AIR LIQUIDE

Creative Oxygen

Environmental Measurements: How to Improve Accuracy

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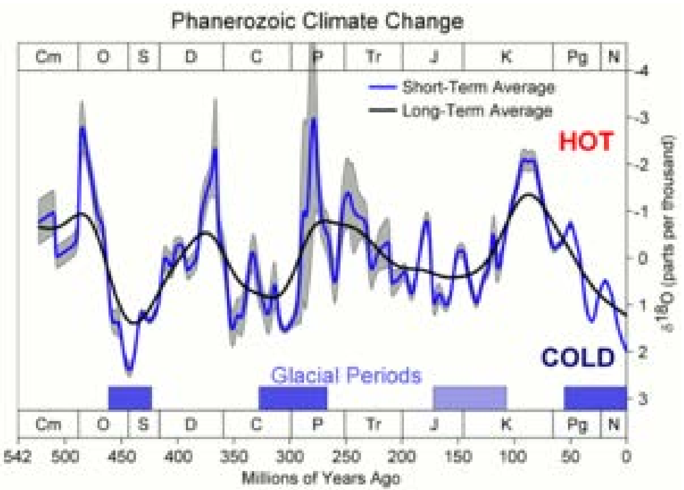
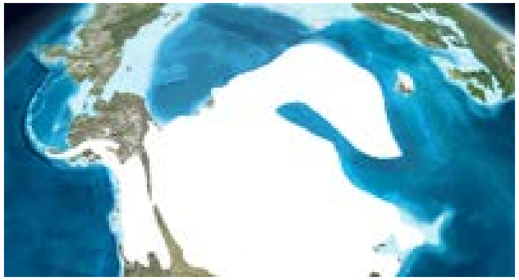
October 14th 2016

Agenda

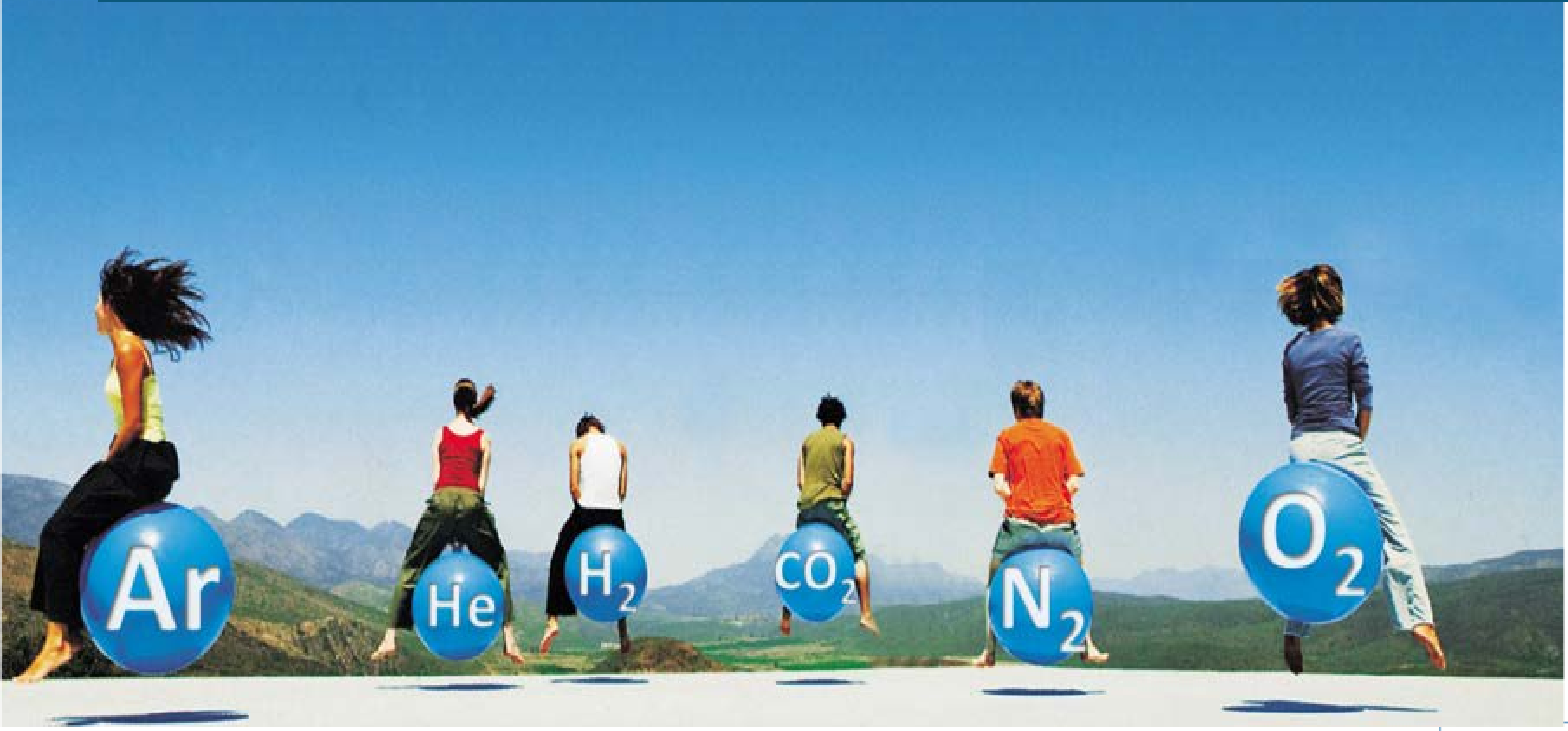
- Stable Isotopes & The Environment
- Alphagaz™ Natural Air
- Summary

Climate change



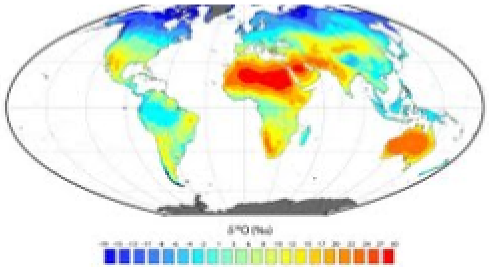


Stable Isotopes & The Environment



Stable Isotopes

- Significant component of environmental research
  - Used to detect, age dating of groundwater, monitoring of landfill contamination, determining source of stray gas in soils…..
  - Isotopes in precipitation, combustion, respiration, volcanic activity, etc…
  - Concentrations for greenhouse gas determination
  - Natural air monitoring



Predicted oxygen isotope ratios of plant leaf water (credit: J. West)

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Carbon Reservoirs

The Global Carbon Cycle

1. Carbon in the atmosphere
2. Carbon dissolved in oceans
3. Carbon contained in terrestrial plants
4. Soil
5. Earths crust
   - Very large reservoir, but interacts very slowly with other reservoirs

Coupling of these reservoirs is very fast (items 1–4)

- During one year about 25% of atmospheric carbon gets exchanged with one of the other reservoirs

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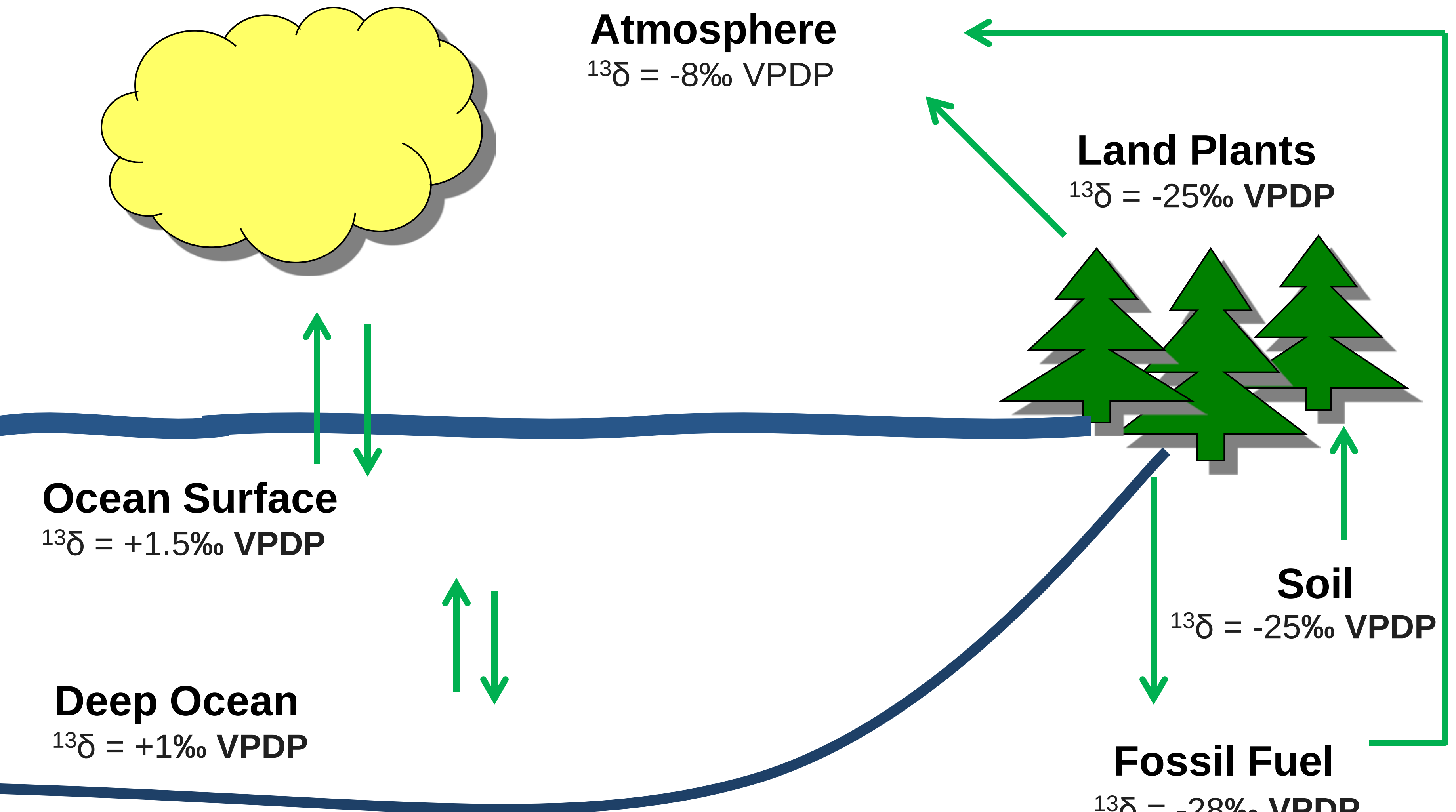
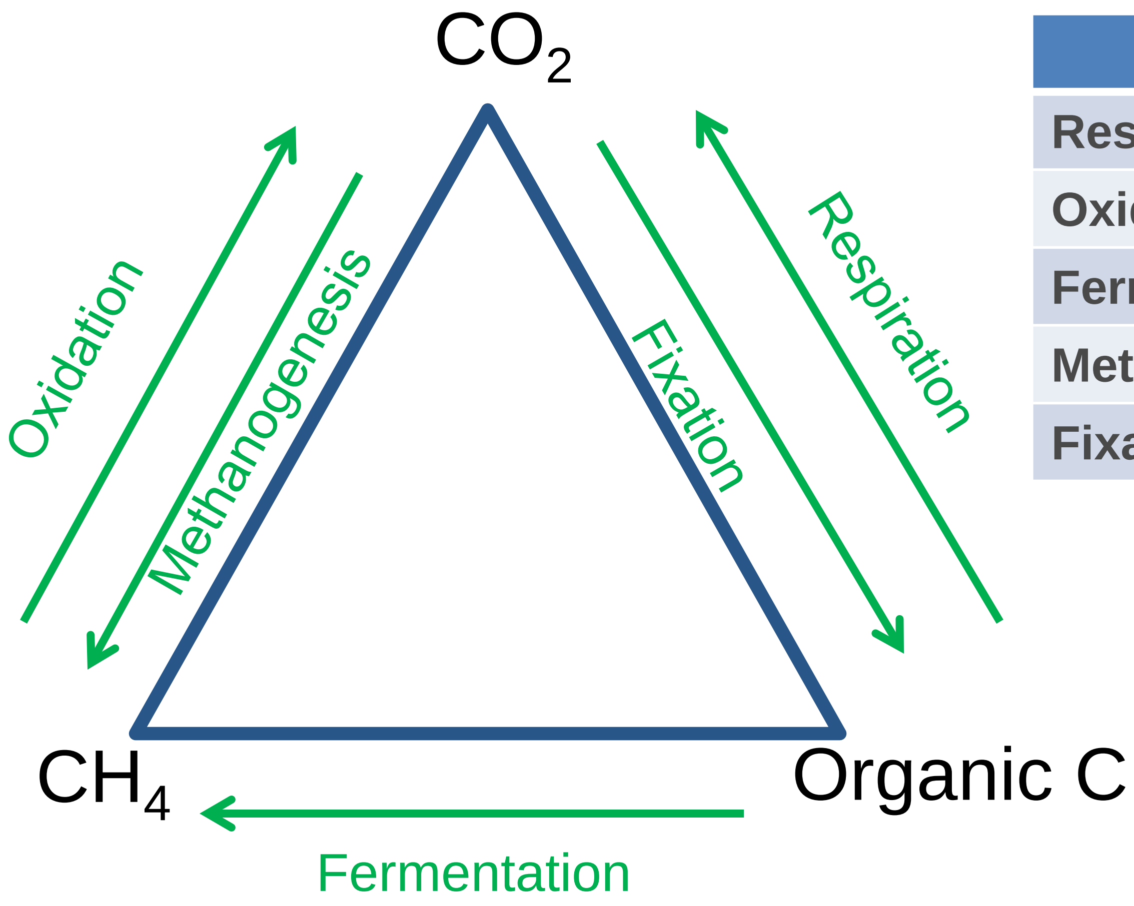
Global Carbon Cycle



Global Carbon Cycle



C-Cycle Processes	
Respiration	$C_{org} \rightarrow CO_2$
Oxidation	$CH_4 \rightarrow CO_2$
Fermentation	$C_{org} \rightarrow CH_4$
Methanogenesis	$CO_2 \rightarrow C_{org}$
Fixation	$CO_2 \rightarrow C_{org}$

Understanding Changes in Earth's Climate

- Long-term and high-precision measurements of GHG are necessary to understand changes in the Earth's climate
  - Assess and monitor the influence of human activity on changes on the worlds climate
  - The most accurate scientific observations are required
- National & International legislation focuses on measurement and reduction of GHG's
  - Significant financial implications for mitigation and process adaptation

Understanding Changes in Earth's Climate

- Global observation networks provide the required observations to monitor the climate and detect small changes
  - Reliable measurement technologies and standards with well characterized uncertainties are essential
  - Stable reference gas standards
  - Metrologically traceable
    - Currently a challenge

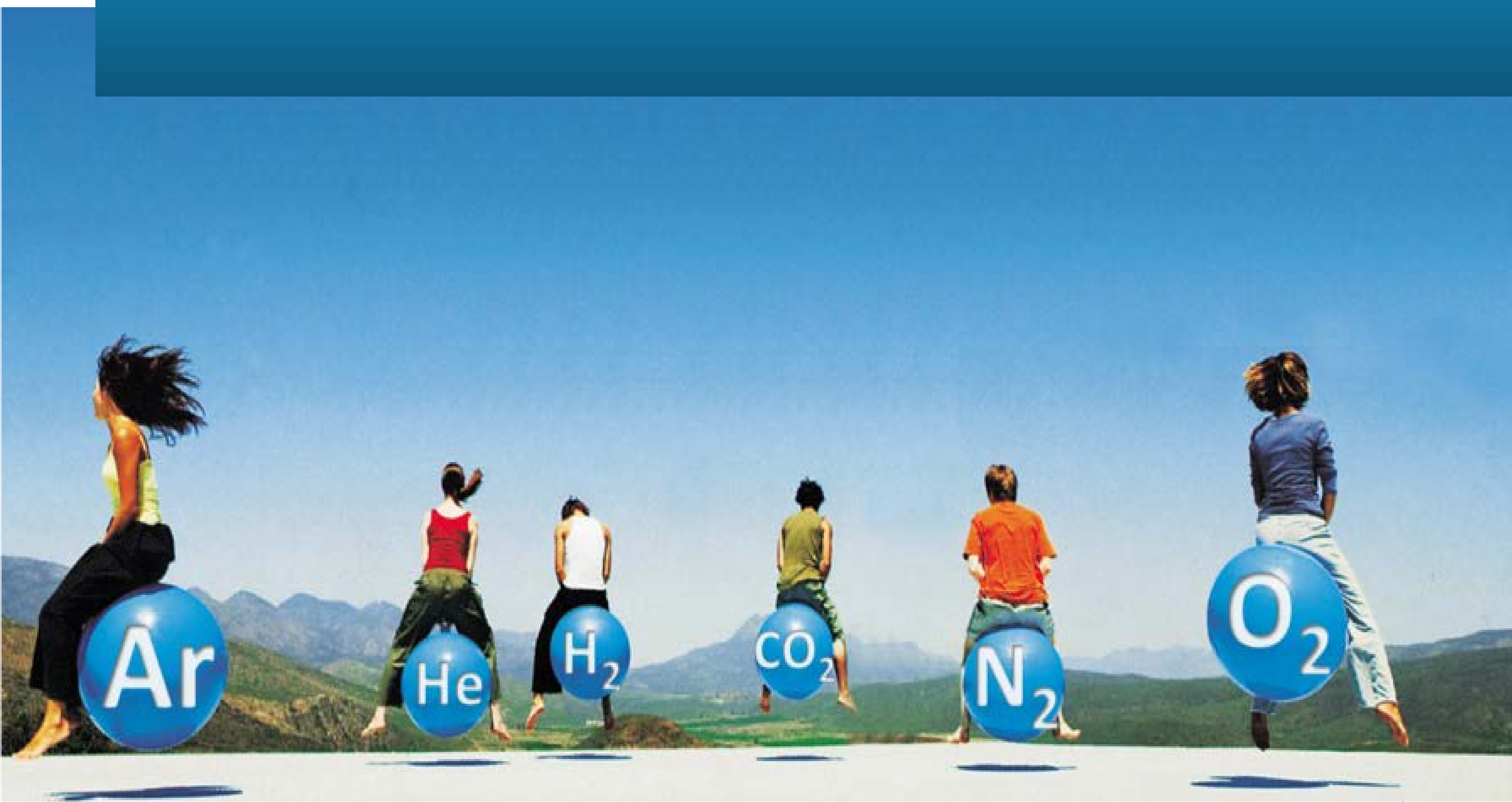
Izana Atmospheric Research Center, Spain

Issue

- Many stations from the monitoring networks as well as R&D centers which study the greenhouse effect are using synthetic air instead of natural air standards
  - Synthetic air has a different isotopic ratio compared to atmospheric natural air
  - Significant errors in the analysis of the greenhouse gas effect
  - **A reliable source of Natural air will reduce measurement errors!**

Jungfraujoch high-Alpine station (3580 m); in the GAW program of the WMO included in the Swiss National Air Pollution Monitoring Network

Alphagaz^{TM} Natural Air

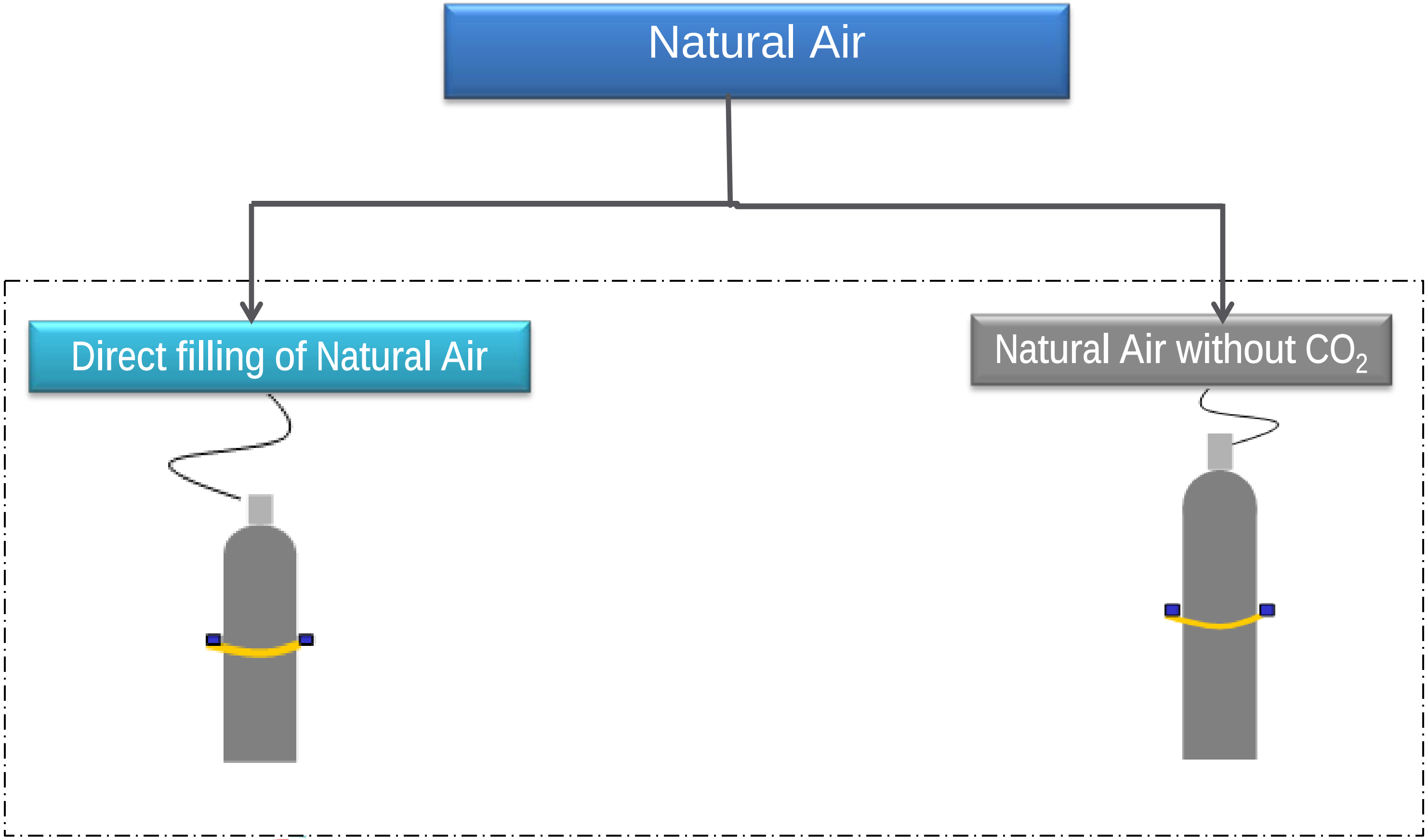


Tropospheric Natural Air

- Natural Air collected at an altitude >2300 meters
  - Natural Air is filled in situ
  - AL supported with Technology developed by NOAA
    - Property of AL

Natural Air

- ALPHAGAZ™ Natural Air
  - Purification to eliminate traces of CO_2



Focus

- Development of new standard material suites to certify
  - CO_2 at ambient levels (available)
- Target uncertainties
  - World Metrological Organization Data Quality Objectives between 0.01% and 0.05% relative
- Production of trace gases
  - ALPHAGAZ™ Natural Air
  - Correct isotopic ratio $^{13}C/^{12}C$ for CO, CO_2, CH_4, N_2O and SF_6

Validated by GAW & ICOS

GHG Atmospheric Research

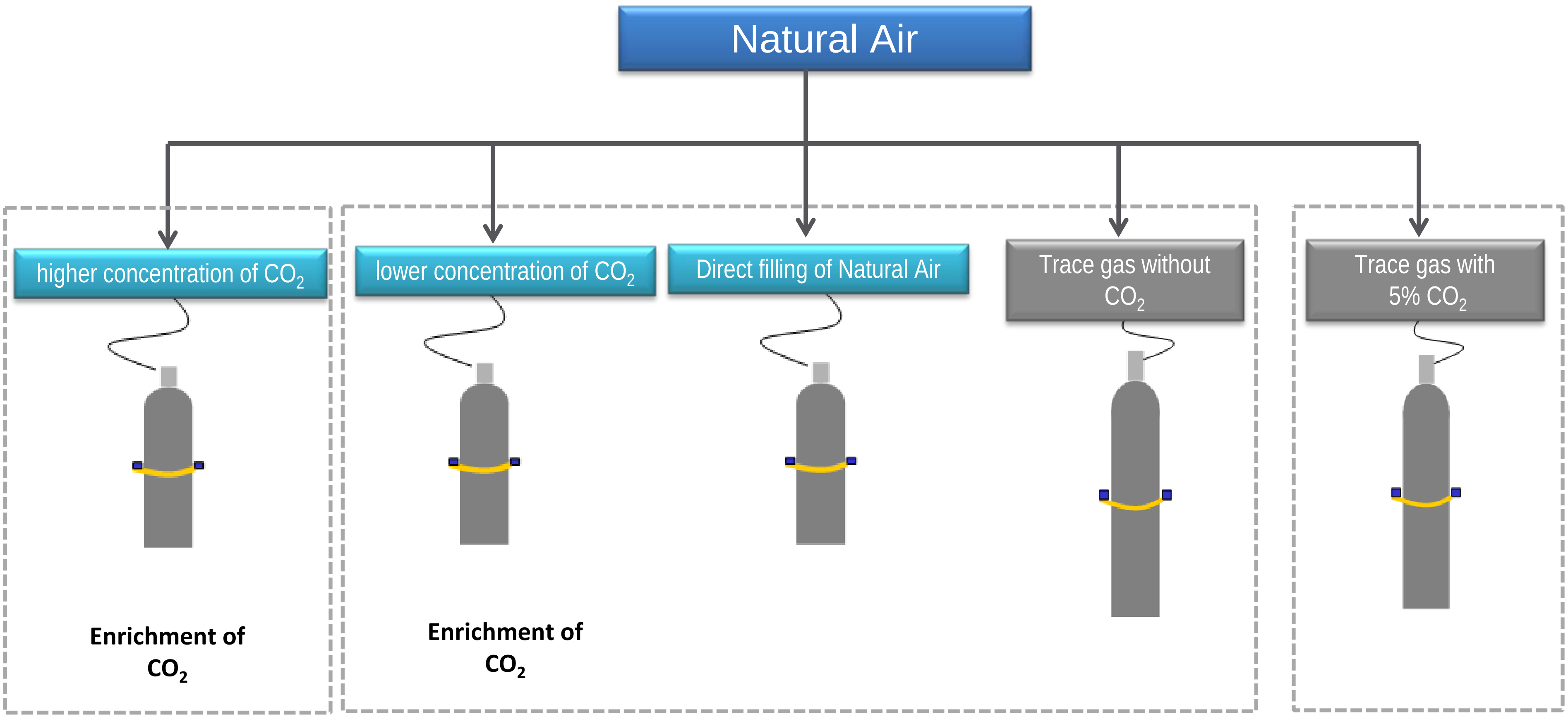
	$\delta^{13}C_{VPDB}$ [‰]	$\delta^{18}O_{VPDB}$ [‰]	$\delta^{18}O_{SMOW}$ [‰]
Natural Air (batch 1)	-8.46	-2.66	28.16
Natural Air (batch 2)	-8.93	-2.76	28.06

	Natural Air	
Component	**Sample 1**	**Sample 2**
O_2	20.97%	20.97%
N_2O	306 ppb	328.5 ppb
Ar	0.957%	0.964%
CH_4	1,828 ppm	1,819 ppm
CO	0.17 ppm	0.157 ppm
CO_2	29.8 ppb	402.7 ppm
SF_6	8.62 ppt	8.64 ppt

Sample 1: CO_2 purification
Sample 2: CO_2 concentration in the natural air

Analysis by The University of Salamanca, Spain

Adjusting Ratios in Natural Air



Adjusting CO_2 Ratios in Natural Air

- NOAA & GAW
  - $\delta^{13}C$ in the unpolluted troposphere: -7.5 → -9 vs. VPDB
- Can adjust the $\delta^{13}C$ ratio

		$\delta^{13}C_{VPDB}$ [‰]
Natural Air		-8.46
Natural Air	Doped with a fossil source of CO_2	-9.01
Natural Air	Doped with a natural source of CO_2	-8.87

Analysis by The University of Salamanca, Spain

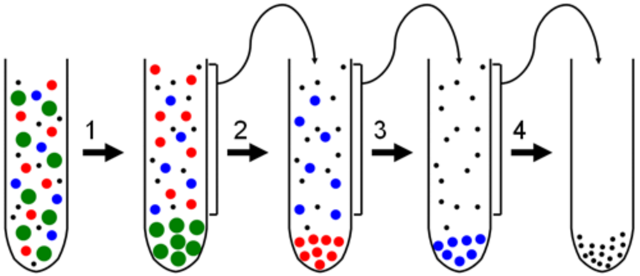
Natural Sources of CO_2

- Refinery source
  - ^{13}C = -40 per mil
  - ^{18}O = -24 per mil
- Natural CO_2 Dome
  - ^{13}C = -3 per mil
  - ^{18}O = -6 per mil
- Grain alcohol processing facility
  - ^{13}C = -11 per mil
  - ^{18}O = -3 per mil
- Ammonia plant
  - ^{13}C = -44 per mil
  - ^{18}O = -27 per mil

- **Available Ranges**
  - **$\delta^{13}C$: -44 to +50**
  - **$\delta^{18}O$: -27 to +50**

Scientific Questions

- Does fractionation occur when making batches of identical mixtures?
  - Does the difference in mass and therefore weight play a roll?
  - Can flow pathways: Direct vs. tortuous - play a role?
- Can the ratios be adjusted?
  - What about homogeneity of the mixture?
- What about the stability of the isotopes & composition of the mixture?



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Concentration Uniformity

- Do cylinders from the same batch have the same δ values?

  - $^{15}N_2O$ / $N_2{}^{18}O$

	δ15N avg	δ15N stdev	δ18O avg	δ18O stdev	N
A1	0.063	0.039	-3.143	0.067	15
A2	0.057	0.049	-3.152	0.045	20
A3	0.056	0.042	-3.140	0.064	28
Total	0.058	0.043	-3.145	0.059	63

- Fractionation does not appear to be an issue during cylinder filling

Values are relative to a standard gas used in the lab.

Brian N. Popp, Professor University of Hawaii, SOEST, Department of Geology & Geophysics1680 East-West Road, Honolulu, Hawaii 96822

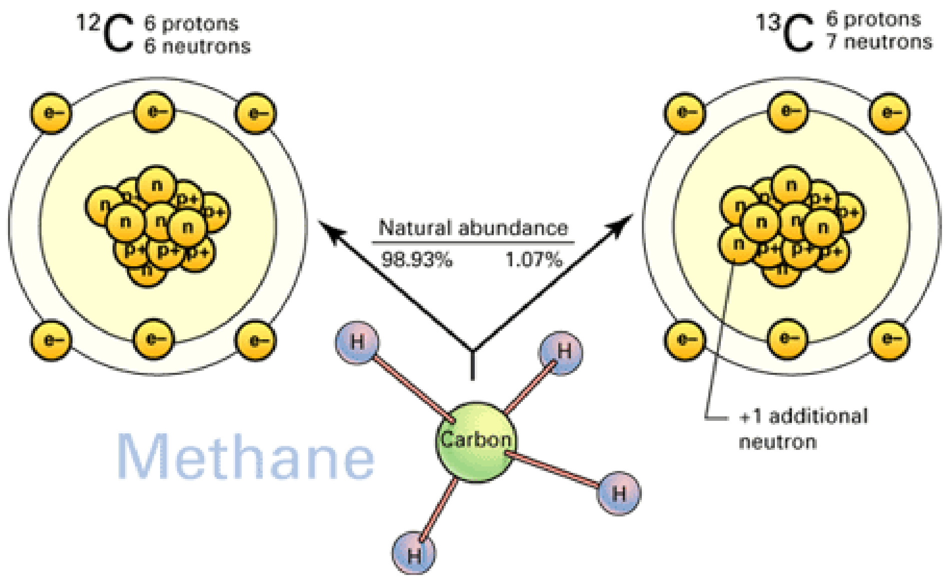
Concentration Uniformity

Cylinder filling as a function of manifold cylinder position vs. direct filling from mother cylinder

	$\delta^{13}C$ Methane							$\delta^{2}H$ Methane					
	Cylinder	#1	#2	#3	avg	stdev	RSD	#1	#2	#3	avg	stdev	RSD
Direct 1	519	-40.4	-40.4	-40.5	-40.4	0.06	0.14%	-59	-59	-59	-59	0.00	0%
Direct 2	521	-40.5	-40.5	-40.5	-40.5	0.00	0%	-60	-59	-59	-59.3	0.58	0.97%
Manifold 1	560	-40.5	-40.4	-40.4	-40.4	0.06	0.14%	-58	-58	-58	-58	0.00	0%
Manifold 2	596	-40.4	-40.5	-40.3	-40.4	0.10	0.25%	-59	-60	-59	-59.3	0.58	0.97%
Manifold 3	597	-40.4	-40.4	-40.4	-40.4	0.00	0%	-59	-61	-60	-60	1.00	1.67%
Pooled					-40.4	0.06	0.15%				-59.1	0.83	1.41%

- Manifold position does not appear to impact $\delta^{13}C$ and $\delta^{2}H$ in methane
- Compares well with direct filling from the mother cylinder

Adjusting Isotope Ratios



C-H Atomic Permutations

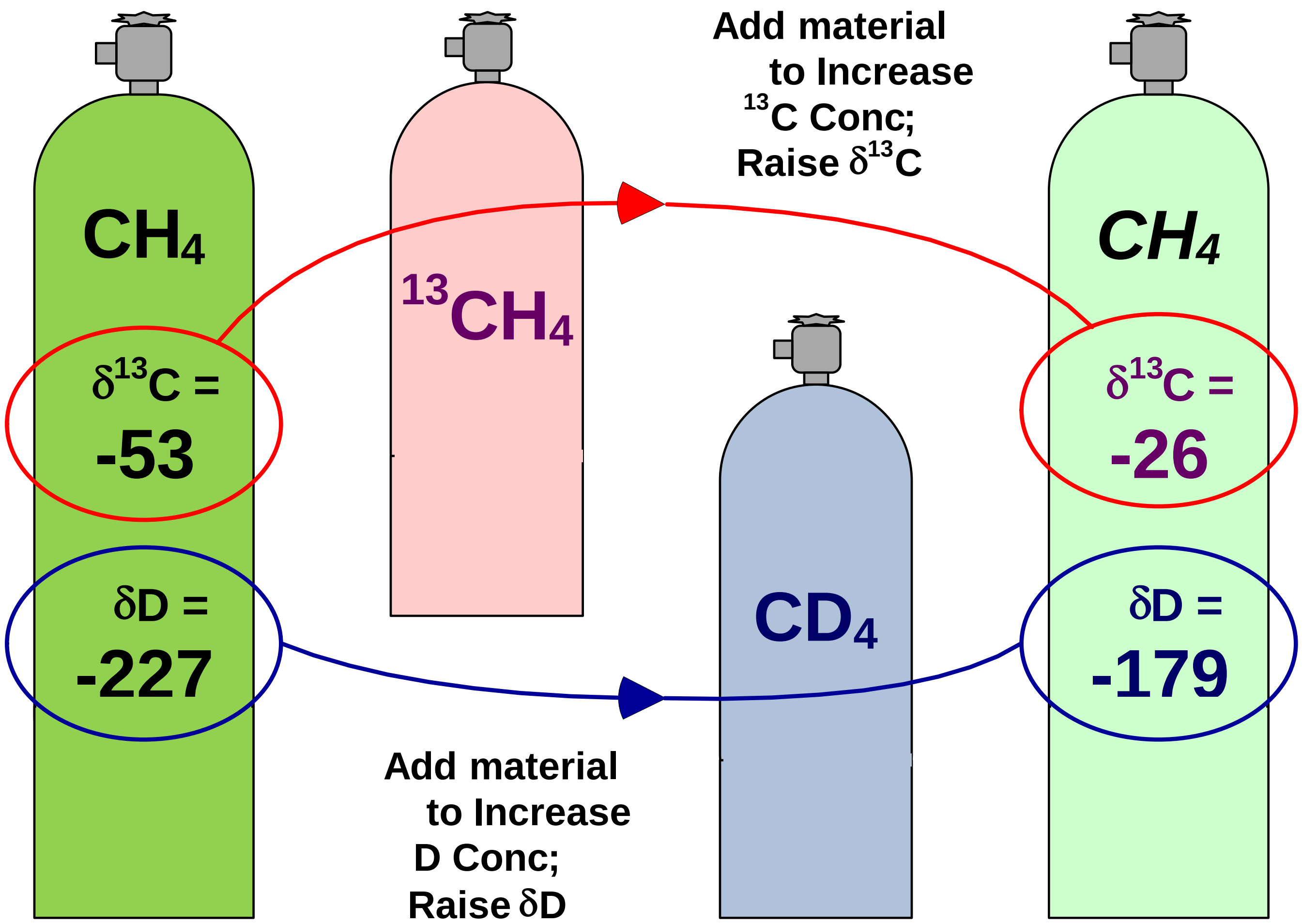
$^{13}CH_4$, $^{13}CDH_3$, $^{13}CD_2H_2$, $^{13}CD_3H$, $^{13}CD_4$

$^{12}CH_4$, $^{12}CDH_3$, $^{12}CD_2H_2$, $^{12}CD_3H$, $^{12}CD_4$

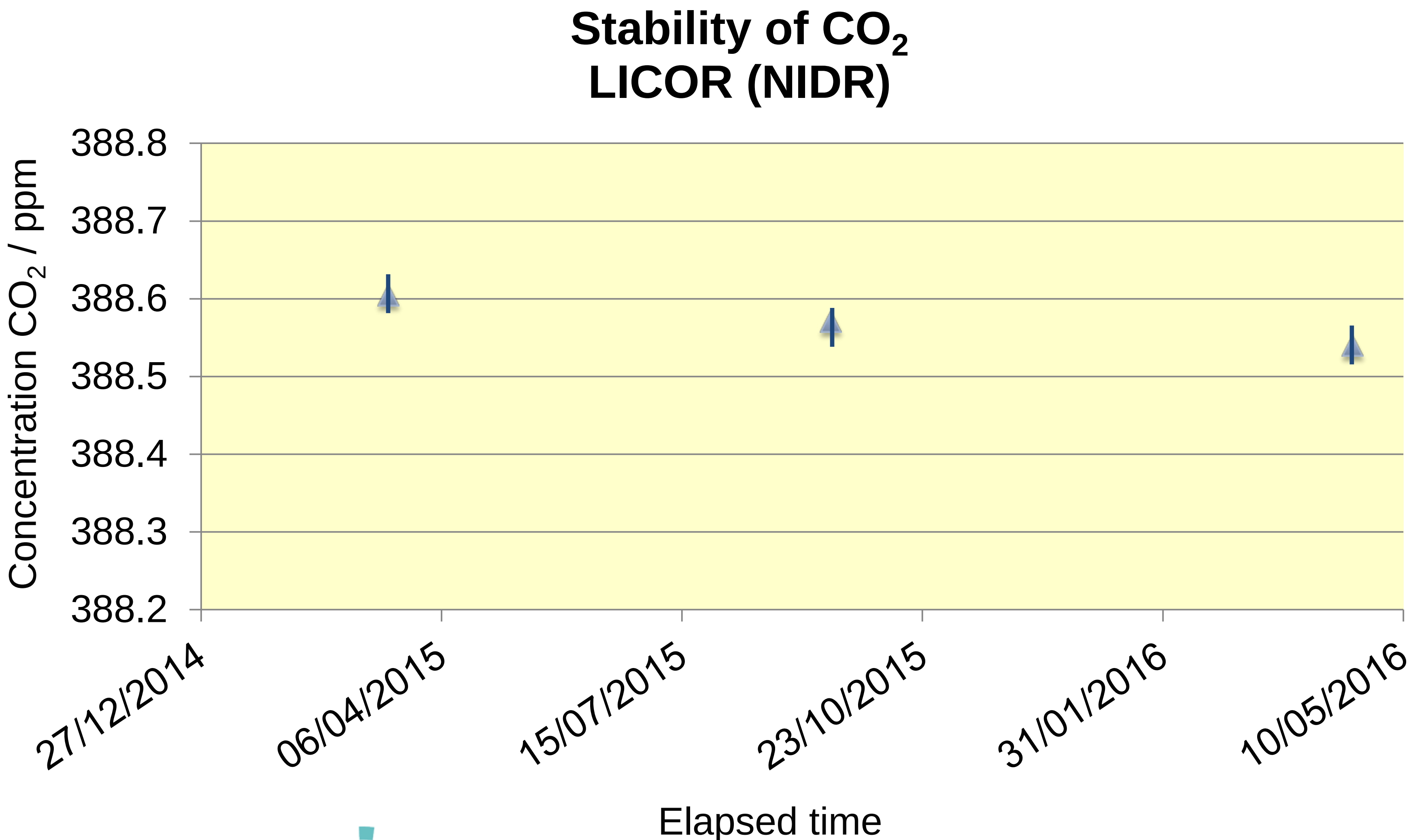
Characterization of source material required!

- 10 Different Molecules!

Adjusting Isotope Concentrations



Stability of CO_2 Concentration



CO_2 concentration measured by Meteorological Research Institute of Japan

Shelflife Study Summary

- Compositional Analysis
  - Uncertainty of mixture ±1%
  - Mixture is within analytical uncertainty over the shelf life

- Isotopic Stability
  - Uncertainty of $\delta^{13}C$: 0.3 per mil
  - Isotopic composition is stable over the shelf life

Stable Isotope Analysis

- Managing analytical uncertainty
  - Eliminate All Excess Error Sources
  - Minimize "Basic" Analysis Uncertainty Sources

  - Reference Material (U_S) 1.0%
  - Analyzer Calibration (U_C) 0.8%
  - Analyzer Precisions (U_P) 0.4%

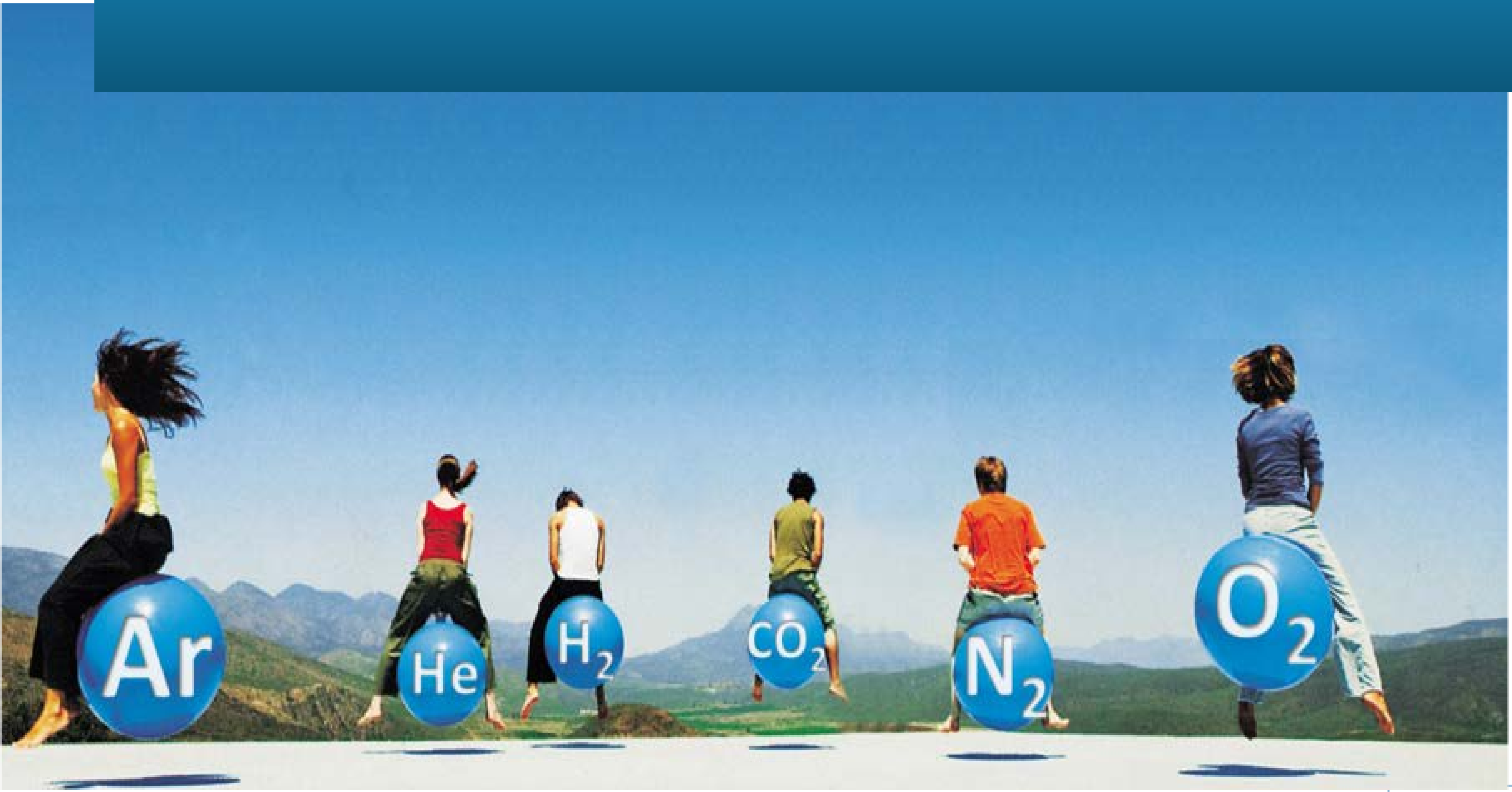
- "Propagation of Error" Calculation
  - Accuracy (U_T) = $\pm \sqrt{(1.0)^2 + (0.8)^2 + (0.4)^2}$
  - Accuracy (U_T) = $\pm$ 1.3 %

Component and Isotope Ranges Available

Concentration / Accuracy	Molecular Composition	Isotopes / Ranges	Repeatability
ppm to %	C_1-C_5 Hydrocarbons	$\delta^{13}C$: -70 to +25; δD: -300 to +50	Component Dependent 0.02 to 10 ‰
	CO_2 / CO	$\delta^{13}C$: -60 to +50	
± 1 to 5%	H_2S	$\delta^{34}S$: -50 to +50	
	N_2	$\delta^{15}N$: -25 to +25	

Composition Analysis ⟷ **Isotope Analysis**

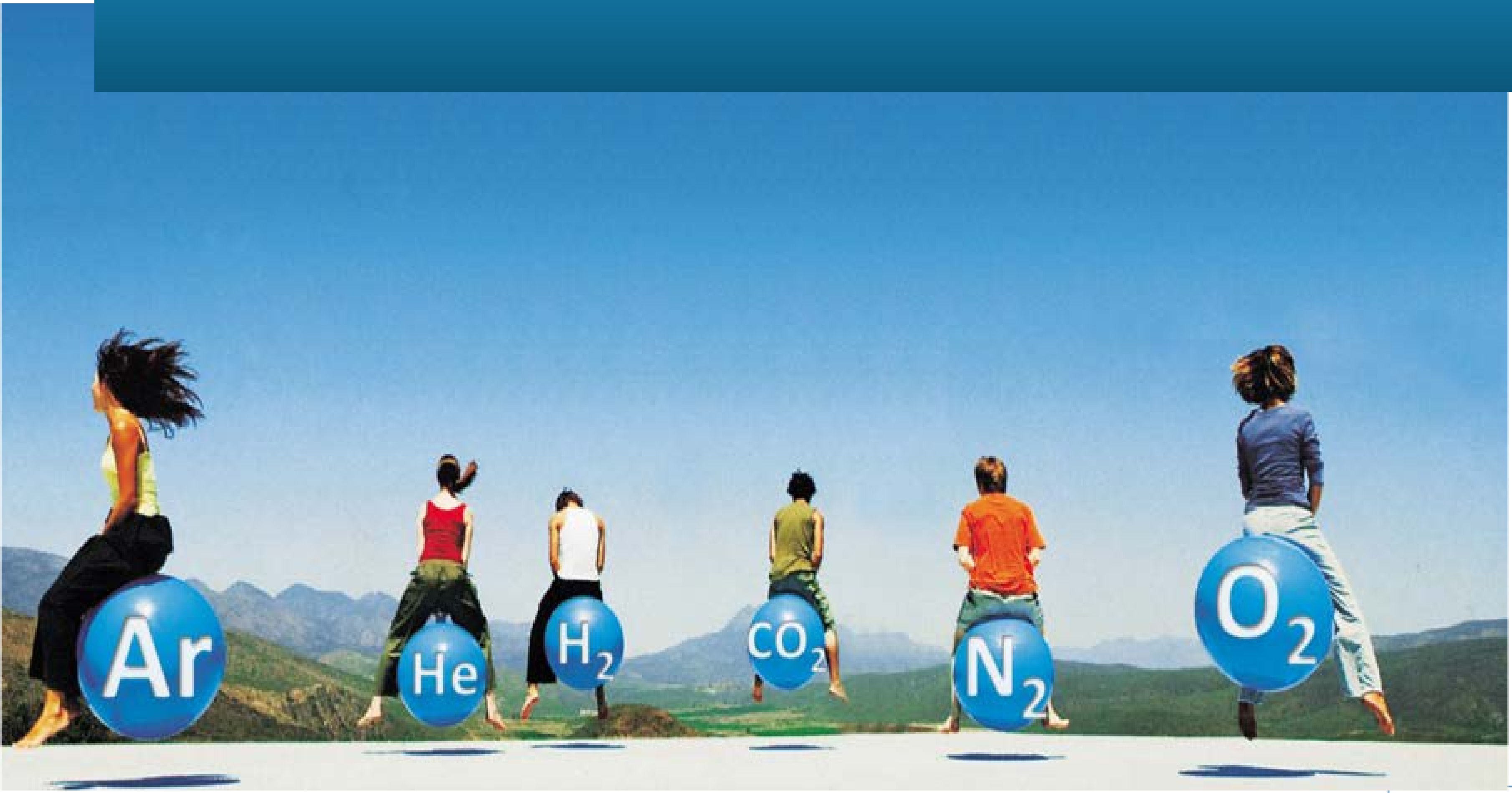
Summary



Summary

- Air Liquide is developing new technologies and applications which
  - Enable our customers to accurately measure emissions, process streams & product quality
- "Off the Shelf"
  - Pure gases
  - Mixtures with fixed composition and isotope ratios
- Custom Mixtures
  - Customer Selected Components and Concentrations
  - Customer Specified Isotope Ratios
    - "Adjusted" by Individual Component

Questions?



THANK YOU FOR YOUR ATTENTION!

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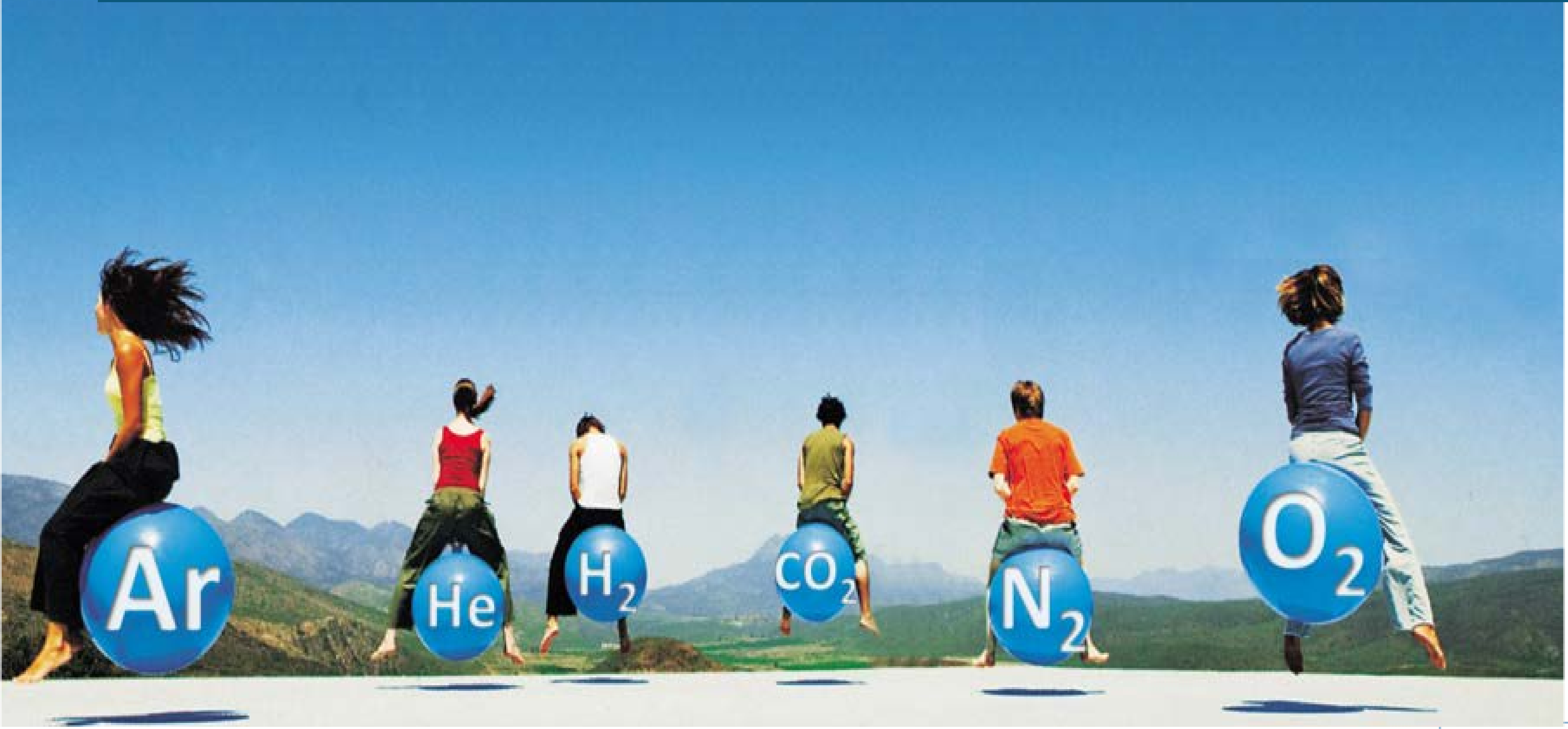
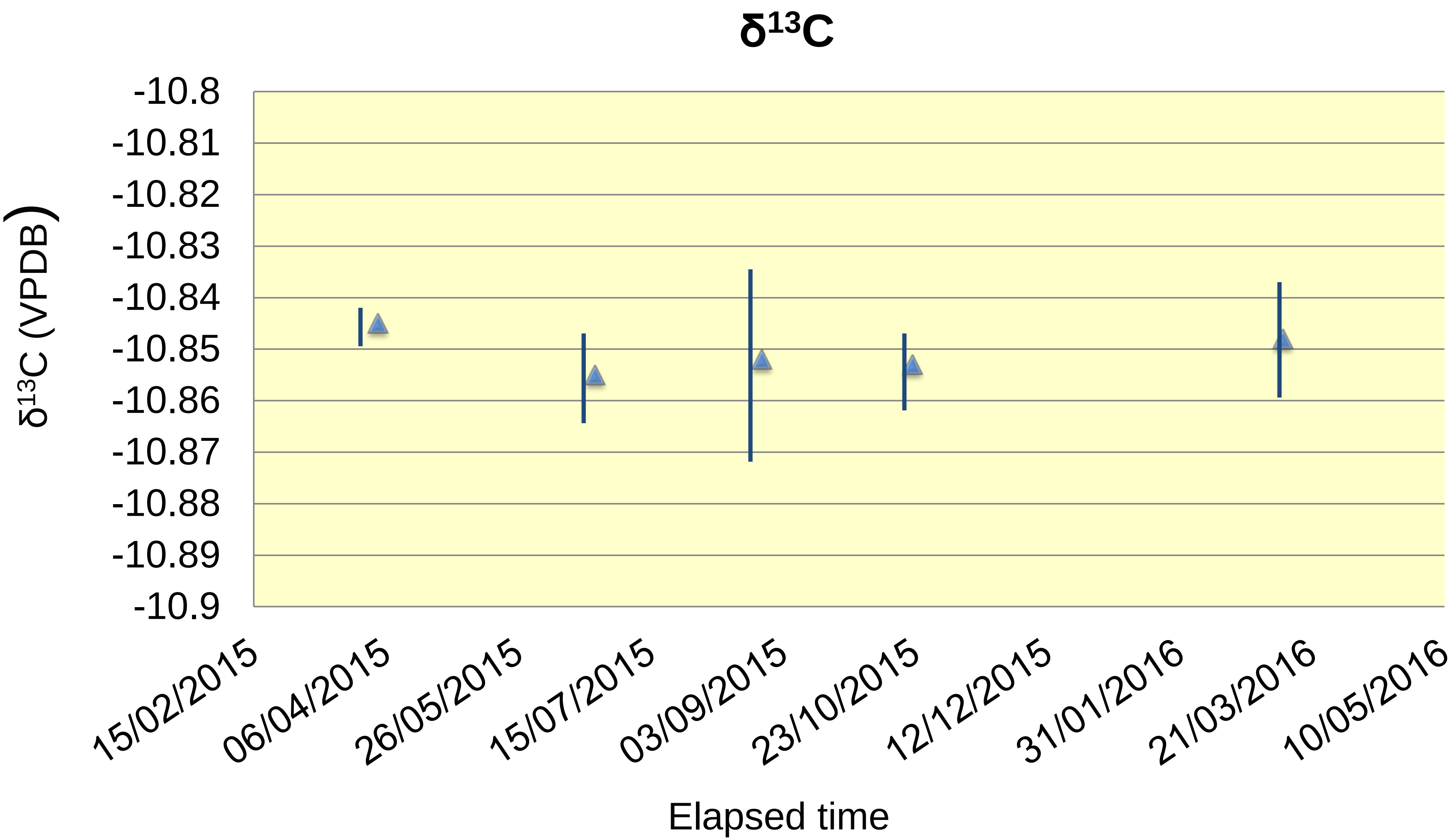
Back-up

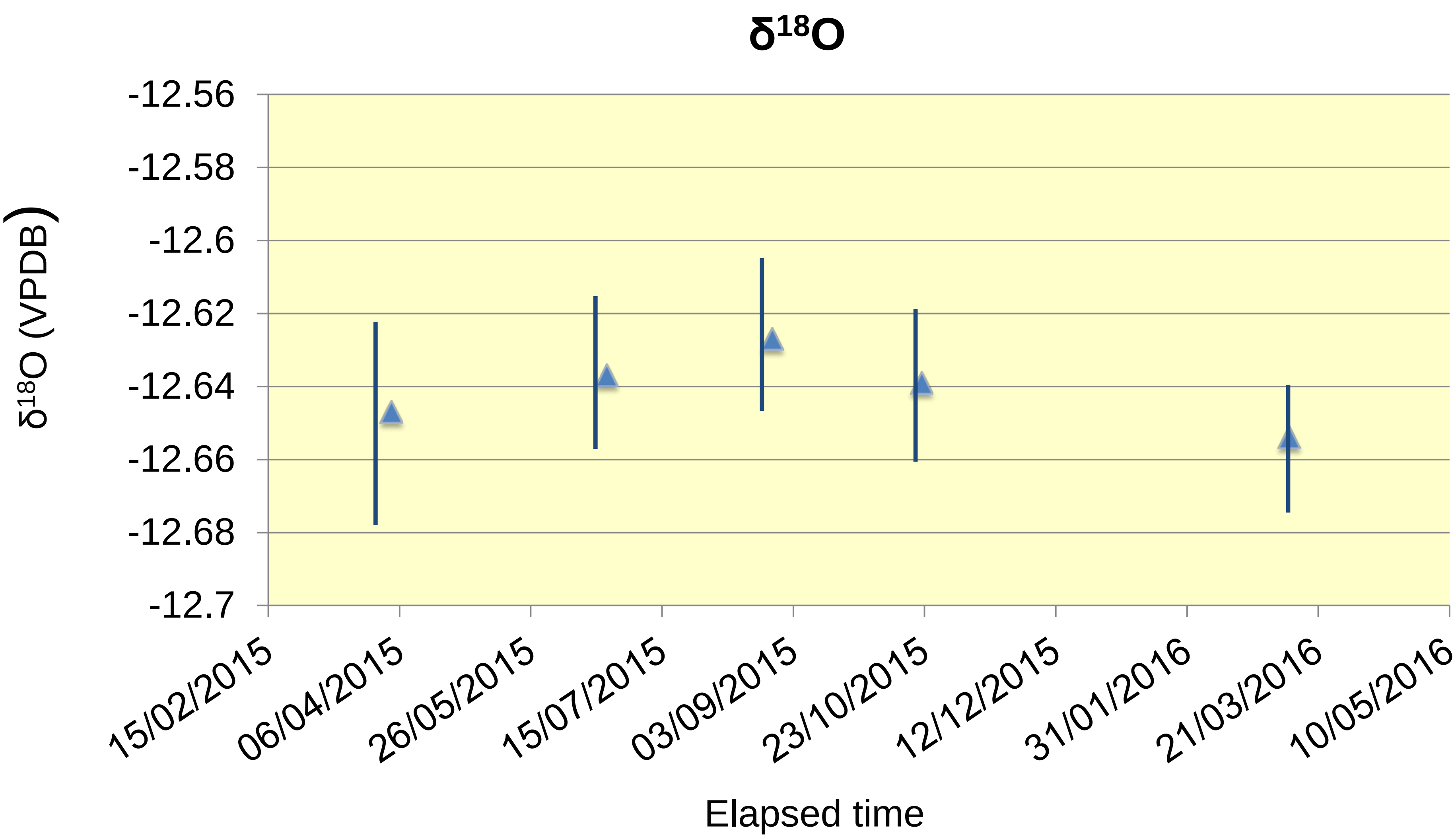


Stability of $\delta^{13}C$ in CO_2



Isotopic Ratio analysis: National Institute of Advanced Industrial Science and Technology (AIST)

Stability of δ^{18}O in CO_2



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