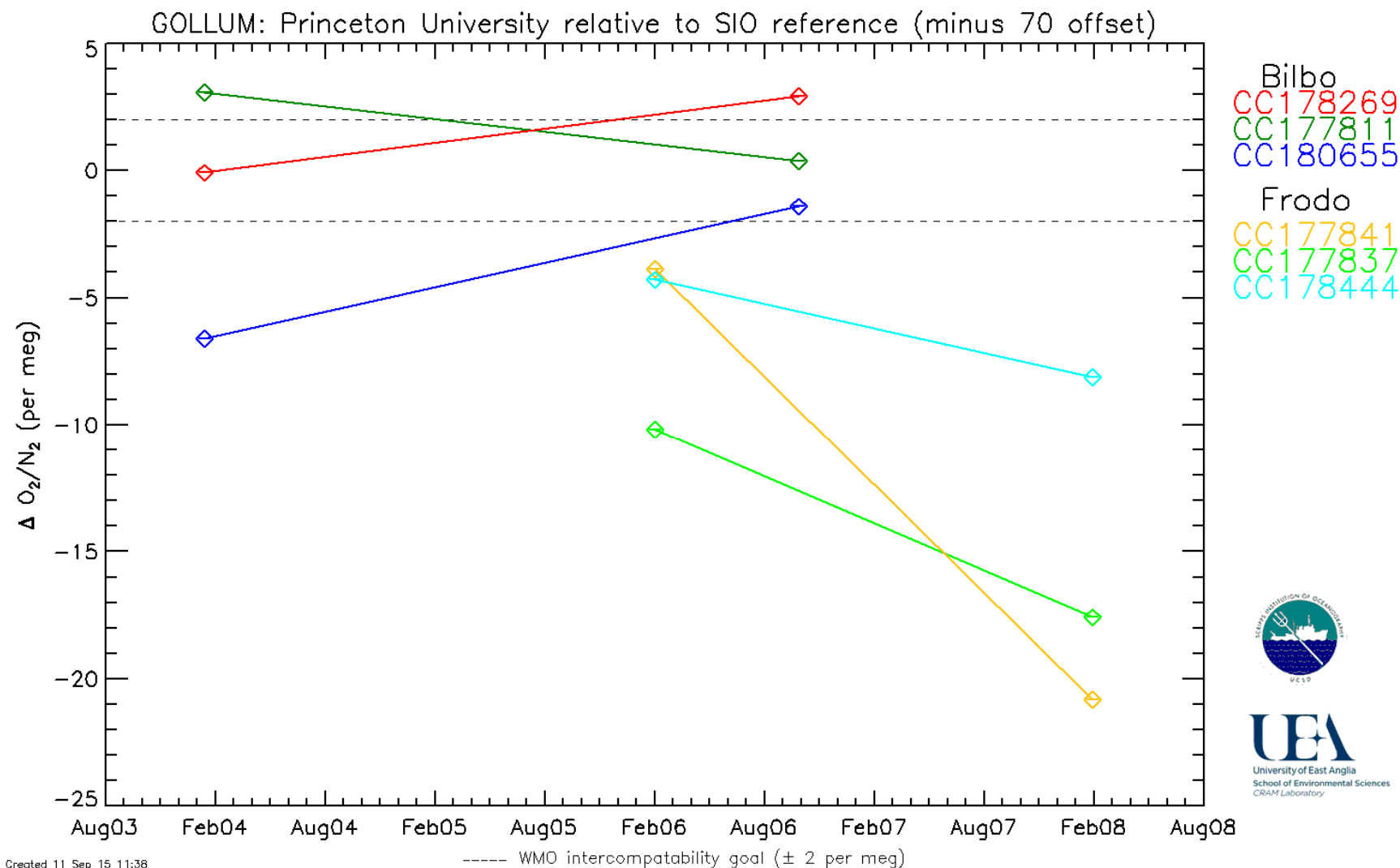
# Results: Max Planck: Relative Ar

GOLLUM: Max Planck Institute for Biogeochemistry relative to SIO reference (minus 130 offset)



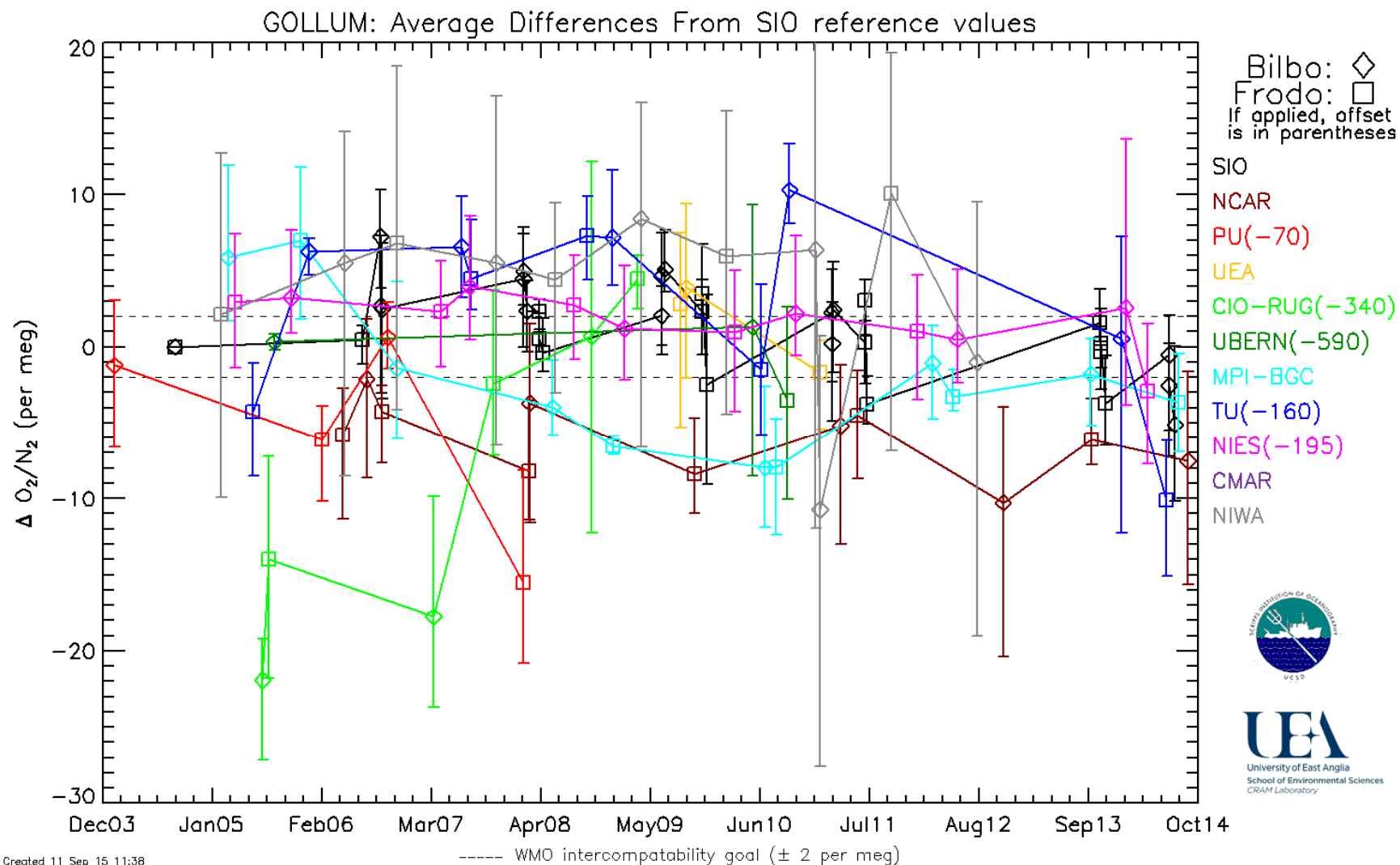
Created 11 Sep 15 11:38

# Results: Princeton University: Relative O<sub>2</sub>

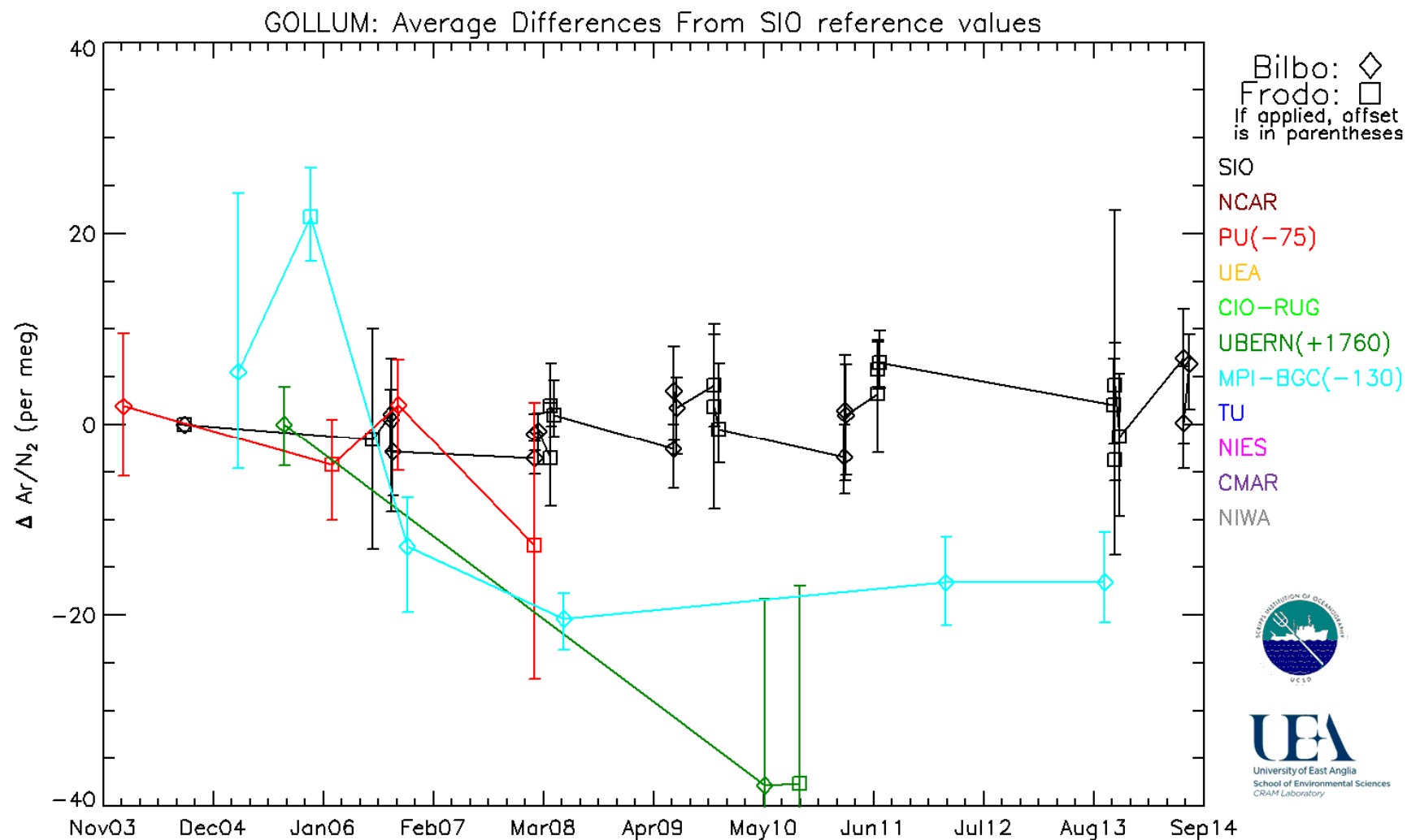


**UEA**  
University of East Anglia  
School of Environmental Sciences  
CRAM Laboratory

# Results: Everyone: Relative O<sub>2</sub>

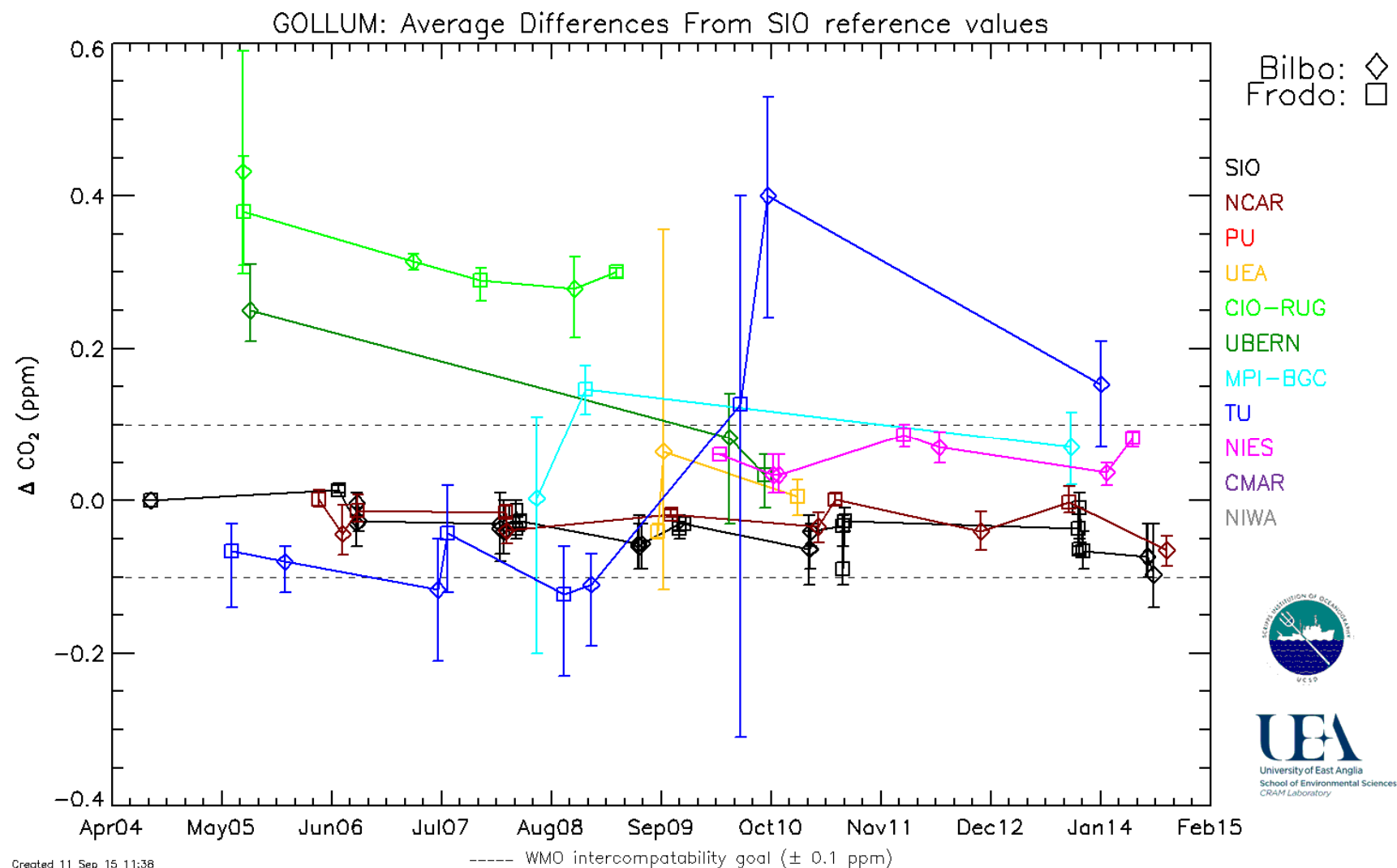


# Results: Everyone: Relative Ar

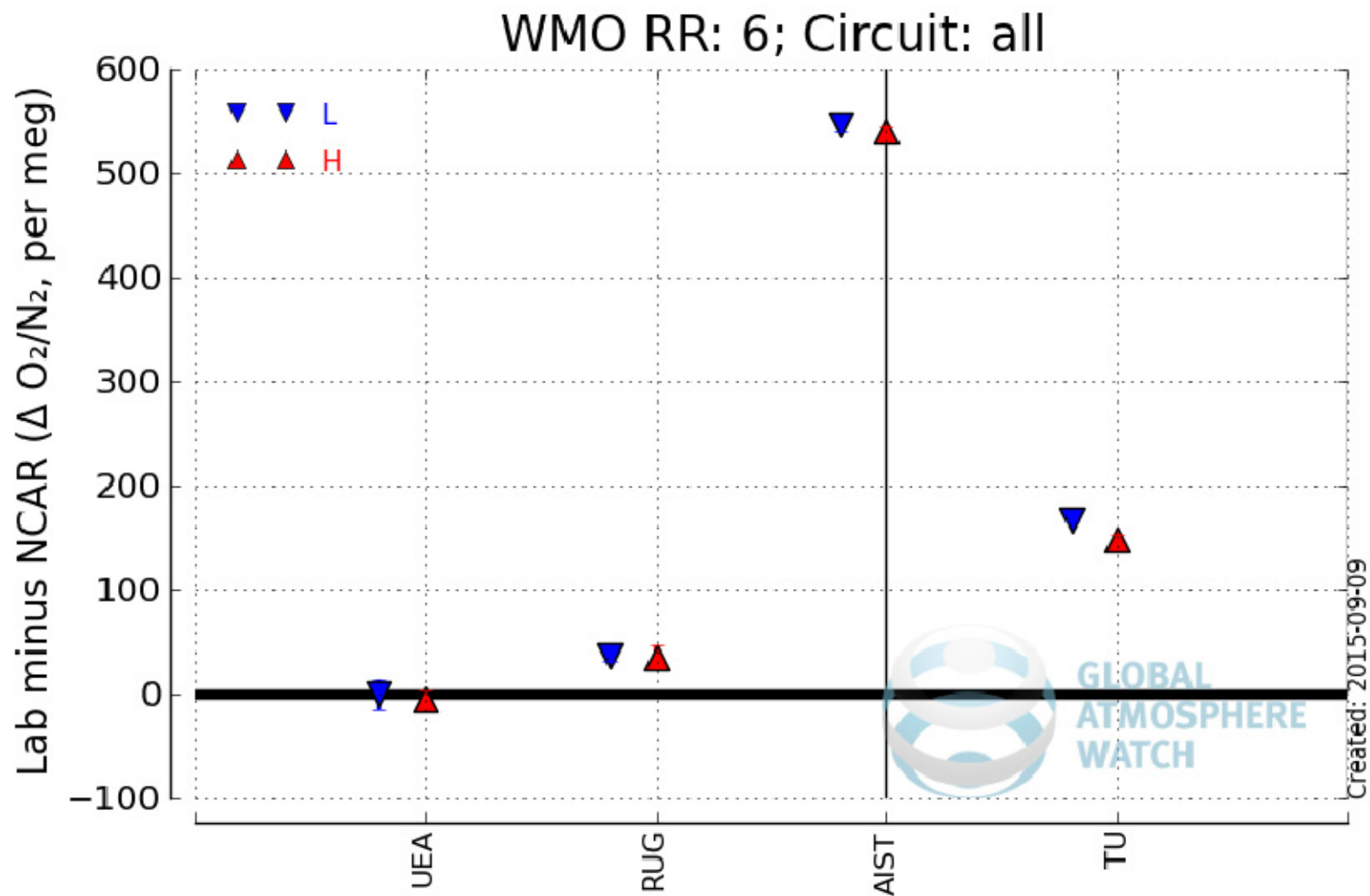


Created 11 Sep 15 11:39

# Results: Everyone: Relative CO<sub>2</sub>



# WMO Round Robin results, 2015



# Maintaining the momentum from this Workshop:

## Part 1: Third APO Workshop

- I've done some extensive research on where we might want to hold the next workshop...





Alpha Phi Omega Fall Rush 2012



Co-ed Service Fraternity

Join the nation's largest collegiate fraternity and become part of a brotherhood that is passionate about service!

Formal Rush  
Tuesday 8/28 & Wednesday  
8/29  
Bobo Spiritual Life Center  
7:00 p.m.

Social Rush  
Wednesday 9/5  
Laser tag & roller skate with  
APO  
Meet at 4:30 p.m.

Dinner with Exec  
Thursday 9/6  
Come eat dinner and get to  
know  
the members of exec.  
6:45 p.m.

Informal Rush  
Friday 9/7  
Bear Park  
4:00 p.m.

Interviews  
Friday 9/7  
Cashion 103  
7:00 p.m.

Service Rush  
Saturday 9/8  
Meet at  
7th & James Church  
10:00 a.m.

For more information contact:

junaid\_gilani@baylor.edu

khadija\_lalani@baylor.edu

www.apoonline/zetaomega

@BaylorAPO



**CONQUER THE PHILIPPINES' HIGHEST**

# MT. APO

*Kidapawan city, North Cotabato*



**FOR MORE DETAILS PLEASE CONTACT:**  
Miguel "MIGS" Mapalad - 0905 268 8275  
Email: miguel.mapalad@yabag.org



**Mt. Apo**

Davao and North Cotabato



**The Mount APO**



**CONQUER THE PHILIPPINES' HIGHEST**

**MT.**

**MT. APO**

*Kidapawan*



**FOR MORE DETAILS PLEASE CONTACT:**  
Miguel "MIGS" Mapalad - 0905 268 8275  
Email: miguel.mapalad@yabag.org



**The Mount APO**

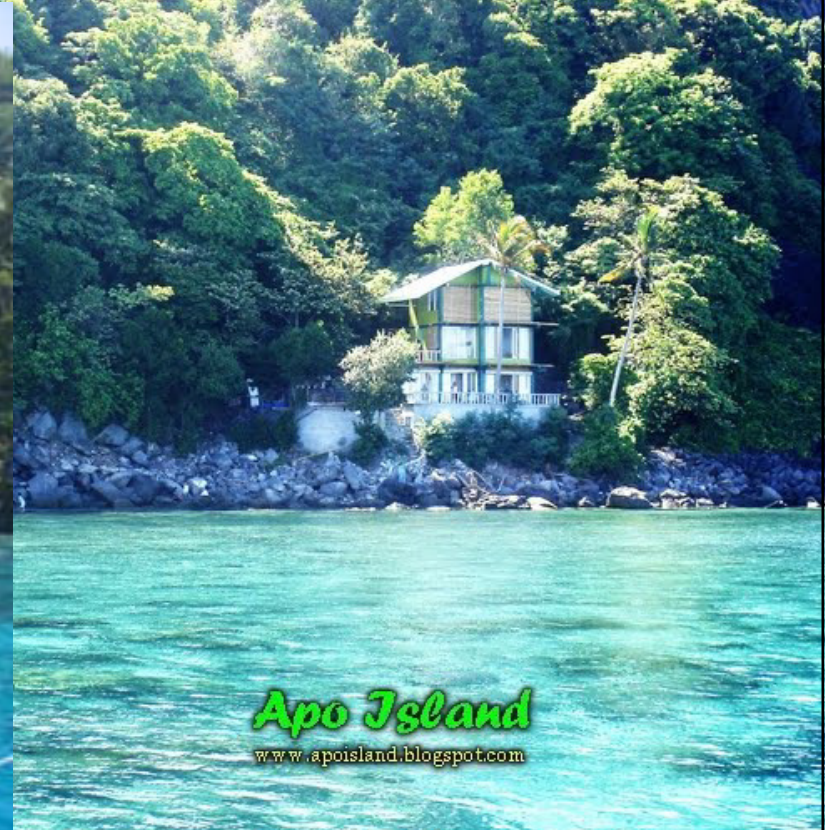




**Apo Island**  
[www.philippinetraveltour.com](http://www.philippinetraveltour.com)



**Apo Island**



**Apo Island**  
[www.apoisland.blogspot.com](http://www.apoisland.blogspot.com)





## APO ISLAND

DAUIN, ORIENTAL NEGROS, PHILIPPINES

9°4'N 123°16'E

AREA : 0.74 km<sup>2</sup> (0.29 sq mi)

Population (2007): 745

Time zone : PST (UTC+8)

Zip code : 6217

Area code : 35

Home to over 650 documented species of fish and estimated to have over 400 species of corals. Most of the Philippines' 450 species of coral can be found in Apo Island.



# Maintaining the momentum from this Workshop:

## Part 2

- EOS article
  - Short report from this Workshop
- GOLLUM mailing list (maintained by myself at UEA)
  - Expand to modelling community too?
    - Currently only ~20 emails per year, so will not be inundated with 'spam'
- GOLLUM website
  - Expand to include other information?
    - E.g. PDFs of all talks from this Workshop?
      - (Can be placed behind a password)
    - E.g. list of APO-relevant papers?

# Maintaining the momentum from this Workshop:

## Part 3: GOLLUM programme

- GOLLUM cylinders
  - Re-hydrotest and refill
    - What concentrations? (Better with range in all 3 cylinders?)
    - Do we want with dip tubes? (previous WMO Recommendations said yes!!)
    - Dew point measured and less than 2 ppm
  - Other participants (CMAR?; AIST?)
  - Produce tables of quantified offsets as in 'Cucumbers' programme
    - 5-year time frames?
- GOLLUM flasks
  - Do we want to resurrect this programme?
- Shared flasks programmes – more?
- Flask sampling co-located with *in situ* stations?
  - Gives Ar/N<sub>2</sub>
  - Provides validation, verification, quality control, intercomparison, etc, etc
- Peer-reviewed paper in 2016/7



# Maintaining the momentum from this Workshop:

## Part 4a: UK funding opportunity



The screenshot shows the NERC Science of the Environment website. The header includes the NERC logo and a navigation menu with links to Home, Funding, Research, Innovation, Skills, News, Events & Publications, and About Us. The breadcrumb trail indicates the path: Home / Research / Partnerships / International research / International Opportunities Fund. The main heading is 'International Opportunities Fund'. Below this, a section titled '- Programme overview' contains the following text:

The aim of the International Opportunities Fund (IOF) Scheme is to provide resources to NERC-supported research groups to allow them to forge long-term partnerships with overseas scientists that add value to existing NERC-funded science

NERC's usual funding schemes encourage international project partnerships and the IOF is not intended to simply support international collaborative research. It has a specific aim of **adding value to existing NERC-funded research, data and knowledge through international collaboration**. Furthermore, the IOF seeks to provide a foundation for long-term partnership and added value that will continue beyond the lifetime of the grant. As such, the IOF aims to support collaborations that are not typically supported through NERC's usual funding schemes.

...should promote excellent research that cannot be delivered by the UK alone.

...some aspects of the research will be more speculative and exploratory than is typical.

...promote UK leadership of international research agenda's and initiatives.

# Maintaining the momentum from this Workshop:

## Part 4b: UK funding opportunity

- Funds available: ~£300,000, i.e. US\$450,000 or 410.000 Euro or A\$650,000 or NZ\$730,000
- Complication: call is for international partnerships/collaboration, but can't give funds to non-UK organisations.
  - But can support travel for foreigners, scientist exchange programmes, workshop, etc.
- Some draft suggestions from me (influenced by both APO needs and meeting call criteria):
  - GOLLUM programme coordination support and expansion
  - Observational Data sets:
    - Develop Obspack O<sub>2</sub>
    - Coordinate for community to submit data to WDCGG
    - But first, improve QC of existing data sets
  - Third APO Workshop (in 3 years)
  - Progress on calibration scales
    - Towards WMO scale?? CCL/WCC??
      - Gravimetric standards work?
      - Pay for postdoc to work at Scripps??

# Maintaining the momentum from this Workshop:

## Part 4c: UK funding opportunity

- More draft suggestions from me (influenced by both APO needs and meeting call criteria):
  - Research O<sub>2</sub> measurement issues such as intake and 'tee' designs that don't fractionate; other examples mentioned in WMO Recommendations
  - Modelling progress that could be done via exchange programmes?
    - Garcia and Keeling update?
  - Help Lingxi and others starting up new O<sub>2</sub>/N<sub>2</sub> programmes (exchange programmes)
  - Impact related activities, e.g. human physiology impacts paper
  - Produce 'Best practices' paper for flask sample collection, analysis, and *in situ* analysis
  - Stimulate more/speedier publications.
  
  - More precise, more stable instruments that consume less calibration gases.
  - Instability in cylinders...