Increasing Accuracy in Environmental Measurements

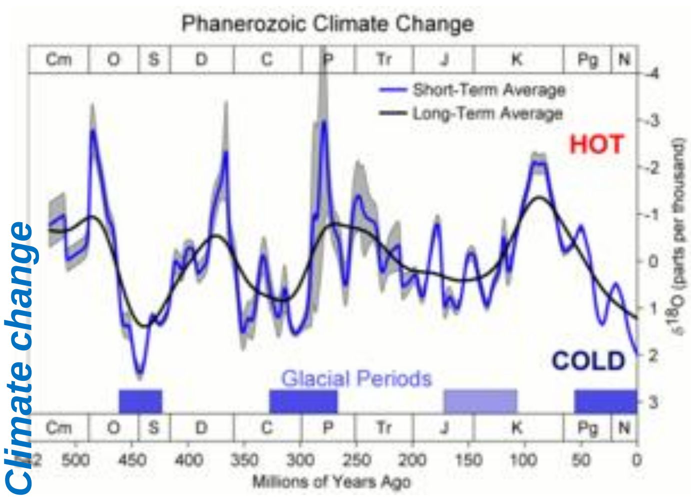
Tracey Jacksier, Adelino Fernandes, Werner Weterings

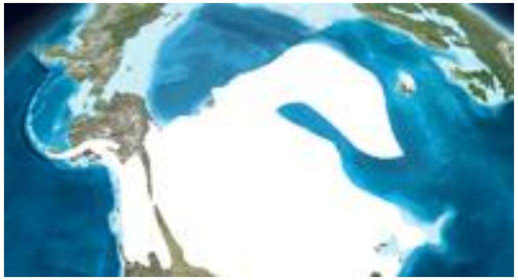
March 2016

Agenda

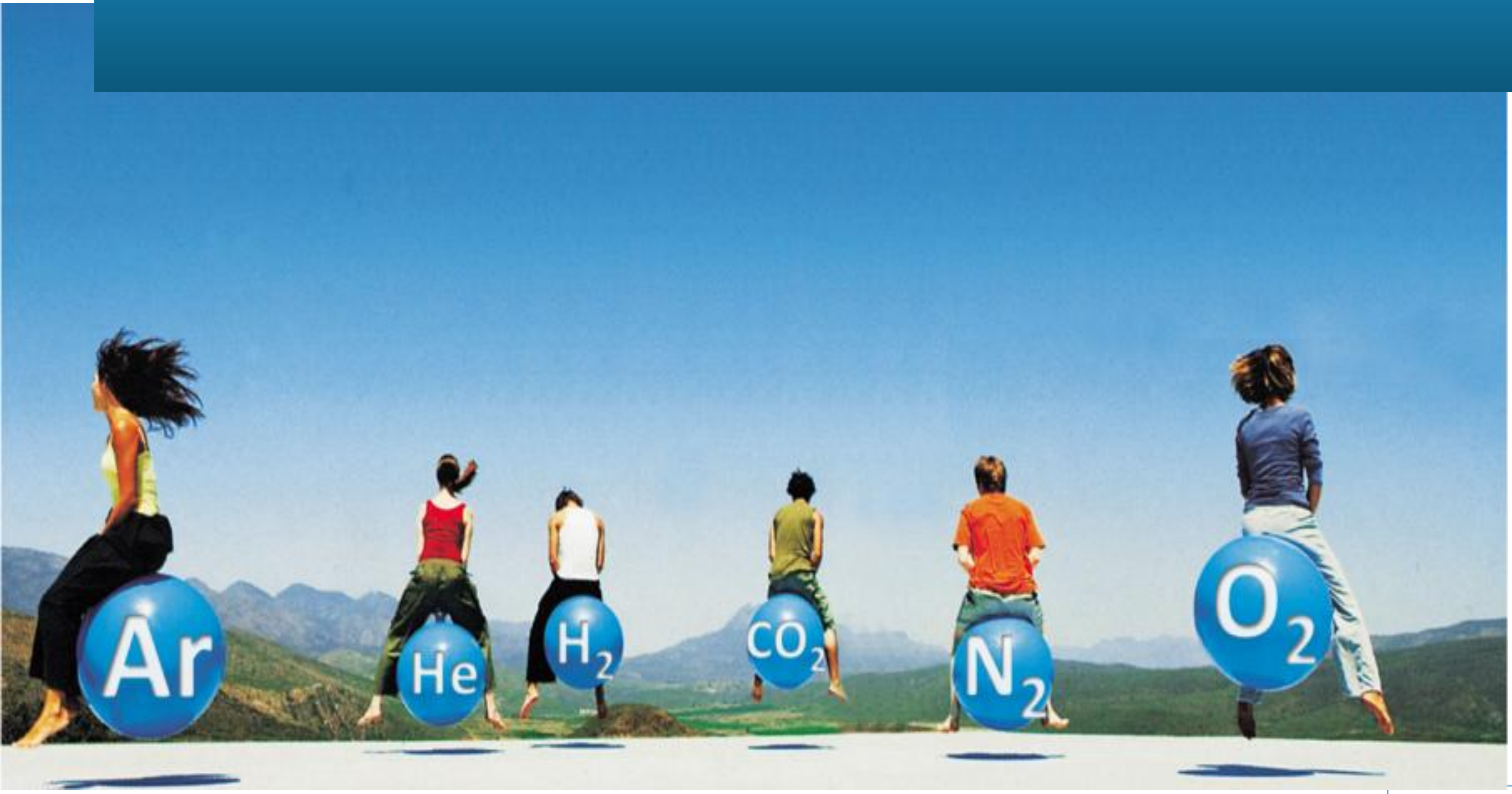
- Stable Isotopes & The Environment
- Alphagaz^{TM} Natural Air
- Summary

Climate change





Stable Isotopes & The Environment



Stable Isotopes

- The Isotopic ratios of gases are a natural bar code to indicate
  - Geographical origin
  - Compounds formation

- Environment
  - Biogenic/Thermogenic Pollution
  - Climate change

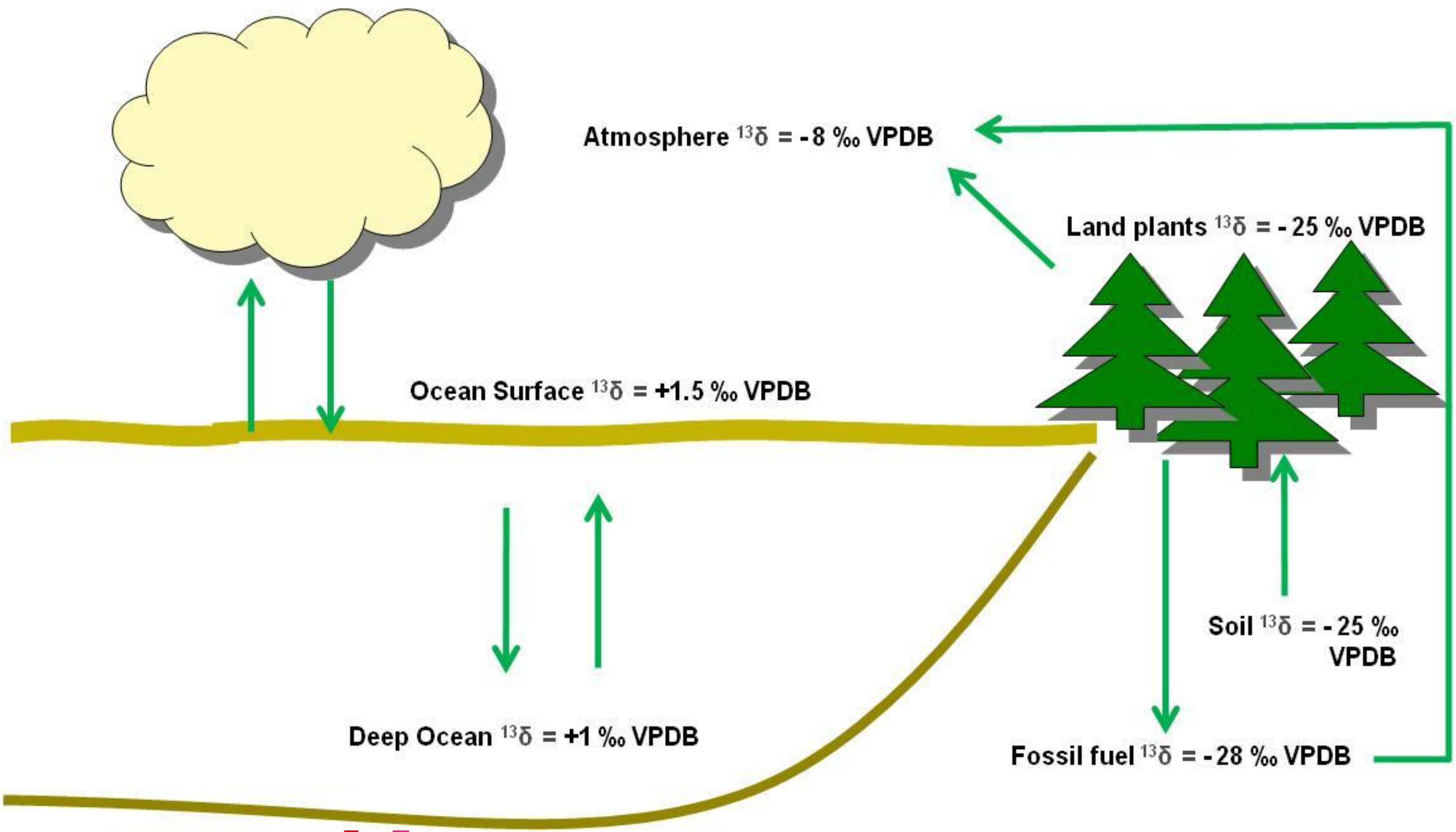
Global Carbon Cycle

- Why measure sources of atmospheric CO_2?
  - Important Greenhouse gas which is regulated by some countries and international agreements
  - Understand changes in the Earth's climate

- Different sources of CO_2 have different signatures
  - Atmospheric gases → -8 ‰
  - Soil → -28 ‰
  - Anthropogenic → <28 ‰

Global Carbon Cycle (Fractionation)

$^{13}\delta$ or Δ13C



Understanding Changes in Earth's Climate

Long-term and high-precision measurements of GHG are necessary to understand changes in the Earth's climate

Global Climate long-term Observing Systems providing the observations required to monitor the climate and detect climate change, with reliable measurement technologies and standards.

Central Analytical Laboratories preparing calibration material and Gas Standards

High-quality, traceable and calibrated in-situ measurements

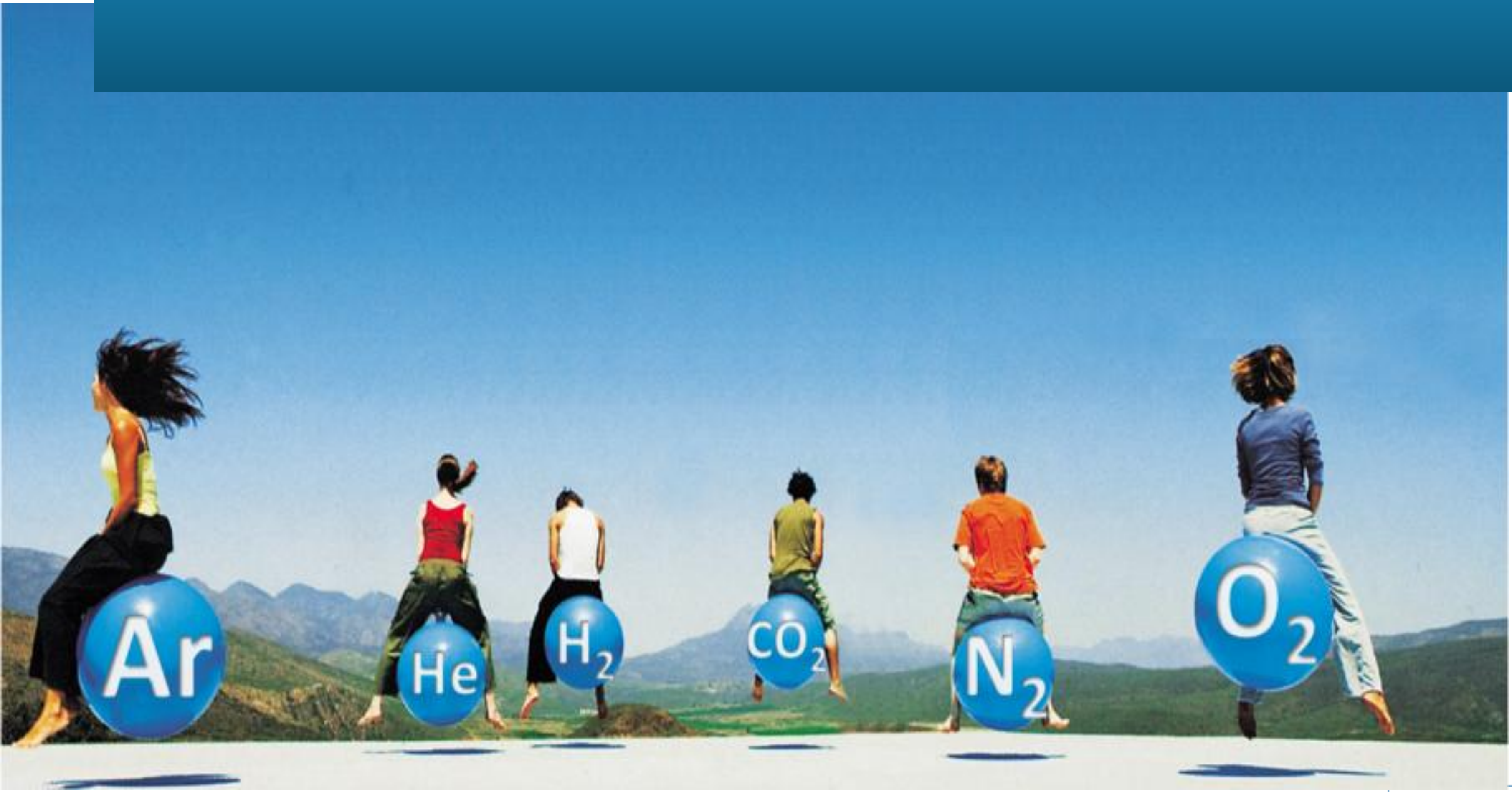
Stable Reference Gas Standards with low uncertainties and metrological traceability providing coherence and confidence through international comparability to meet World Meteorology Organization (WMO) and Regulatory requirements

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™ Natural Air



Focus

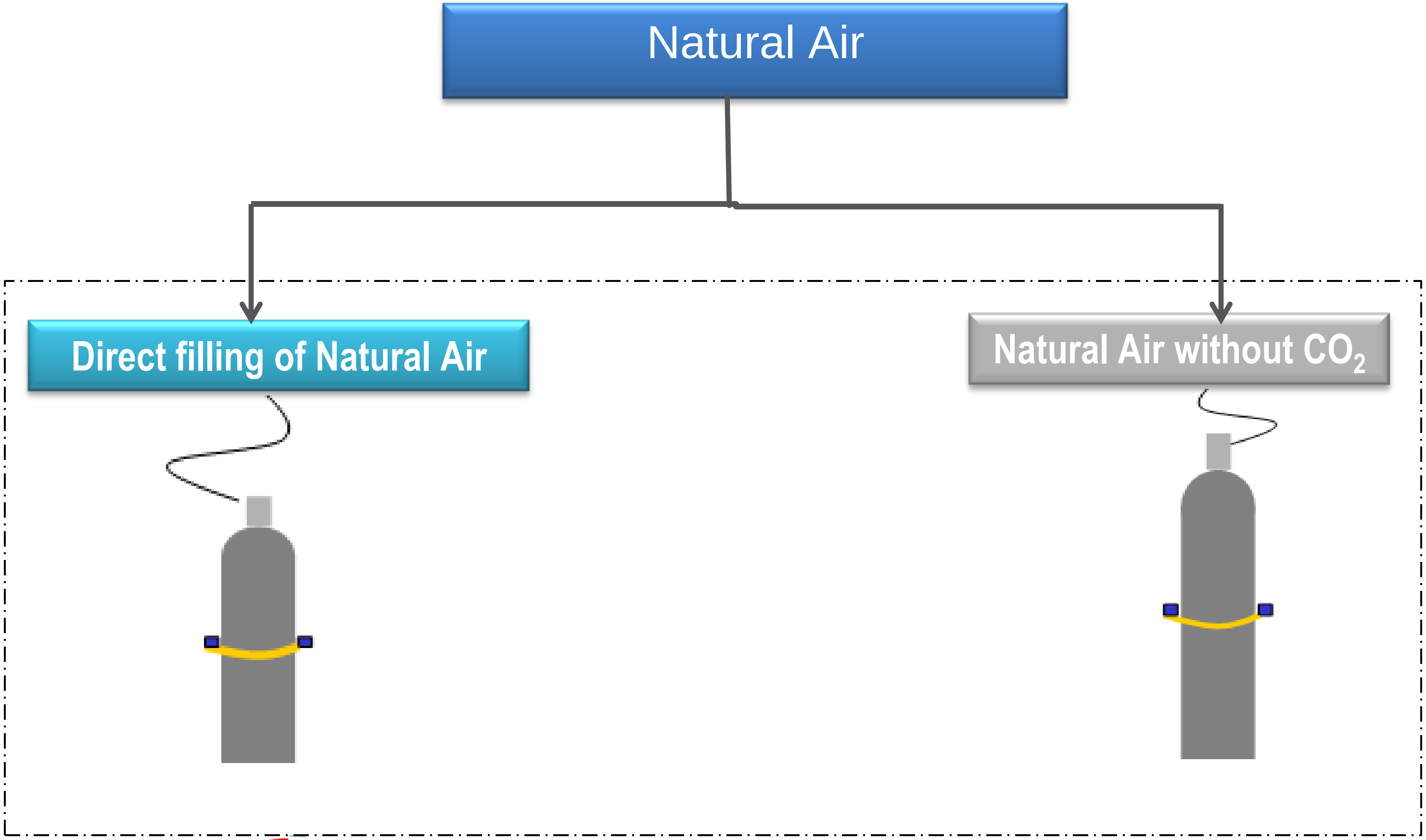
- Development of new standard material suites to certify
  - CO_2 at ambient levels (available)
  - CH_4 at ambient levels (available)
- Target uncertainties
  - World Metrological Organization Data Quality Objectives between 0.01% and 0.05% relative
- Production of trace gases
  - *ALPHAGAZ*™ Natural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

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

ALPHAGAZ™ Natural Air

- Purification to eliminate traces of CO_2



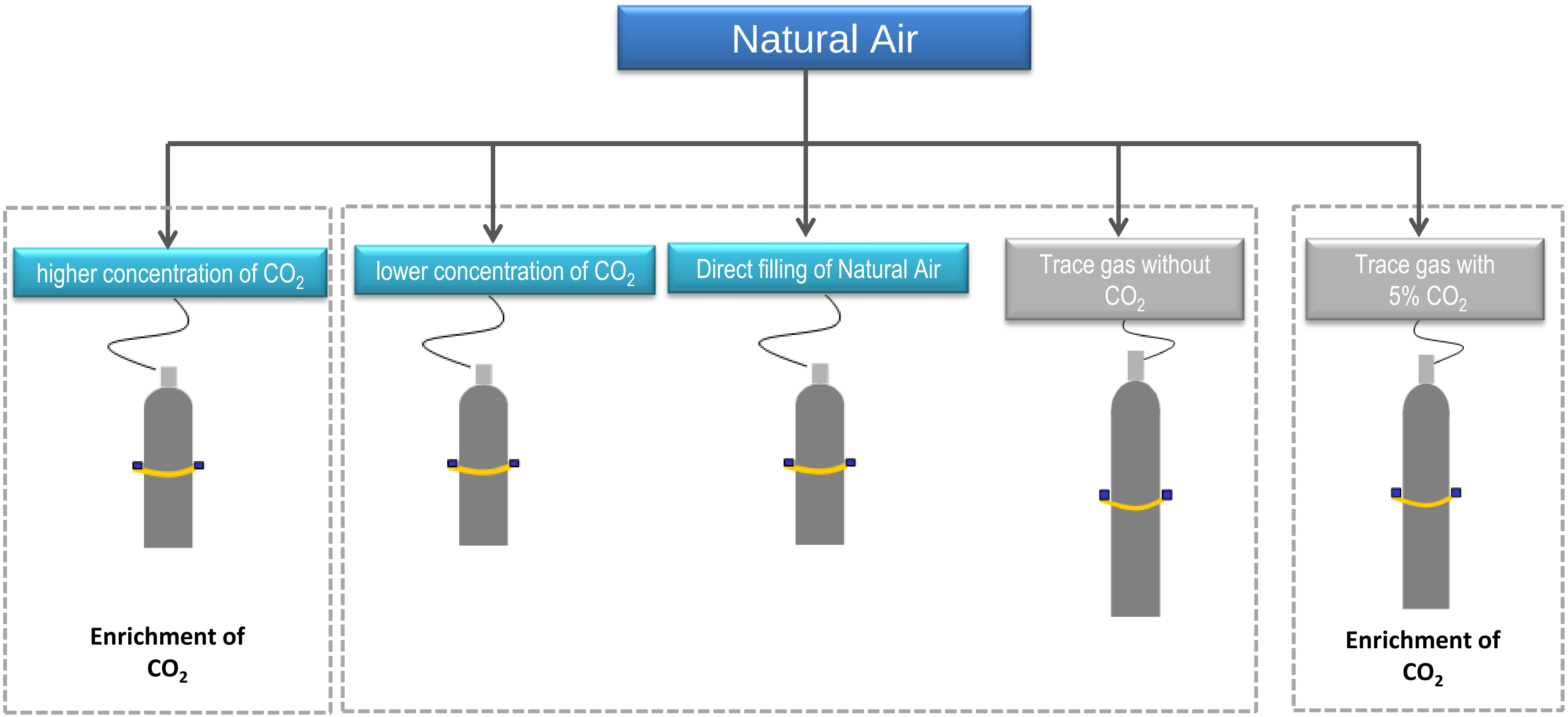
GHG Atmospheric Research

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

	Natural Air	
Component	**Natural Comp**	**Purified Comp**
O_2	20.97%	20.97%
N_2O	329 ppb	306 ppb
Ar	0.964%	0.957%
CH_4	1,819 ppb	1,828 ppb
CO	0.157 ppm	0.170 ppm
CO_2	402.7 ppm	29.8 ppb
SF_6	8.64 ppt	8.63 ppt

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

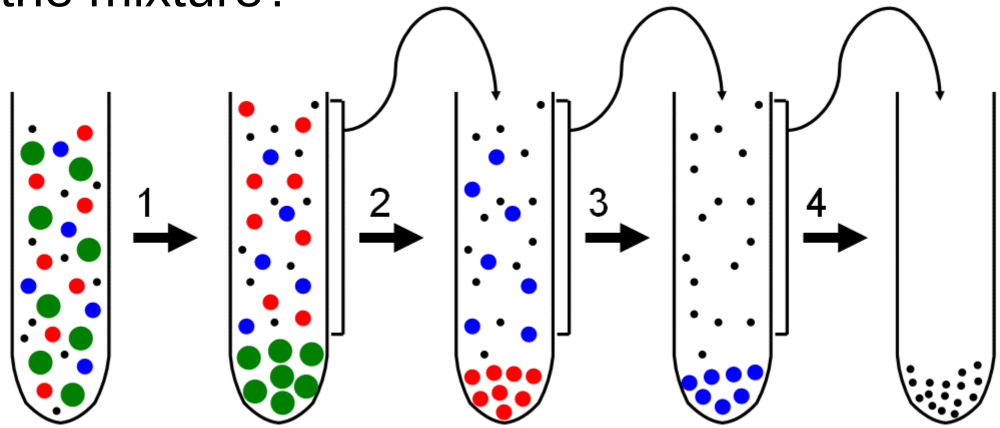
Natural Sources of CO_2

- 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?



Concentration Uniformity

- Do cylinders from the same batch have the same δ values?
  - $^{15}N_2O$ / $N_2{}^{18}O$

	δ^{15}N avg	δ^{15}N stdev	δ^{18}O avg	δ^{18}O 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

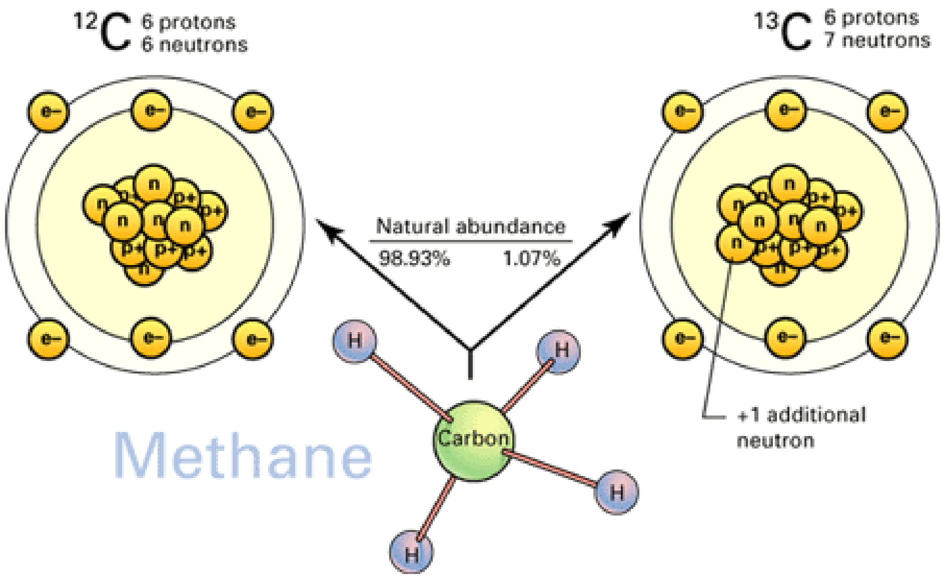
Concentration Uniformity

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

	δ13C Methane								δ2H 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

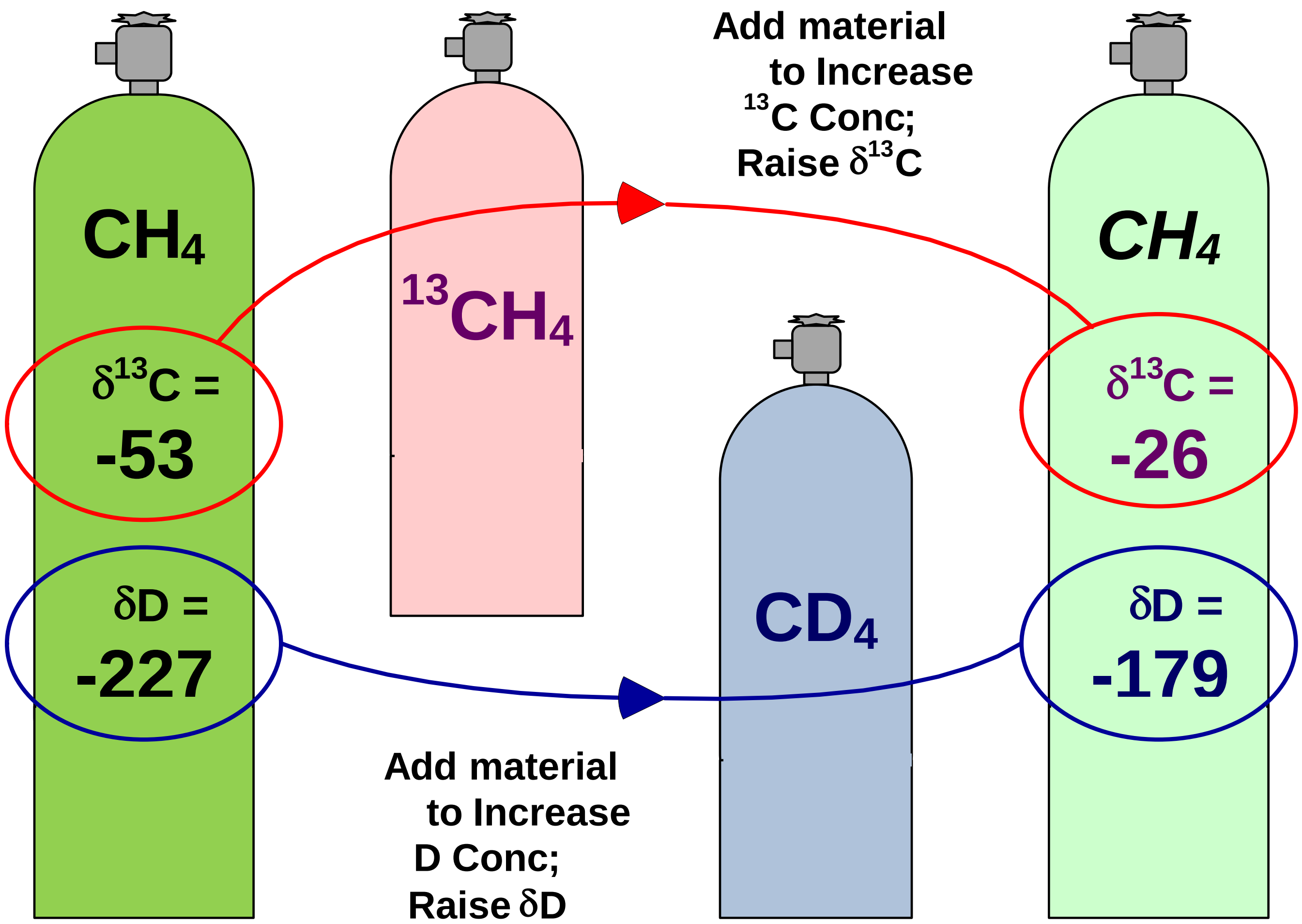
$^{13}CH_4$, $^{13}CDH_3$, $^{13}CD_2H_2$, $^{13}CD_3H$, $^{13}CD_4$

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

- 10 Different Molecules!

Characterization of source material required!

Adjusting Isotope Concentrations



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 Precision (U_P) 0.4%

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

AL Commercial Products

- Stable Isotopes
  - First offer launched in 2013 for Oil & Gas
  - Today: Environment, Food Authentication, Pharma, Medical
- “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

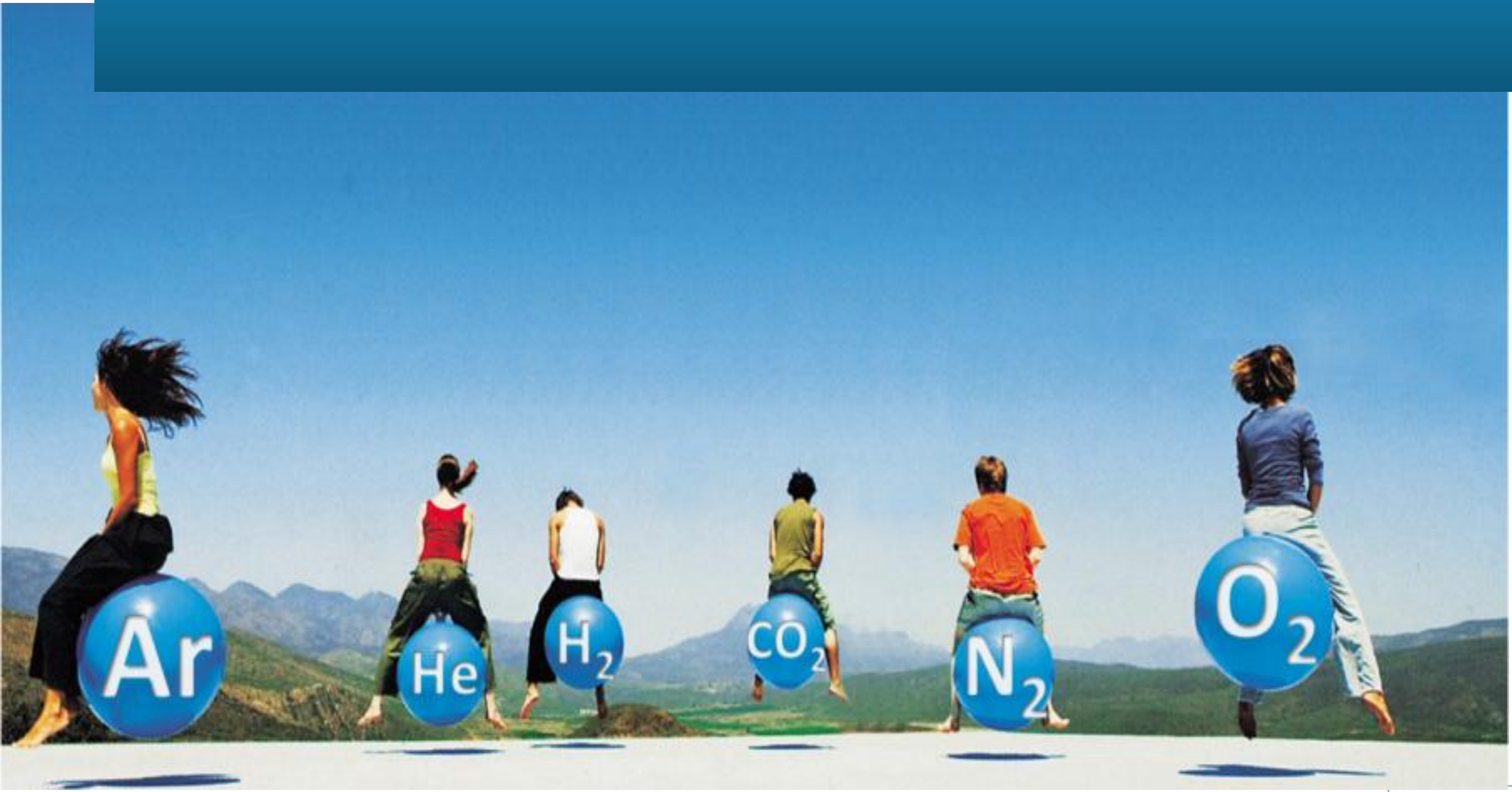
Air Liquide Stable Isotopes

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**

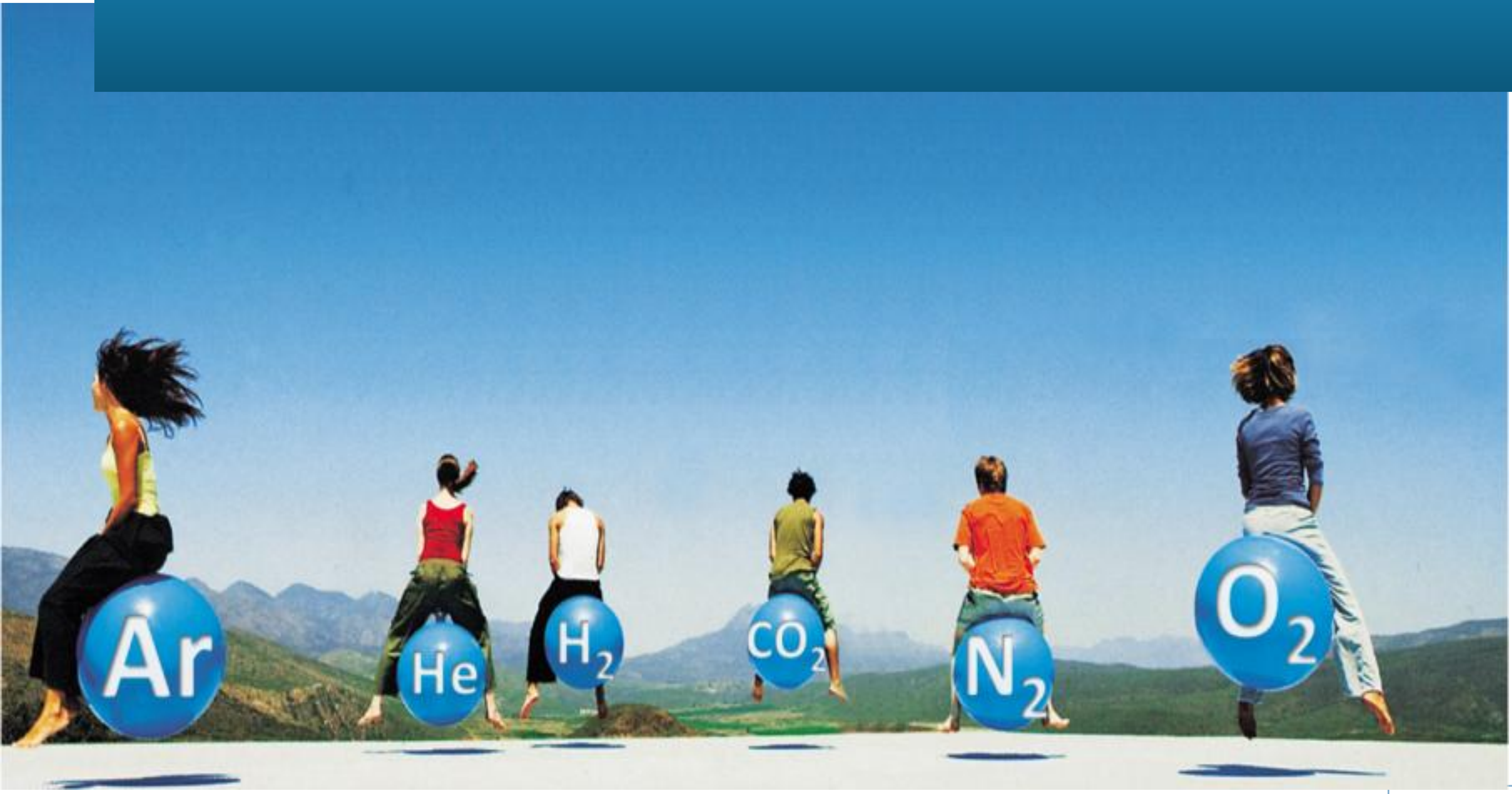
Summary



Summary

- Air Liquide is developing new technologies and applications which
  - Enable our customers to accurately measure emissions, process streams & product quality
  - Addresses market demands
  - Realize value for our customers
- Innovation is the key to success
  - What can we do for you?

Questions?



THANK YOU FOR YOUR ATTENTION!

www.airliquide.com