3. iceGGO-2 (CO_2)

3.1. Round-robin cylinders (iceGGO-2)

The second experiment (2012), the iceGGO-2, focused on a comparison of CO_2 standard gas scales by circulating high-pressure cylinders. Details of the nine sample cylinders used for this round-robin experiment are listed in Table 5. Six cylinders filled by JFP using a volumetric method were provided by TU for the iceGGO-2 experiment. These six cylinders were prepared using purified natural air as a matrix gas, and their CO_2 concentrations ranged from about 340 ppm to 409 ppm. The parent CO_2 gas in these cylinders was derived from combusted petroleum; the $\delta^{13}C$ values of their CO_2 were deduced to be around –30 ‰.

Three other cylinders containing relatively high $^{13}CO_2$ concentrations were provided by NIES to examine isotope effects of CO_2 analyzers, because such effects would confound interpretation of apparent differences in the isotopic compositions of round-robin samples and calibration gases. Two cylinders (CPB16443 and CPB29524) were filled with dry natural air, including CO_2 at concentrations of about 405 ppm and 410 ppm, respectively. The $\delta^{13}C$ values of the CO_2 in these cylinders were measured by the NIES to be –8.8 ‰ and –9.0 ‰, respectively. A third cylinder (CPB28548) was specially prepared using an enriched $^{13}CO_2$ gas ($\delta^{13}C$ = +57.3 ‰) in purified natural air with a CO_2 concentration of ~370 ppm (Tohjima et al., 2009).

Table 5. The nine cylinders used in the iceGGO-2 experiment.

Cylinder Identification	CO_2 Concentration* (ppm)	Matrix gas	Manufacturer	Filling method	$\delta^{13}C$ of CO_2 (‰)
CPB10204	339.93	Purified natural air	JFP	Volumetric	
CPB10206	369.80	Purified natural air	JFP	Volumetric	
CPB10208	390.02	Purified natural air	JFP	Volumetric	
CPB10210	409.91	Purified natural air	JFP	Volumetric	
CPB10213	429.72	Purified natural air	JFP	Volumetric	
CPB10216	449.95	Purified natural air	JFP	Volumetric	
CPB28548	370.06	Purified natural air	NIES		+57.3[&]
CPB16443	406.02	Dry natural air	NIES		-8.8[#]
CPB29524	409.31	Dry natural air	NIES		-9.0[#]

*Measured by NIES

[#]Measured by Cavity Ring-Down Spectroscopy (CRDS) of NIES

[&]Measured by isotope ratio mass spectrometry (IRMS) of NIES (Tohjima et al., 2009)

3.2. Measurement methods (iceGGO-2)

Five laboratories (AIST, NIES, JMA, NIPR, and TU) participated in the iceGGO-2 round-robin experiment from May to August 2012. Table 6 provides details of the CO_2 analytical methods used by the five laboratories. All participants used a non-dispersive infrared (NDIR) analyzer to measure CO_2 concentrations. However, the models of the NDIR instruments differed: the AIST, NIES, and TU used a LI-6252 model (LI-COR); the AIST and TU used a model VIA-500R (Horiba); and the JMA and NIPR used a model VIA-510R (Horiba).

The JMA measurements were based on the WMO X2007 scale (Zhao and Tans, 2006), which has been propagated from the NOAA/GMD. The NDIR analyzers differ from the JMA and NOAA, although no consideration is given to associated isotope effects on the WMO scale transfer from the NOAA to the JMA. Three laboratories, TU, AIST, and NIPR,

used the same TU2010 scale, which was developed recently by the TU. The NIES09 scale was based on eight cylinders prepared by a one-step dilution method with a precision of 0.04 ppm (Machida et al., 2011). All laboratories used a gas mixture that included CO_2 derived from combustion of fossil fuel ($\delta^{13}C$ of about –30 ‰) in purified natural air as a calibration gas.

Table 6. The five laboratories and the analytical methods, instruments, and calibration scales they used to measure CO_2 during the iceGGO-2 experiment.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
AIST	NDIR	LI-6252, Licor	TU2010 Scale	340 ppm - 450 ppm	6	May 20-25, 2012
AIST	NDIR	VIA-500R, Horiba	TU2010 Scale	340 ppm - 450 ppm	5 or 6	May 15-17, 2012
NIES	NDIR	LI-6252, Licor	NIES09 Scale	340 ppm - 450 ppm	8	April 29-May 1, 2012
JMA	NDIR	VIA-510R, Horiba	WMO X2007 Scale	320 ppm - 480 ppm	9	June 12-15, 2012
NIPR	NDIR	VIA-510R, Horiba	TU2010 Scale	370 ppm - 420 ppm	6	October 18-24, 2012
TU	NDIR	LI-6252, Licor	TU2010 Scale	380 ppm - 450 ppm	7	July 25- August 1, 2012
TU	NDIR	VIA-500R, Horiba	TU2010 Scale	380 ppm - 450 ppm	7	July 25- August 1, 2012

3.3. Results of iceGGO-2

Table 7 summarizes the CO_2 concentrations measured in the nine round-robin cylinders by five laboratories using three different NDIR models. The analytical precision of most of the measurements in all laboratories was less than 0.04 ppm, although the TU and AIST results indicated that the precision was higher for measurements made with the VIA-500R than with the LI-6252. The TU assayed six cylinders containing combusted

petroleum CO_2 at both the beginning and the end of the experiment to evaluate the stabilities of the CO_2 contents during the experimental period. No significant drift of CO_2 concentration was observed in any of the six cylinders. The results for three other cylinders examined by the NIES were found to be stable during the experimental period. Thus, no correction for drift has been applied to the measurement results reported by any of the laboratories. The CO_2 concentrations of three cylinders reported by the NIES were corrected for isotope effects of +0.06 ppm for CPB16443 and CPB29524 and of +0.29 ppm for CPB28548 in accord with the method of Tohjima et al. (2009). The reported values from all other laboratories, however, were not corrected for isotope effects.

Table 7. CO_2 concentrations (ppm) and reported analytical precisions in parentheses during the iceGGO-2.

	Cylinder Identifications								
Laboratory	CPB10204	CPB10206	CPB10208	CPB10210	CPB10213	CPB10216	CPB28548	CPB16443	CPB29524
AIST (LI-6252)	340.11 (0.020)	369.98 (0.019)	390.19 (0.017)	410.08 (0.016)	429.86 (0.013)	450.08 (0.016)	369.93 (0.018)	406.04 (0.013)	409.33 (0.021)
AIST (VIA-500R)	340.10 (0.009)	369.95 (0.011)	390.19 (0.006)	410.07 (0.011)	429.86 (0.006)	450.10 (0.013)	370.17 (0.010)	406.16 (0.011)	409.45 (0.013)
NIES (LI-6252)	339.93 (0.024)	369.80 (0.014)	390.02 (0.017)	409.91 (0.018)	429.72 (0.023)	449.95 (0.024)	370.06*(0.017) (+0.29)**	406.02*(0.016) (+0.06)**	409.31*(0.008) (+0.06)**
JMA (VIA-510R)	340.10 (0.018)	369.91 (0.020)	390.05 (0.013)	409.97 (0.012)	429.69 (0.012)	449.97 (0.007)	369.98 (0.018)	405.99 (0.014)	409.27 (0.006)
NIPR (VIA-510R)	-	370.06 (0.020)	390.25 (0.020)	410.16 (0.020)	-	-	370.08 (0.010)	406.15 (0.020)	409.44 (0.010)
TU (LI-6252)	340.11 (0.037)	369.99 (0.020)	390.21 (0.026)	410.13 (0.035)	429.94 (0.026)	450.12 (0.042)	369.93 (0.018)	406.11 (0.028)	409.40 (0.025)
TU (VIA-500R)	340.12 (0.009)	370.00 (0.012)	390.25 (0.014)	410.12 (0.011)	429.92 (0.015)	450.08 (0.018)	370.26 (0.013)	406.22 (0.009)	409.52 (0.011)

*Corrected by isotope effect
**Isotope effect

Figure 2 shows differences in CO_2 concentrations measured by each laboratory (Laboratory X) and NIES for the six cylinders containing combusted petroleum CO_2. The differences (Laboratory X minus NIES) among the laboratories ranged from –0.03 ppm to +0.26 ppm. The differences for the TU, AIST, and NIPR exceeded +0.1 ppm, whereas the

difference between the JMA and NIES depended largely on the CO_2 concentration. The concentrations measured with the two different instruments (VIA-500R and LI-6252) by the TU and AIST were in good agreement, although there was a small systematic difference (less than ~0.05ppm) between the two laboratories. These results mainly reflect differences in the standard gas scales for the CO_2 calibrations among the laboratories. Isotope effects are ruled out because the same combusted petroleum CO_2 was the CO_2 source in both the round-robin samples and the calibration gas cylinders.

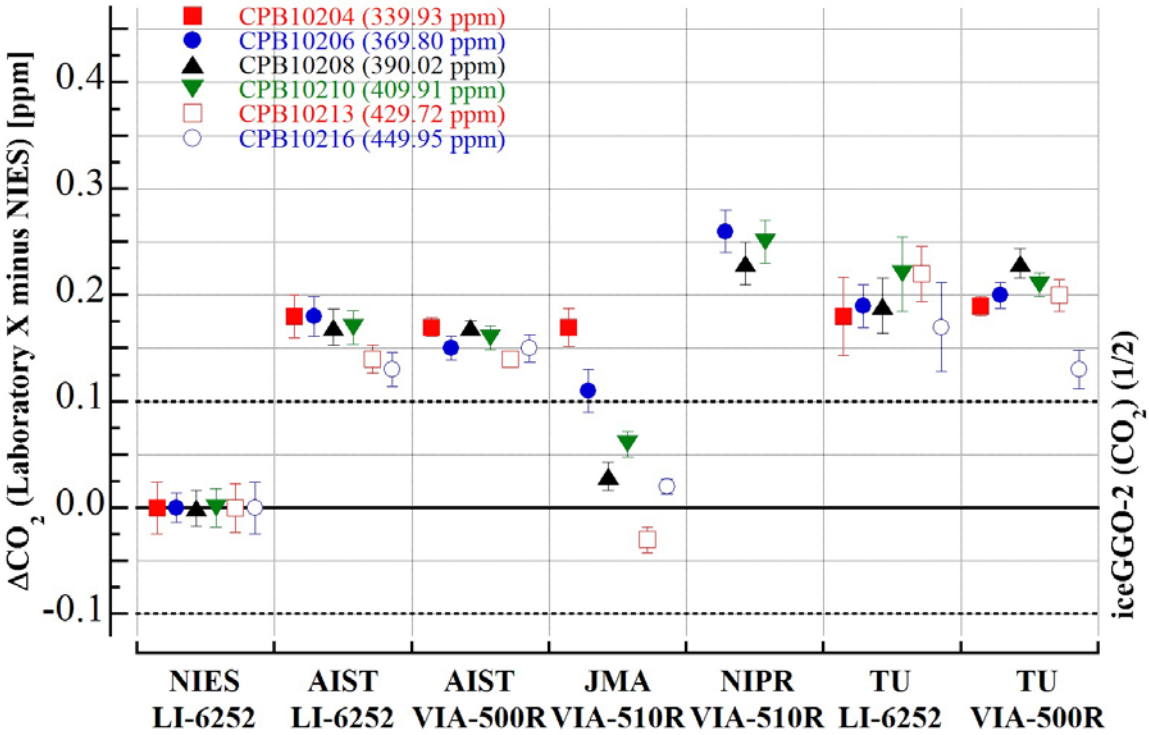

Figure 2. Differences (Laboratory X minus NIES) of CO_2 concentrations for six round-robin cylinders measured for the iceGGO-2. The error bars represent the ± measurement precision reported by each laboratory. The dashed lines around the zero line identify the WMO criterion (±0.1 ppm) in the Northern Hemisphere for network compatibility.

Figure 3 shows differences in CO_2 concentrations measured by each laboratory (Laboratory X) and the NIES for natural air samples in the CPB16443 and CPB29524 cylinders and the CPB28548 ($^{13}CO_2$ enriched) cylinder. The isotopic compositions of CO_2 in these three cylinders were different from those in the CO_2 calibration gases used in all laboratories to examine the isotope effect on the NDIR analysis. The differences (Laboratory X minus NIES) among the laboratories and NDIR models ranged from –0.15 ppm to +0.21 ppm in these three cylinders. The measurements of the two natural air sample cylinders agreed well within the analytical precision in all laboratories. However, there was a large difference (±0.1 ppm) between the concentrations determined with the VIA-500R and LI-6252 analyzers for two natural air samples analyzed by the TU and AIST. The deviations of the analyses were larger for the enriched $^{13}CO_2$ sample cylinder than for the two natural air sample cylinders. These results reflect not only differences in CO_2 calibration standard scales but also isotope effects associated with the NDIR models.

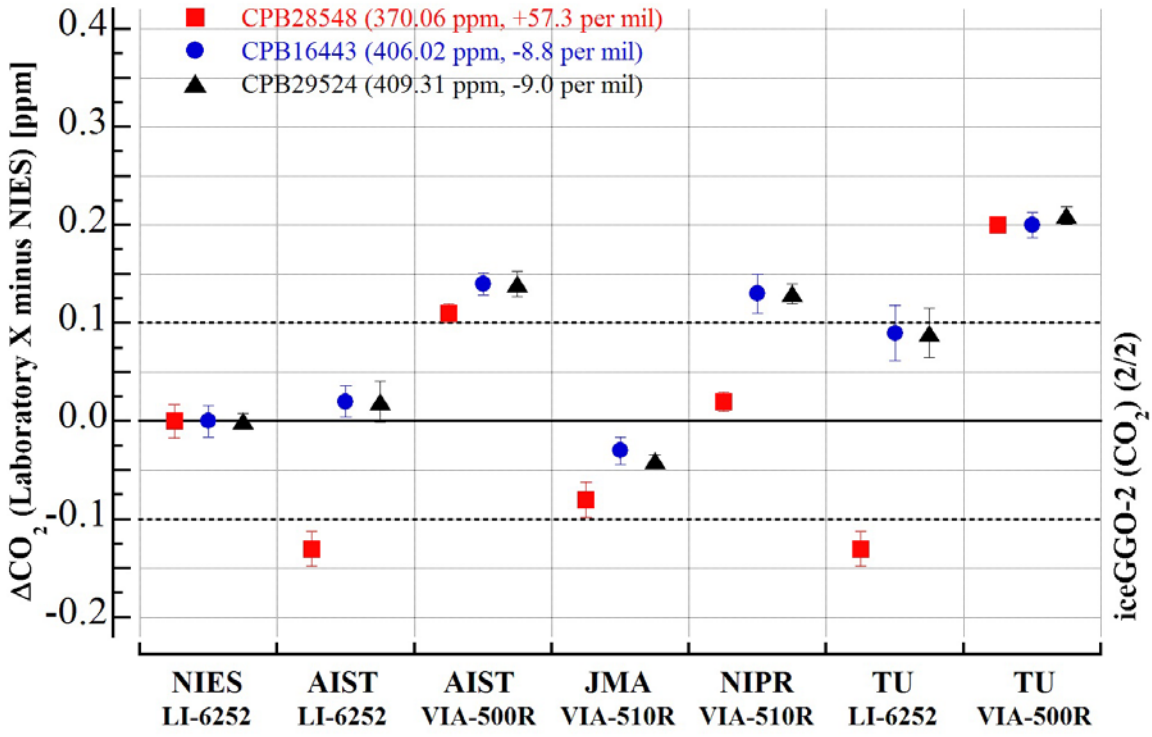

Figure 3. Differences (Laboratory X minus NIES) of CO_2 concentrations for three round-robin cylinders measured for the iceGGO-2. The error bars represent the ± measurement precisions reported by each laboratory. The dashed lines around the zero line identify the WMO criterion (±0.1 ppm) in the Northern Hemisphere for network compatibility.

4. iceGGO-3 (CO_2)

4.1. Round-robin cylinders (iceGGO-3)

The third experiment (iceGGO-3), which took place in 2014, was a comparison of CO_2 concentrations in high-pressure cylinders. Table 8 provides details about the three sample cylinders used in the round-robin experiment. The samples in these three cylinders contained CO_2 at concentrations of about 380 ppm, 400 ppm, and 418 ppm, respectively. The samples were prepared from pure CO_2 and purified natural air with a three-step