

2009-20 Deep Nutrient Comparison and Data Report

Kristina Brown and Fiona McLaughlin, December 30, 2010

Background:

Water column profiles of seawater samples collected and analyzed for the determination of Orthophosphate (PO_4) during the 2009-20 Canada Basin JOIS cruise were observed to fall on the high side of historical deep water data distributions (> 250m depth as depicted in Appendix Figures A1 & A2). As a similar deviation was seen in the 2008-30 Nitrate + Nitrite (NO_3) sample analysis, 2009-20 PO_4 data were immediately compared with historical deep water values, averaged between 2003 and 2006, following the methods outlined in the 2008-30 NO_3 deep water comparison. Since the multitude of daily calibration and check standards run over the duration of the 2009-20 JOIS cruise illustrated satisfactory instrument operation (Appendix Table A7; see 2009-20 Nutrient Analysis report by Linda White), in order to investigate other potential sources of higher PO_4 values to the 2009 data set, (for example, progressive instrument drift in the evaluation of standards), comparisons were made for all three nutrient parameters, NO_3 , PO_4 , and Reactive Silicate (SiO_4), measured during the 2009-20 cruise.

Appendix Figures A1 & A2 (PO_4), A3 & A4 (SiO_4) and A5 & A6 (NO_3), depict 2009-20 nutrient depth profiles with respect to historical data. From these figures it can be seen that 2009 PO_4 values appear high compared to previous years, while 2009 SiO_4 values fall on the low side of historical trends, and 2009 NO_3 data profiles track in line with historical data. The inconsistent behaviour between the 3 nutrients suggests the cause of such deviations is sample analysis/instrument function, despite daily calibration checks indicating otherwise. The following report investigates of the role of sample analysis/instrument function in the deviation of 2009 PO_4 & SiO_4 deep water measurements from previous year's data.

Investigation Methods:

Following the methods utilized to investigate the influence of instrument drift on the 2008-30 NO_3 data set (see "**2008-30 NO3 Data Correction Report 17Dec 2010.pdf**" for a detailed description of the comparison methods), data from the LSSL 2009-20 cruise were evaluated against historical data from deep water stations throughout the Canada Basin. Deep water nutrient samples from CB stations visited from 2003-2006 (LSSL 2003-21, 2004-16, 2005-04, & 2006-18) were evaluated and Table 1 lists the details of the 2003-2006 data used in comparisons. Each 2003-2006 depth average is composed of data from at least 3 years, with the average standard deviation falling in line with historically reported Sp values for each nutrient (PO_4 +/- 0.02 mmol/m³; SiO_4 +/- 0.14 mmol/m³; NO_3 +/- 0.21 mmol/m³).

As detailed in Linda White's nutrient analysis report, the main colorimeters used for nutrient analysis onboard the LSSL in 2008 were significantly damaged during container loading at IOS in July 2008. Damage to the main colorimeters was found to be extensive and although parts were replaced, the colorimeter is believed to be the main contributor to variability in the data (see Linda White's 2009 nutrient analysis report). Data from 2007 were not included because questions about the PO_4 reagents; data from 2008 was not included because the 2008 and 2009 data sets were corrected at the same time.

Data from the 2003-2006 data sets found to fulfill the 2008-30 report criteria were then used to determine average values for each deep water depth (ie. 1500m, 2000m, 2250m, 2500m, 3000m etc) at each station listed in Table 2. 59 deep water (> 1500m) samples analyzed for each of the three nutrients over the 2009-20 cruise were then compared to the 2003-2006 deep station averages (> 3000m station depth). Note standard deviation is used in the following analysis, not pooled standard deviation which underestimates the variability of the analyses.

Table 1. 2003-2006 Data Used for Deep Water Comparison. Average deep water values for each nutrient comparison were compiled for stations with at least 3 years (2003 to 2006 inclusive) of samples from each depth. Standard deviations listed indicate the average spread in the compared data sets for each nutrient.

	Number of Data Points Per Depth Compared	PO ₄ StDev	SiO ₄ StDev	NO ₃ StDev
Average	3.48	0.02	0.14	0.21
StDev	0.62	0.01	0.06	0.13
Max	6.00	0.05	0.24	0.62
Min	3.00	0.00	0.03	0.02
n		50	39	50

Table 2. 2003-2006 Stations utilized in 2009 vs (2003-2006) comparison.

CB2	CB3	CB4	CB5	CB7	CB8
CB9	CB10	CB11	CB13	CB15	CB17
CB18	CB21	CB22	CB27	CB29	

Results: 2009-20 Drift

PO₄: Figure 1 illustrates the results of the deep water comparison for 2009-20 PO₄ data. The difference between the 2009 value and the calculated 2003-2006 average at each station/depth compared is plotted against the date each sample/cast was analyzed aboard the LSSL. While calculated differences in deep water concentrations show a weaker trend with date analyzed ($R^2 = 0.1764$), all 2009 data points are observed to be higher (by + 0.02 to + 0.12 mmol/m³) than historical deep water averages, with a trend of the highest offsets at the beginning of the cruise and falling to within reported error limits by the end of the cruise. This suggests a drift in instrument measurement over the course of the cruise. The trend line in Figure 1 suggests a 2009 PO₄ data are affected by a drift in instrument operation on the order of -0.002 mmol/m³/day (a decrease by 10% of reported error per day) superimposed on an offset from expected deep water values on the order of +0.08 to +0.04 mmol/m³.

SiO₄: Figure 2 illustrates the results of the deep water comparison for 2009-20 SiO₄ data. As in Figure 1, the difference between the 2009 value and the calculated 2003-2006 average at each station/depth compared is plotted against the date each sample/cast was analyzed aboard the LSSL. As seen in Figure 1, calculated differences in deep water concentrations of SiO₄ also show a weak trend with date analyzed ($R^2 = 0.1028$); however, contrary to PO₄ results, SiO₄ data points begin at parity with historical averages, and proceed to fall below historical deep water values as the cruise progresses (date of analysis increases). The trend line in Figure 2 suggests 2009 SiO₄ data are affected by a drift in instrument measurement on the order of -0.02 mmol/m³/day (a decrease by 10% of reported error per day).

NO₃: Figure 3 illustrates the results of the deep water comparison for 2009-20 NO₃ data. As in Figures 1 & 2, the difference between the 2009 value and the calculated 2003-2006 average at each station/depth compared is plotted against the date each sample/cast was analyzed aboard the LSSL. From this comparison, Figure 3 illustrates no trend ($R^2 = 0.00004$) between differences in deep water values and date analyzed; however, NO₃ data do appear to exhibit a minimal, but consistent, offset (~ - 0.15 mmol/m³) with respect to historical deep water averages. As an offset on the order of 0.15 mmol/m³ falls within the reported 95% confidence limit for 2009 NO₃ data (+/- 0.2 mmol/m³) these data have not been corrected.

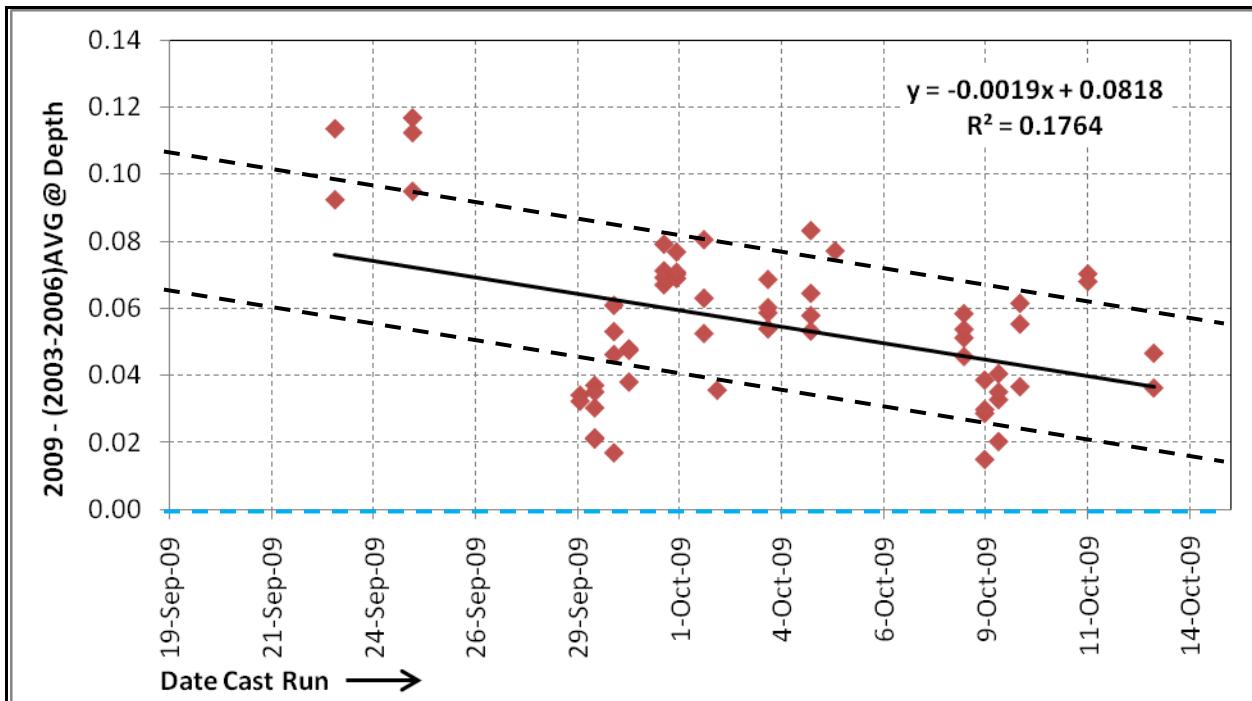


Figure 1. PO₄ Average Difference [2009 – (2003-2006 Average @ Station Depth)] vs Date Sample Run. PO₄ data compared only at stations > 3000m. Solid black line represents the trend line fit to the data, defined by $y = -0.0019x + 0.0818$, where x is the day each sample is run (September 19th = 0); black hatched lines are the expected error limits projected from the trend line, +/- 0.02 mmol/m³, or the reported 95% confidence limits for the 2009 data set.

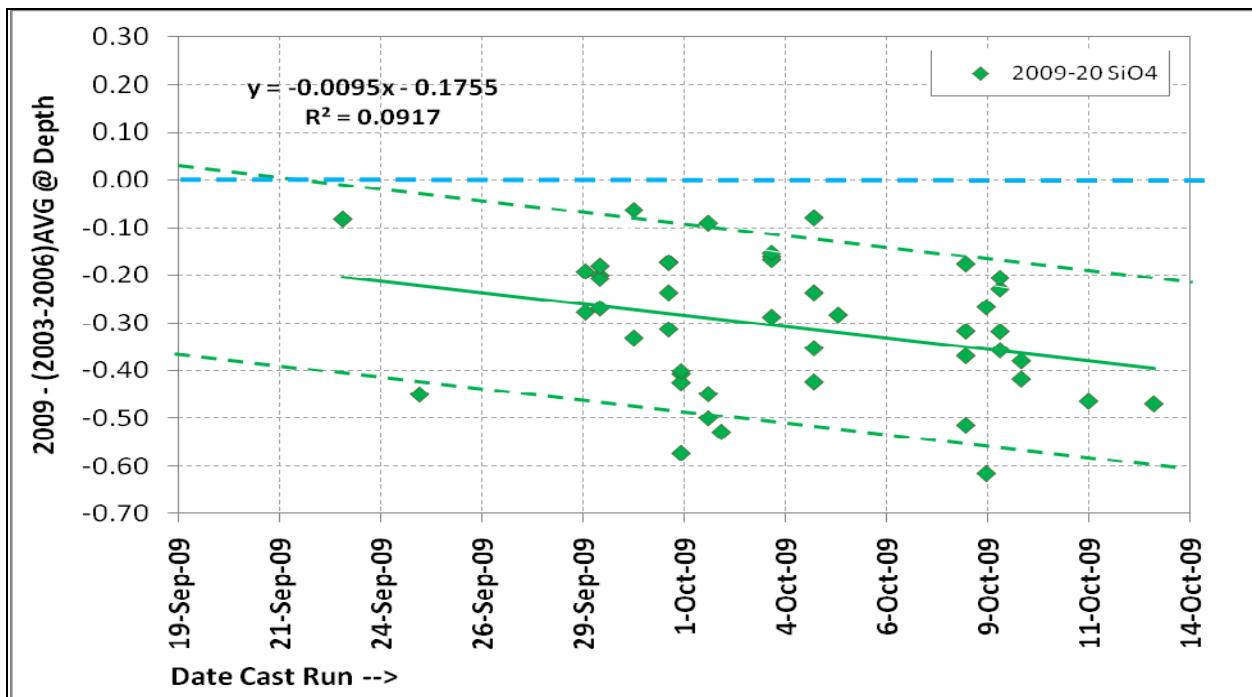


Figure 2. SiO₄ Average Difference [2009 – (2003-2006 Average @ Station Depth)] vs Date Sample Run. SiO₄ data compared only at stations > 3000m. Solid black line represents the trend line fit to the data, defined by $y = -0.0095x - 0.1755$, where x is the day each sample is run (September 19th = 0); green hatched lines are the

expected error limits projected from the trend line, +/- 0.2 mmol/m³, or the reported 95% confidence limits for the 2009 data set.

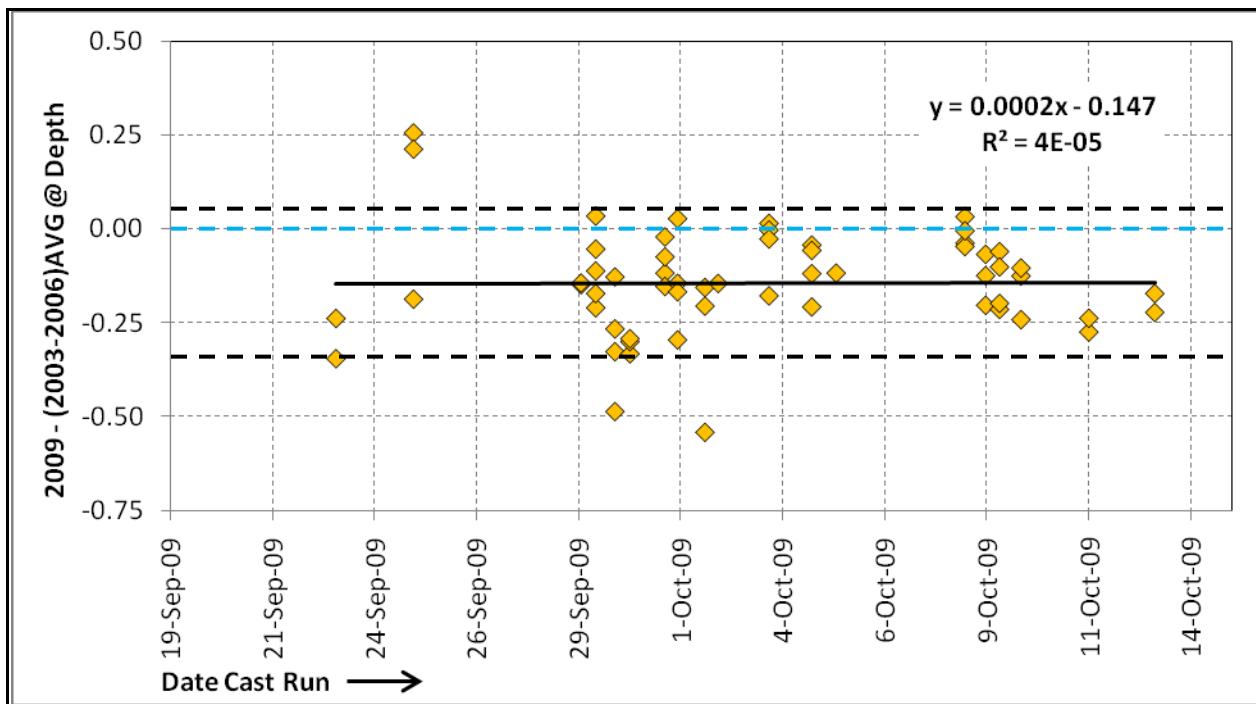


Figure 3. NO₃ Average Difference [2009 – (2003-2006 Average @ Station Depth)] vs Date Sample Run. NO₃ data compared only at stations > 3000m. Solid black line represents the trend line fit to the data, defined by $y = 0.0002x - 0.147$, where x is the day each sample is run (September 19th = 0); black hatched lines are the expected error limits projected from the trend line, +/- 0.2 mmol/m³, or the reported 95% confidence limits for the 2009 data set.

Results: Data Correction

2009 PO₄ Data: The slope depicted in Figure 1 ($y = -0.0019x + 0.0818$, where x is the day each sample is run (September 19th = 0)) was used to apply a linear correction to PO₄ samples analyzed aboard the LSSL during the 2009-20 cruise. This is based on the assumption that the negative slope & offset depicted in Figure 1 are a result of a linear drift in the instrument output over the course of the cruise, and not due to daily fluctuations in the instrument response. Note, however, that Figure 1 also illustrates substantial variation in measurements carried out within the same day, overprinted with an apparent trend in negative drift over the duration of the cruise. The error at the 95% confidence limit based on duplicate analysis during the cruise is +/- 0.02 mmol/m³ (2 sigma), limits which do not envelope the visible within-day drift seen in Appendix Figures A31, A32, & A33, illustrating the difference of 2009 data from historic deep water values with respect to the day of analysis and cast run (see Within-Day Drift & Reported Standard Error section below).

Figure 4 illustrates the data depicted in Figure 1, including recalculated data values corrected for instrument drift according to the equation $y = -0.0019x + 0.0818$, where x is the day each sample is run (September 19th = 0). Red diamonds depict original data, as in Figure 1, whereas pink diamonds illustrate the corrected data. The flat (slope = -0.00005) trend line associated with corrected 2009 data illustrates that remaining variability in the values is not dependant on the date samples were analyzed, and therefore, is no longer associated with instrument drift.

The 2009-20 PO₄ data set (all samples) were also corrected using the linear drift correction depicted by the trend line equation, $y = -0.0019x + 0.0818$, where x is day run in order from beginning of cruise. Appendix Figures A8 & A9 illustrate corrected PO₄ data compared to historical deep water column profiles. Examples of individual station profiles are depicted in Appendix Figures A12 – A19, where red filled circles denote original 2009-20 PO₄ data, and purple hollow circles denote corrected data points.

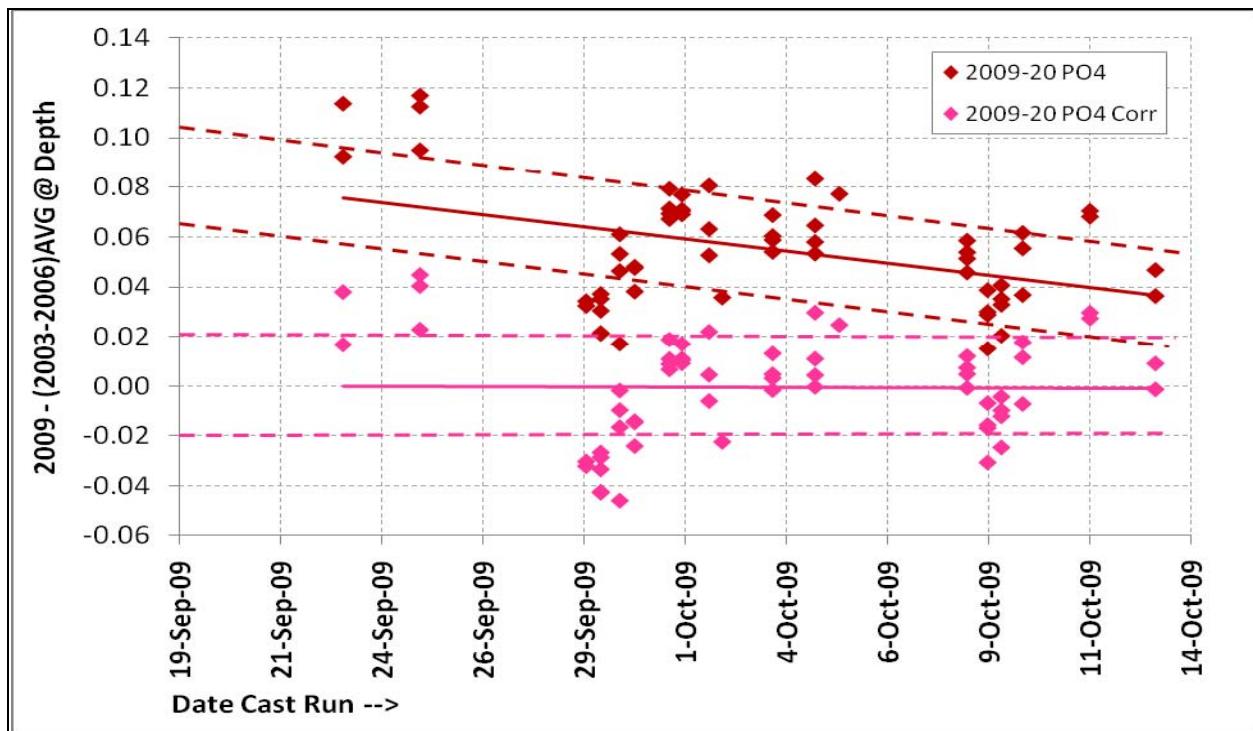


Figure 4. As in Figure 1, PO4 Average Difference [2009 – (2003-2006 Average @ Station Depth)] vs Date Sample Run, original & corrected data. PO4 data points corrected according to the relationship defined by $y = -0.0019x + 0.0818$, where x is the day each sample is run (September 19th = 0). Hatched lines are the expected error limits projected from the trend line, $\pm 0.02 \text{ mmol/m}^3$, or the reported 95% confidence limits for the 2009 data set.

2009 SiO₄ Data: The slope depicted in Figure 2 ($y = -0.0095x - 0.1755$, where x is the day each sample is run (September 19th = 0)) was used to apply a linear correction to SiO₄ samples analyzed aboard the LSSL during the 2009-20 cruise. This is based on the assumption that the negative slope & offset depicted in Figure 2 are a result of a linear drift in the instrument output over the course of the cruise, and not due to daily fluctuations in the instrument response. Note, however, that Figure 2 also illustrates substantial variation in measurements carried out within the same day, overprinted with an apparent trend in negative drift over the duration of the cruise. The error at the 95% confidence limit based on duplicate analysis during the cruise is $\pm 0.2 \text{ mmol/m}^3$ (2 sigma), limits which do not envelope the visible within-day drift seen in Appendix Figures A34, A35, & A36, illustrating the difference of 2009 data from historic deep water values with respect to the day of analysis and cast run (see Within-Day Drift & Reported Standard Error section below).

Figure 5 illustrates the data depicted in Figure 2, including recalculated data values corrected for instrument drift according to the equation $y = -0.0095x - 0.1755$, where x is the day each sample is run (September 19th = 0). Dark Green diamonds depict original data, as in Figure 2, whereas Light Green diamonds illustrate the corrected data. The flat (slope = -0.00001) trend line associated with corrected 2009 data illustrates that remaining variability in the 2009-20 Deep Nutrient Comparison and Data Report Kristina Brown and Fiona McLaughlin, Dec 30, 2010

values is not dependant on the date samples were analyzed, and therefore, is no longer associated with instrument drift.

The 2009-20 SiO₄ data set (all samples) were also corrected using the linear drift correction depicted by the trend line equation, $y = -0.0095x - 0.1755$, where x is day run in order from beginning of cruise. Appendix Figures A10 & A11 illustrate corrected SiO₄ data compared to historical deep water column profiles. Examples of individual station profiles are depicted in Appendix Figures A20 – A27, where red filled circles denote original 2009-20 SiO₄ data, and purple hollow circles denote corrected data points.

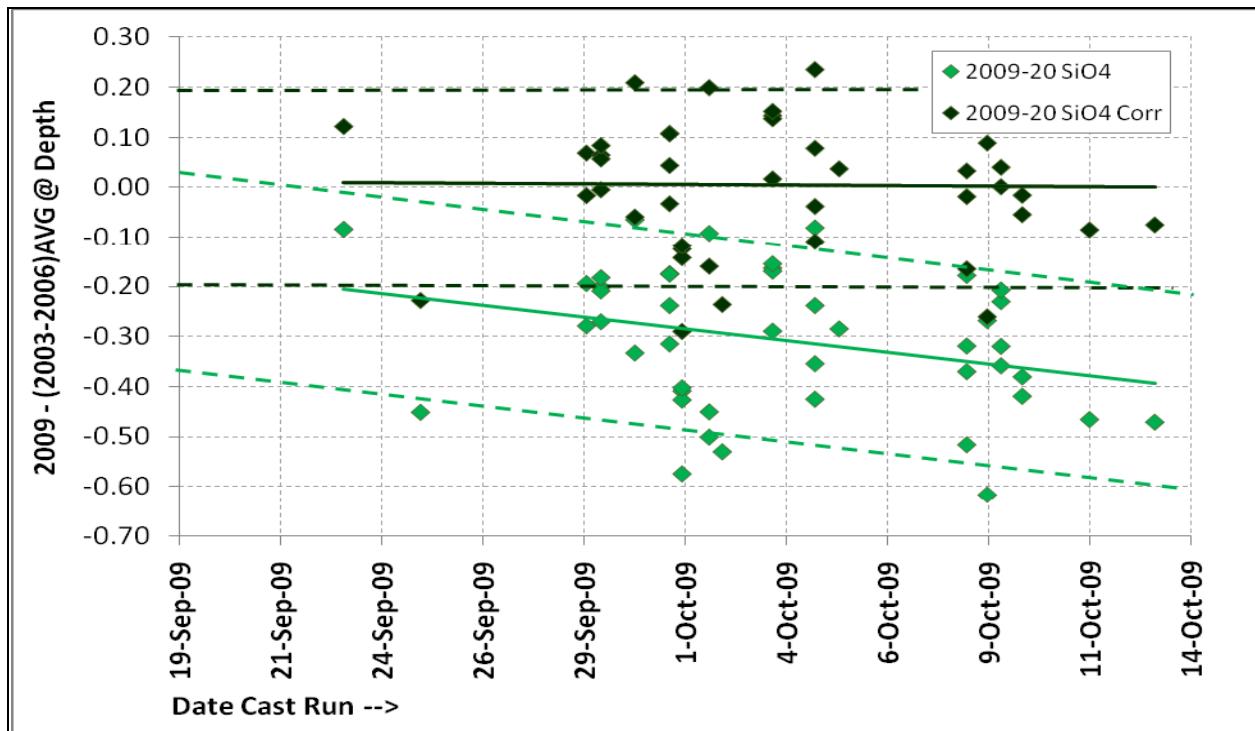


Figure 5. As in Figure 2, SiO₄ Average Difference [2009 – (2003–2006 Average @ Station Depth)] vs Date Sample Run, original & corrected data. SiO₄ data points corrected according to the relationship defined by $y = -0.0095x - 0.1755$, where x is the day each sample is run (September 19th = 0). Hatched lines are the expected error limits projected from the trend line, $\pm 0.2 \text{ mmol/m}^3$, or the reported 95% confidence limits for the 2009 data set.

One station, CB22, was occupied at the beginning and end of the cruise (casts 6 and 52) and comparison of these data illustrate that the corrections applied were appropriate. Table 3 shows the corrected PO₄, corrected SiO₄, and NO₃ data from these two casts compared with previous years.

Table 3. CB22 Nutrient data analyzed on board in 2009 (Cast 6 & 52) compared with corrected values (this analysis) and measurements from previous years.

CB22	PO ₄ [mmol/m ³]					SiO ₄ [mmol/m ³]					NO ₃ [mmol/m ³]		
	Approx Depth (m)	2009 (6)	2009 (6) Corr	2009 (52)	2009 (52) Corr	2008	2009 (6)	2009 (6) Corr	2009 (52)	2009 (52) Corr	2008	2009 (6)	2009 (52)
3200	1.13	1.06	1.06	1.03	1.08	13.8	14.0	13.4	13.8	14.0	14.7	14.9	
2545	1.12	1.05	1.06	1.02	1.06	13.2	13.4	12.9	13.3	13.8	14.7	14.8	
2030	1.11	1.03	1.04	1.00	1.03	11.5	11.7	11.1	11.5	11.6	14.3	14.4	14.4
1525	1.04	0.96	0.98	0.95	0.97	9.1	9.3	8.7	9.1	9.0	13.5	13.6	13.6
1015	1.00	0.92	0.94	0.90	0.93	7.5	7.7	7.2	7.6	8.0	12.9	13.0	12.9
815	0.99	0.91			0.92	7.1	7.3			7.4	12.8		12.8
715	1.00	0.92	0.93	0.89		7.3	7.5	6.9	7.3		12.9	13.0	
510			0.90	0.86	0.89			6.7	7.1	7.0		12.8	
430	0.97	0.89	0.90	0.86	0.89	6.9	7.2	6.7	7.0	7.5	12.6	12.8	12.7
315	0.97	0.90	0.90	0.86	0.87	8.0	8.2	7.8	8.2	8.3	12.3	12.1	12.7
225	1.21	1.13	1.55	1.51	1.17	17.0	17.2	28.5	28.9	19.1	11.7	14.0	
200	1.58	1.50	1.48	1.44	1.74	26.9	27.1	26.5	26.9	33.1	13.7	13.6	12.6
190	1.87	1.79	1.92	1.88	1.95	34.1	34.3	36.5	36.9	36.9	15.3	15.9	15.4
180	2.00	1.92	1.98	1.94	2.01	36.7	36.9	37.0	37.4	36.2	15.8	16.1	15.6
160	1.94	1.87	1.96	1.92	1.86	31.4	31.6	34.2	34.6	30.3	14.4	15.4	15.0
130	1.83	1.75	1.70	1.66	1.72	27.1	27.3	24.6	25.0	25.1	12.8	12.0	13.8
70	0.86	0.79	0.79	0.75	0.76	4.0	4.2	3.5	3.8	4.5	0.6	0.4	
22	0.54	0.47	0.55	0.51	0.57	3.0	3.2	3.0	3.4	2.9	0.0	0.0	
7	0.61	0.53	0.50	0.46	0.47	3.1	3.3	2.9	3.3	3.3	0.0	0.0	0.1

Corrected Data Considerations

Within-Day Drift & Reported Standard Error

As Figures 1, 2 & 3 illustrate a considerable spread in 2009 deep water values over the course of a run day (further exemplified in Appendix Figures A28- A36) the reported standard error envelope is slightly higher for this data set for each of the nutrients to include this within day variability.

PO₄: The reported standard error as calculated from duplicate analyses (n= 206) is **+/- 0.01 mmol/m³** (see Linda White's 2009-20 Nutrient cruise report). On board analysis gives a standard error at the 95% confidence limit as **+/- 0.02 mmol/m³** (2 sigma); this 95% confidence interval, however, does not account for the within-day drift of the analysis system, as evidenced by differences in Canada Basin deep water (> 2500 m), and therefore the reported standard error is increased to **0.025 mmol/m³**, yielding a standard error at the 95% confidence limit as **+/- 0.05 mmol/m³** (2 sigma) to account for the differences seen with respect to deep water values (n=59).

SiO₄: The reported standard error as calculated from duplicate analyses (n= 197) is **+/- 0.10 mmol/m³** (see Linda White's 2009-20 Nutrient cruise report). On board analysis gives a standard error at the 95% confidence limit as **+/- 0.20 mmol/m³** (2 sigma); this 95% confidence interval, however, does not account for the within-day drift of the analysis system, as evidenced by differences in Canada Basin deep water (> 2500 m), and therefore the reported standard error of **0.30 mmol/m³**, yielding a standard error at the 95%

confidence limit as +/- 0.60 mmol/m³ (2 sigma) to account for the differences seen with respect to deep water values (n=59).

Comparison to Frozen Samples

Duplicate samples were collected during the 2009-20 LSSL cruise and transported back to IOS to be analyzed and compared with those samples run on board. In an attempt to check the applied correction to the 2009-20 data set, frozen deep water samples from a selection of 2009 deep stations were removed from their freezer storage and run on the Astoria at IOS on April 8, 2010, by Linda White and Kenny Scozzafava. Results from these runs are illustrated in Appendix Figures A12- A19 for PO₄ and Appendix Figures A20-A27 for SiO₄, which compare the original 2009-20 data set, 2009-20 corrected data, 2009-20 freezer stored samples (identified as Frozen) and samples from the 2008-30 & 2006-18 LSSL cruises.

Corrections to Other Data

Leg 1 samples (frozen), Underway System & Sea Ice samples analyzed onboard during LSSL 2009-20 should also be corrected for drift.

Appendix Figure List & Captions

Figures A1 & A2 (PO₄), A3 & A4 (SiO₄), A5 & A6 (NO₃). All 2009-20 Nutrient data collected and analyzed on the Louis S. St. Laurent (red filled circles) compared to historical Canada Basin data from 2003-21, 2004-16, 2005-04, 2006-18, 2007-20 & 2008-30.

Figure A7. LSSL 2009-20 calibration and check standards run for each of the three nutrient parameters over the course of the cruise. As virtually all plots of the standard runs show little deviation over the course of the cruise, instead of showing plots here, details on the average, standard deviation, maximum, minimum, slope (with respect to day run) and correlation coefficient (with respect to day run) are listed at the bottom of the table.

Figures A8 & A9 (PO₄), A10 & A11 (SiO₄). As in Figures A1 – A6, 2009-20 Nutrient data collected and analyzed on the Louis S. St. Laurent (red filled circles) and corrected values (dark green open circles) compared to historical Canada Basin data from 2003-21, 2004-16, 2005-04, 2006-18, 2007-20 & 2008-30.

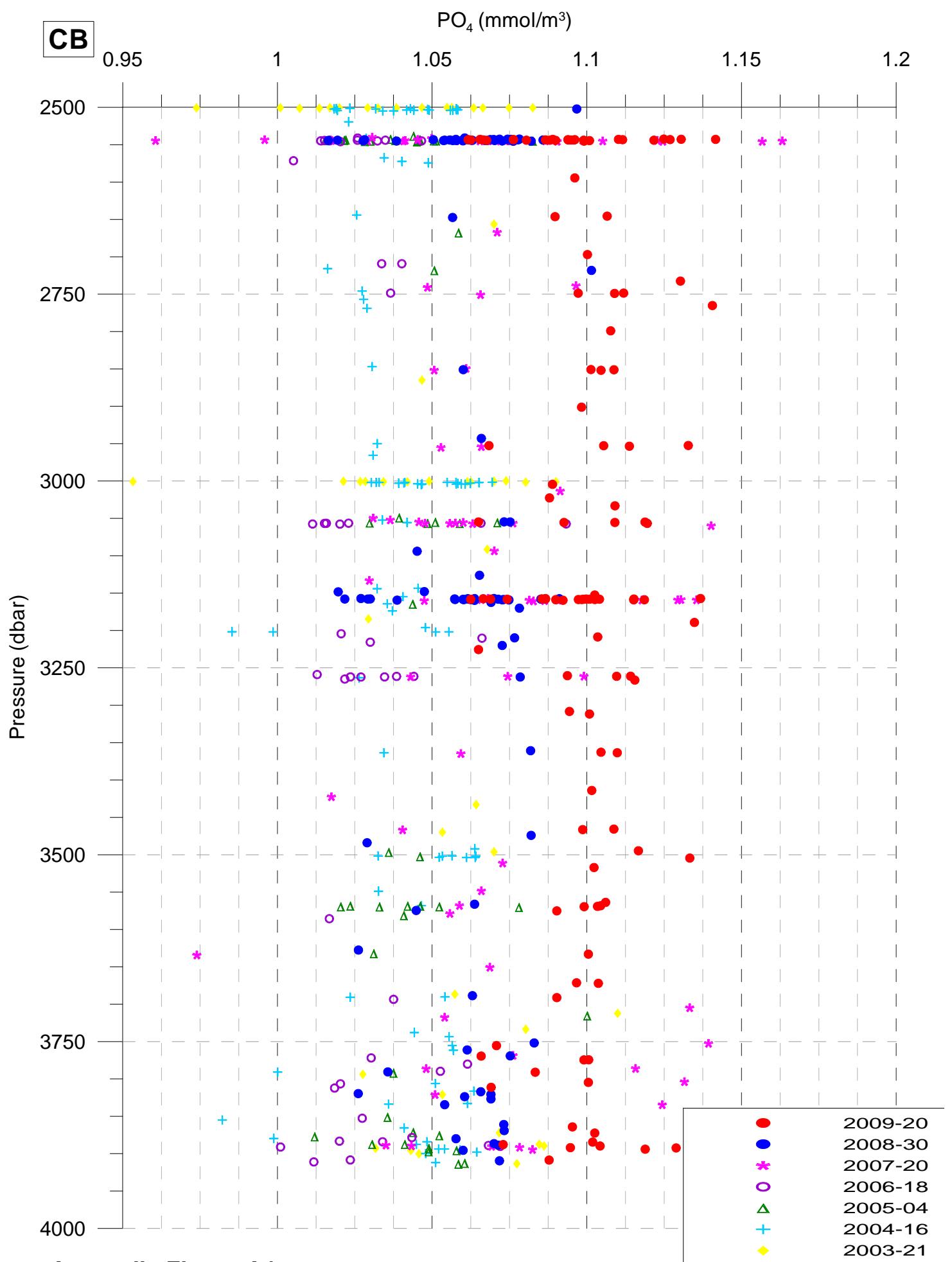
Figures A12-A19 (CB21, CB22, CB40, CB61, CB6e, CB7, CB9 & STNA): PO₄ data analyzed on board (red filled circles) and corrected PO₄ values (dark green open circles), compared with 2009-20 frozen samples (green open triangles) analyzed at IOS on the Astoria, April 8, 2010. 2008-30 (blue filled circles) & 2006-18 (pink open circles) data analyzed on board included for comparison.

Figures A20-A27 (CB21, CB22, CB40, CB61, CB6e, CB7, CB9 & STNA): SiO₄ data analyzed on board (red filled circles) and corrected SiO₄ values (dark green open circles), compared with 2009-20 frozen samples (green open triangles) analyzed at IOS on the Astoria, April 8, 2010. 2008-30 (blue filled circles) & 2006-18 (pink open circles) data analyzed on board included for comparison.

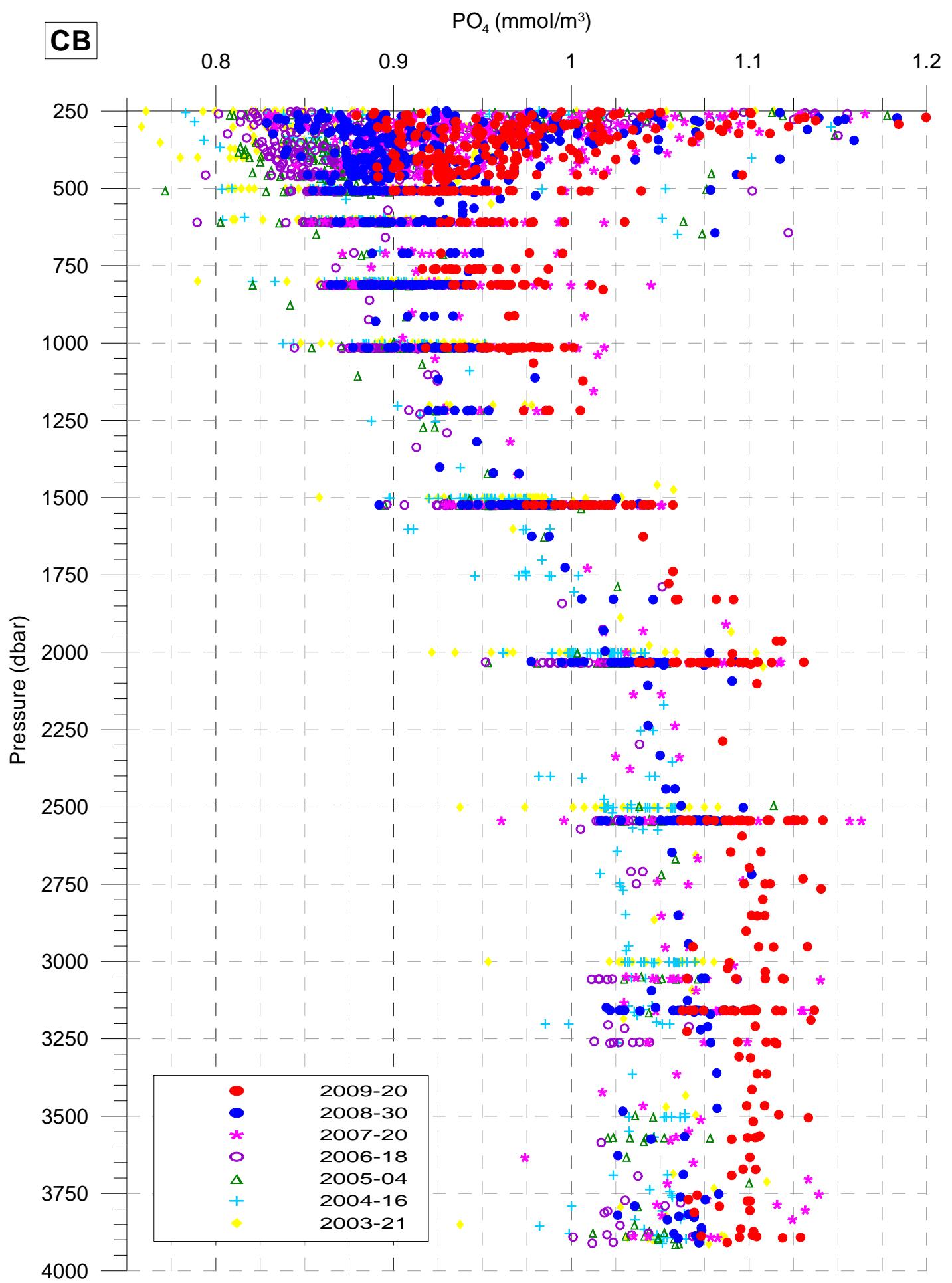
Figures A28, & A29 (NO₃): 2009-20 NO₃ (2009 – (2003-2006)AVG) plotted against date of sample run and colour coded for cast number. A28: Casts 0 – 27, A29: Casts 27-52

Figures A30 & A31 (PO₄): 2009-20 PO₄ (2009 – (2003-2006)AVG) plotted against date of sample run and colour coded for cast number. A30: Casts 0 – 27, A31: Casts 27-52

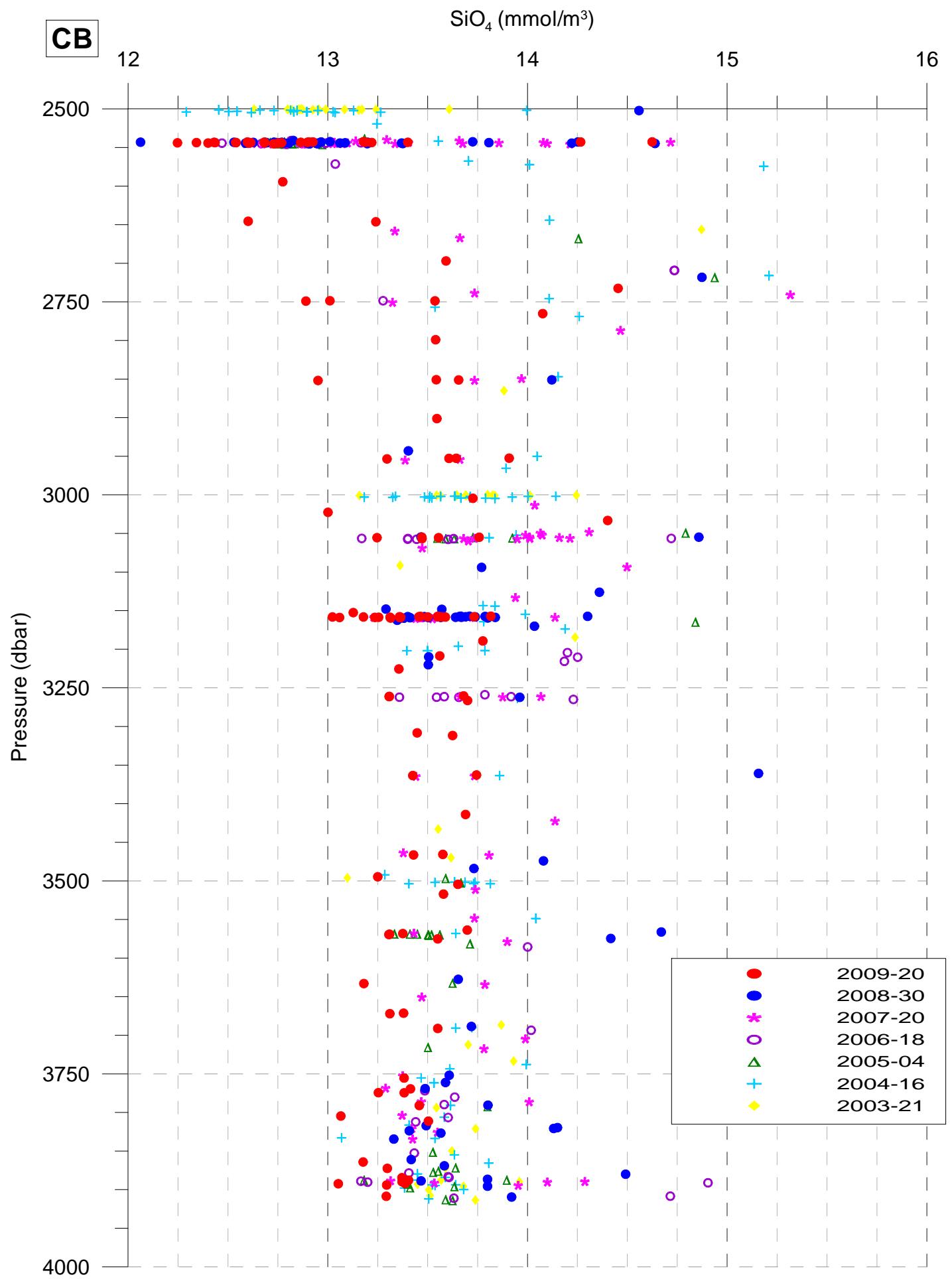
Figures A32 & A33 (SiO₄): 2009-20 SiO₄ (2009 – (2003-2006)AVG) plotted against date of sample run and colour coded for cast number. A32: Casts 0 – 27, A33: Casts 27-52



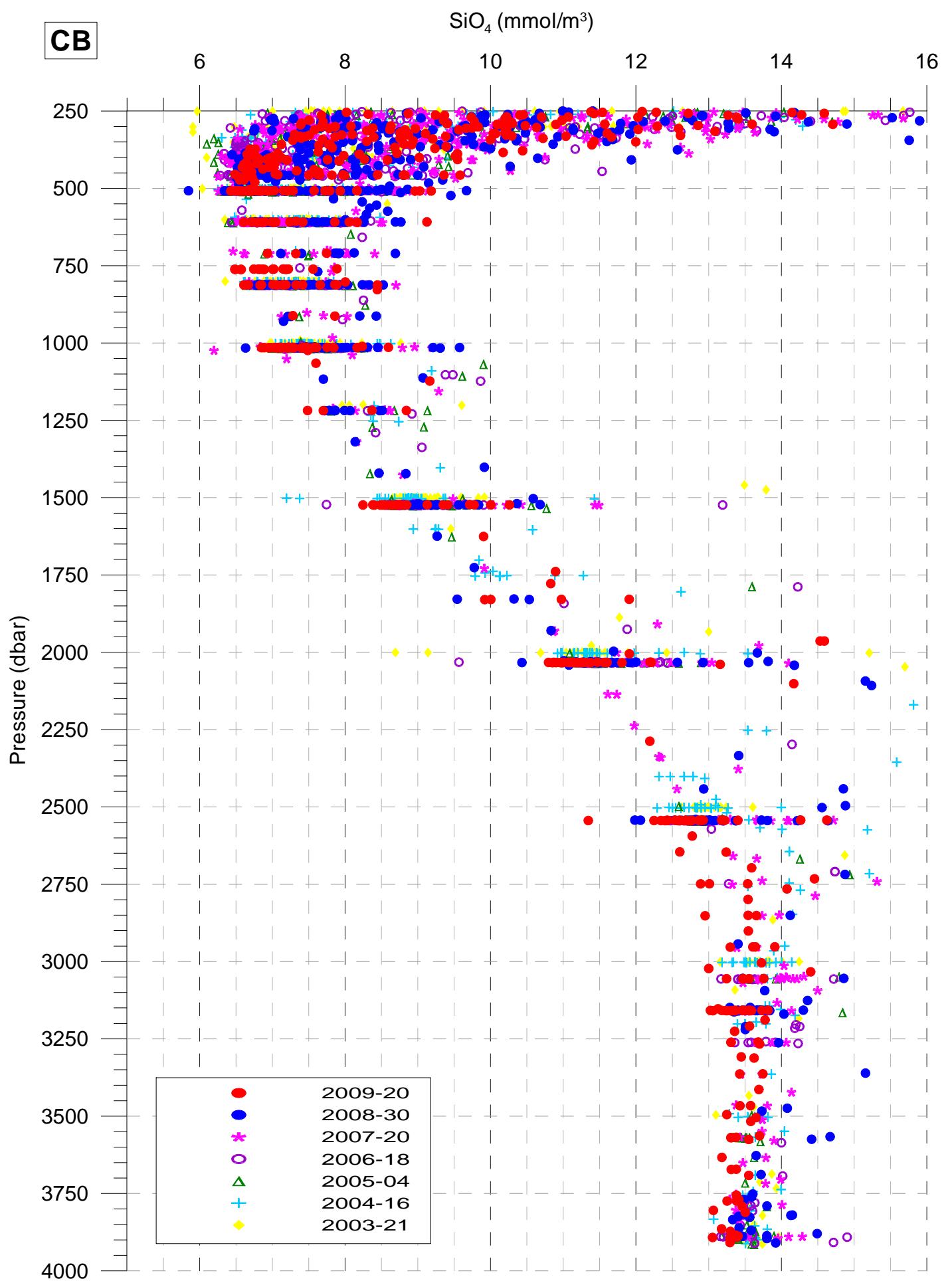
Appendix Figure A1



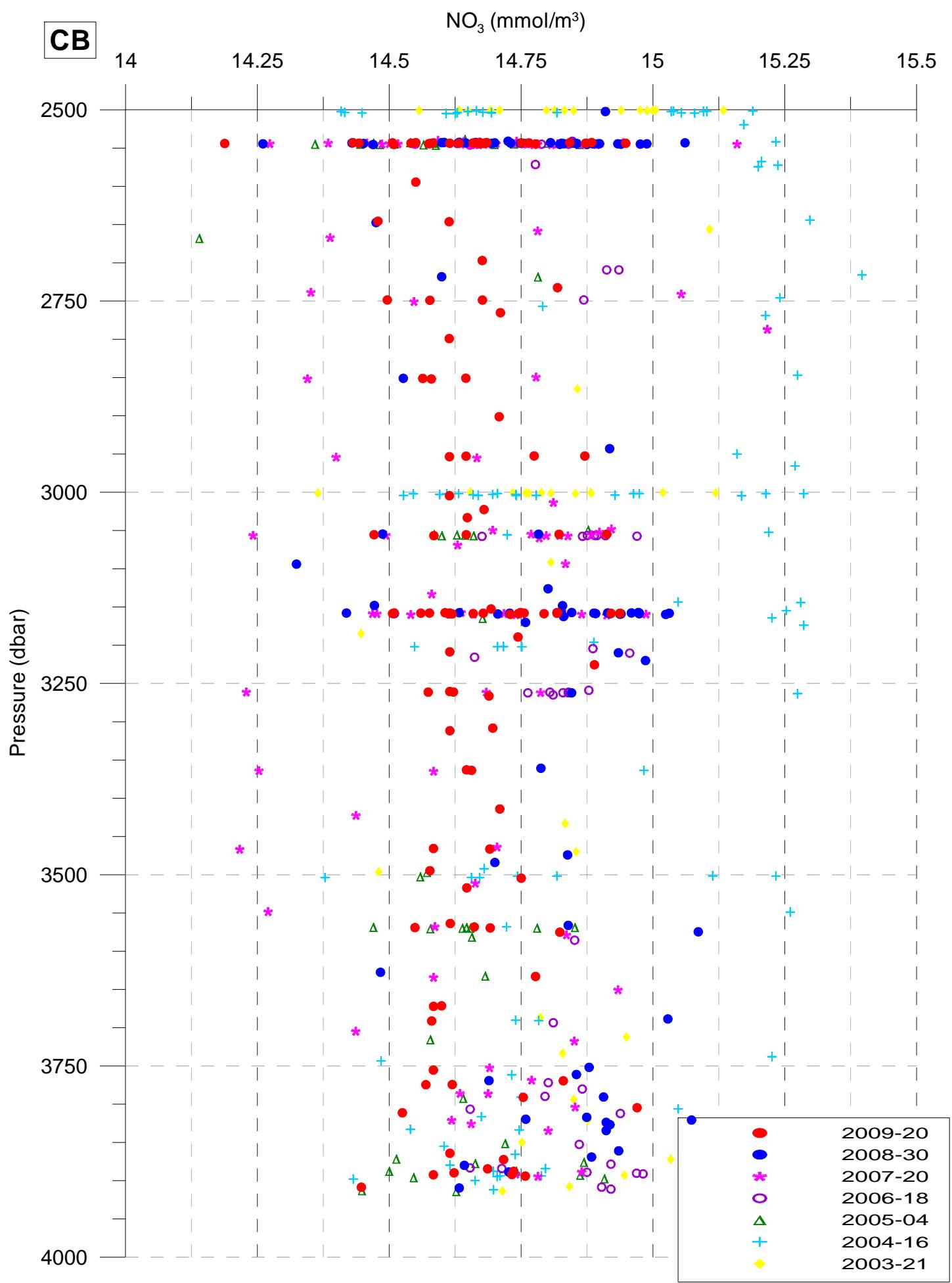
Appendix Figure A2



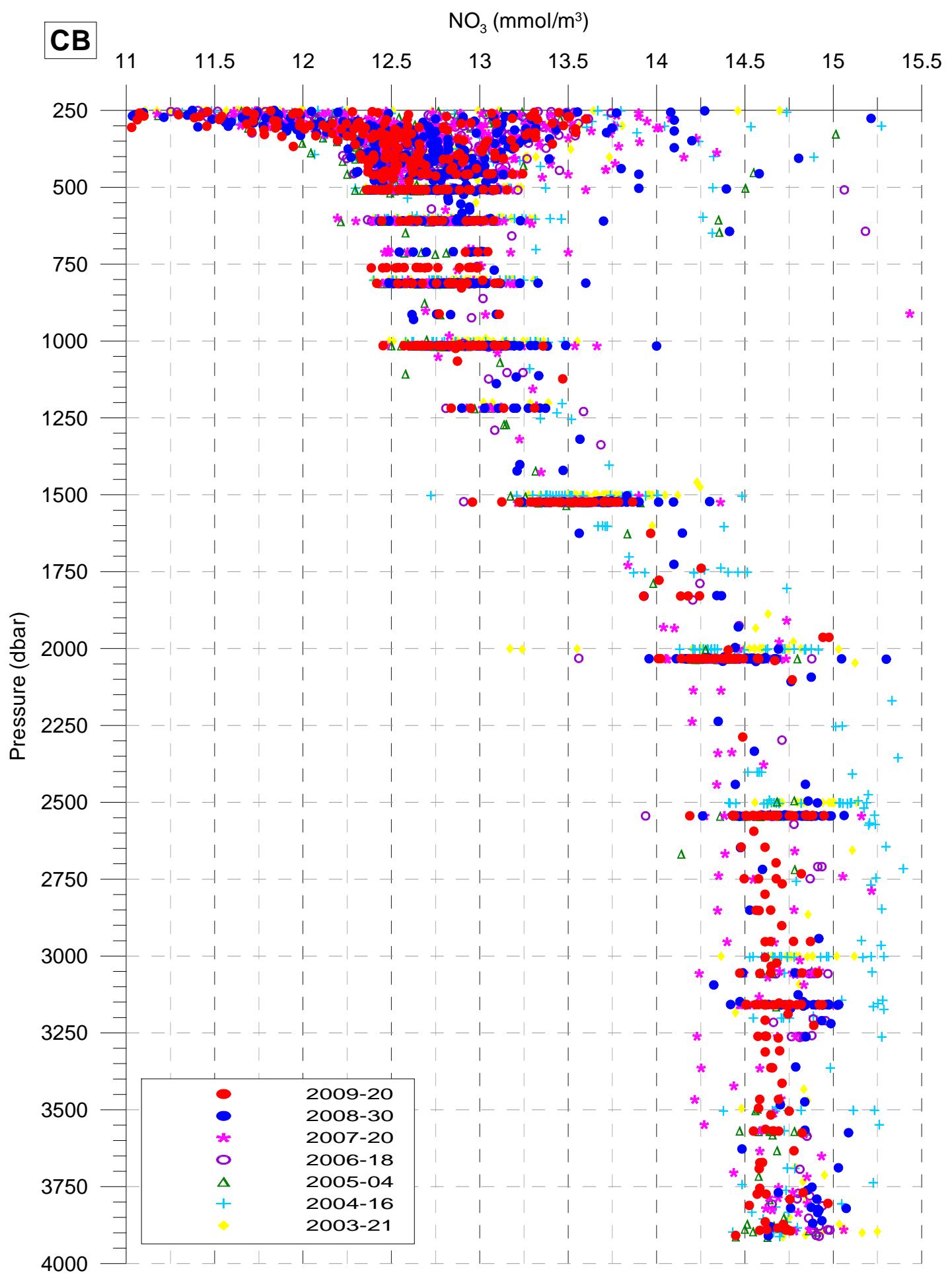
Appendix Figure A3



Appendix Figure A4



Appendix Figure A5

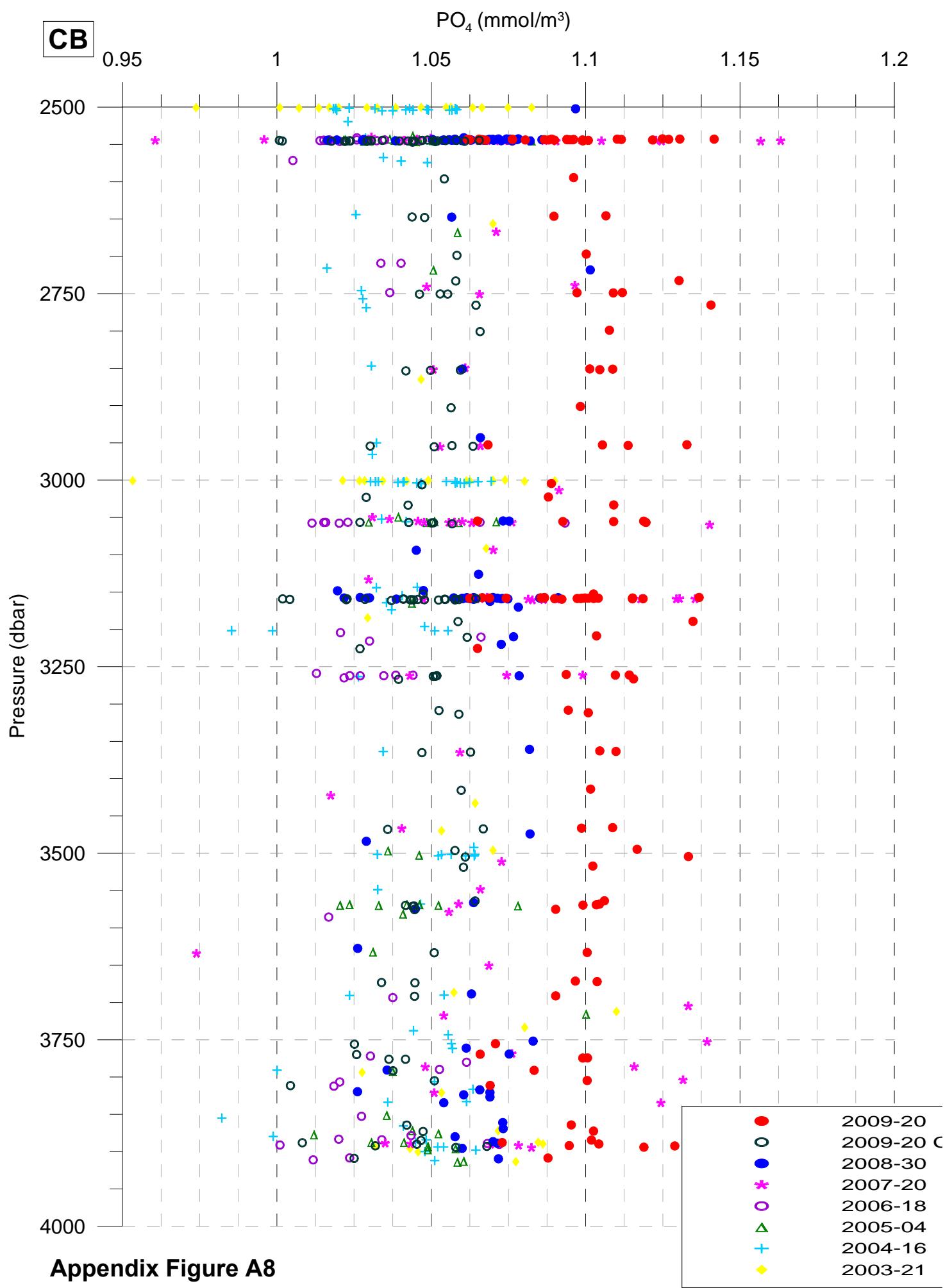


Appendix Figure A6

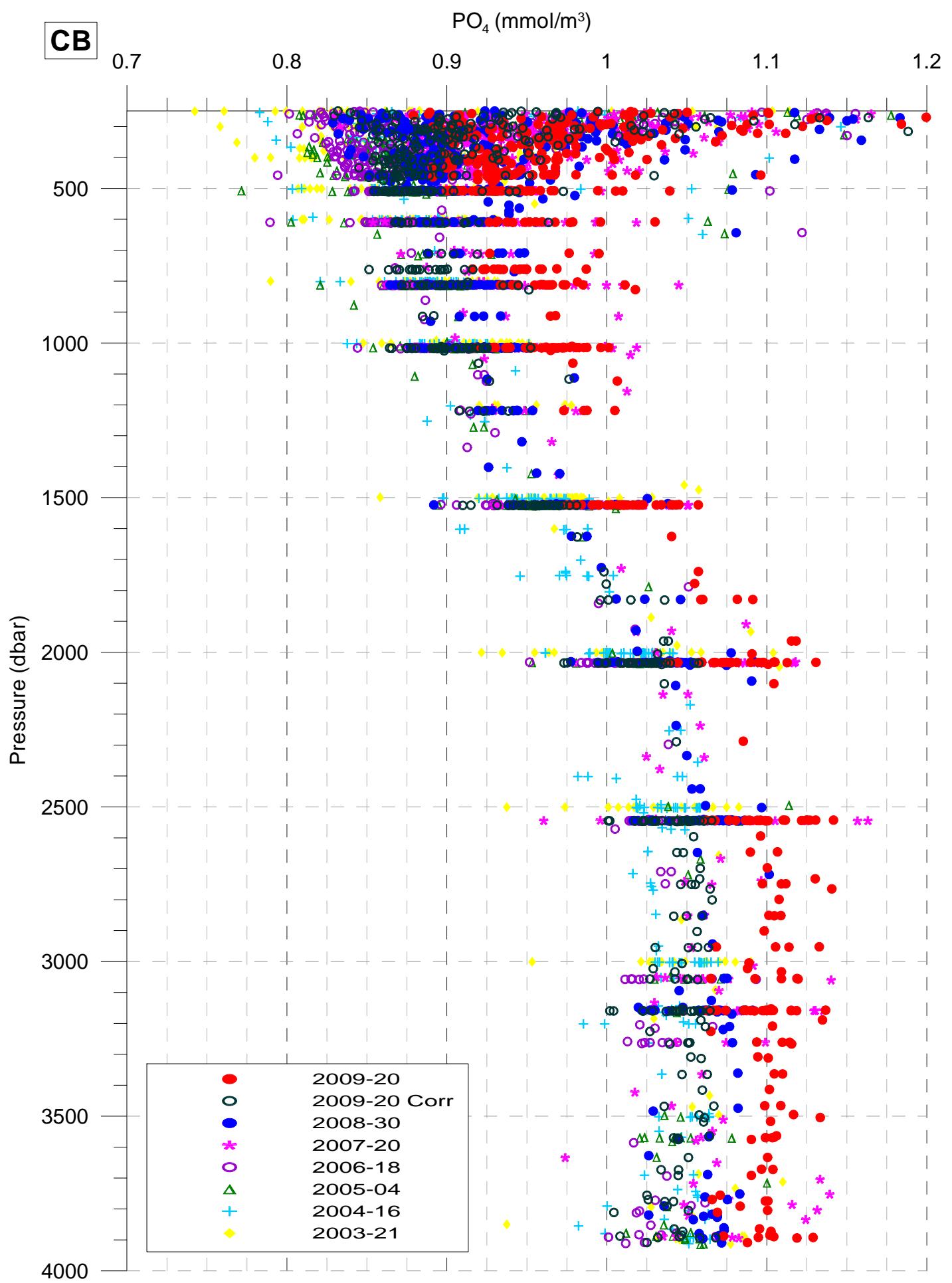
LSSL 2009-20 Standard Runs NO3, SiO4, PO4

Date	DAY	DMQ Nitrate um/l	WAKO Nitrate 20 um/l	WAKO Nitrate 0 um/l	Med CHK Nitrate um/l	FRSH Nitrate 13.5um/l	FRZN Nitrate 13.0um/l	KANSO AY Nitrate um/l	DMQ Silicate um/l	WAKO Silicate 50 um/l	WAKO Silicate 0 um/l	Med CHK Silicate um/l	FRSH Silicate 8.7um/l	FRZN Silicate 8.1um/l	KANSO AY Silicate um/l	DMQ Phosphate um/l	Med CHK Phosphate um/l	FRSH Phosphate 1.02um/l	FRZN Phosphate 0.99um/l	KANSO AY Phosphate 0.5 +/-0.02um/l	
		Expected Value	20.00	0.00	16.00	13.50	13.00	6.35		50.00	0.00	32.00	8.70	8.10	30.30		1.60	1.02	0.99	0.56	
20-Sep-09	0	-0.12			16.08			6.27	-0.30			31.84			29.70	-0.10	1.59			0.56	
20-Sep-09	0							6.28							29.75					0.56	
21-Sep-09	1	-0.08	19.94	0.06		13.49	13.01	6.21	-0.27	50.03	0.06		8.64	8.09	29.89	-0.09		1.02	0.99	0.55	
21-Sep-09	1					13.48	13.07	6.37					8.74	8.08	30.00			1.02	1.00	0.56	
23-Sep-09	3	-0.08	20.05		16.04	13.23	12.97	6.18	-0.36	49.90		31.95	8.59	8.07	30.41	-0.09	1.56	1.04	1.01	0.59	
23-Sep-09	3		20.09		16.08	13.30	13.01	6.15		50.05		32.01	8.70	8.01	30.35		1.56	1.03	1.00	0.61	
23-Sep-09	3				16.06							32.01					1.56				
23-Sep-09	3				16.03							32.02					1.57				
25-Sep-09	5		20.05	0.11	16.09	13.33	12.91	6.27		50.15	0.17	32.00	8.48	8.03	29.94		1.56	1.03	1.01	0.56	
25-Sep-09	5				15.98	13.34	13.07	6.25				31.94	8.53	8.08	29.90		1.58	1.03	1.02	0.58	
25-Sep-09	5				16.08							31.99					1.60				
25-Sep-09	5				15.95							32.11					1.58				
27-Sep-09	7	-0.09	20.16		16.08	13.35	12.97	6.31	-0.39	50.34		31.51	8.58	8.02	29.70	-0.09	1.59	0.99	0.98	0.55	
27-Sep-09	7				16.09	13.41	12.97	6.28		50.28		31.67	8.58	8.08	29.76		1.60	1.00	0.99	0.57	
28-Sep-09	8	-0.09	19.81	0.09	16.07	13.25	12.92	6.16		49.96		32.00	8.55	8.03	29.83	-0.08	1.59	0.99	1.00	0.55	
28-Sep-09	8				16.08	13.19	12.85	6.20				32.10	8.44	8.02	29.74		1.59	0.99	0.99	0.58	
28-Sep-09	8				15.90							31.90					1.59				
29-Sep-09	9	-0.13	19.99	0.10	15.92	13.06	12.66	6.25	-0.35	50.25	0.16	31.93	8.51	8.01	29.94	-0.10	1.60	1.03	0.94	0.53	
29-Sep-09	9					13.42	12.72	6.21				31.62	8.01		30.14		1.00	0.94	0.55		
30-Sep-09	10		20.17		16.07	13.08	12.76	6.22		49.99		32.03			29.79		1.61	1.06	0.99	0.57	
30-Sep-09	10					13.15	12.80	6.26						29.62			1.04	0.98	0.57		
01-Oct-09	11	-0.11	20.08		16.02	13.35	12.83	6.19	-0.38	49.95		31.91	8.38	8.00	29.69	-0.07	1.62	1.03	0.99	0.55	
01-Oct-09	11				16.06	13.38	12.86	6.49				31.99	8.45	7.90	29.73		1.60	1.03	0.99	0.57	
02-Oct-09	12	-0.10	20.14		15.92		12.82	6.32	-0.38	50.21		31.73		7.95	29.98	-0.10	1.59		0.98	0.58	
02-Oct-09	12				15.94		12.81	6.25				31.90		7.88	29.92		1.60		0.99	0.60	
02-Oct-09	12				15.88							31.90					1.61				
4-Oct-09	14		20.04	-0.12	16.01	13.13	12.78	6.20	-0.37	50.58	0.10	32.03		8.03	30.08	-0.12	1.61	1.02	0.98	0.56	
4-Oct-09	14				15.90	13.34	12.65	6.12				32.04	8.50	7.97	29.72		1.60		0.98	0.56	
4-Oct-09	14				16.02							32.02					1.59				
05-Oct-09	15	-0.11	20.00				6.18	-0.27	50.03			31.94			29.53	-0.09	1.62			0.56	
05-Oct-09	15				16.05			6.24				31.96			29.58		1.59			0.56	
07-Oct-09	17	-0.09	20.28	0.10	16.13	13.35	12.71	6.18	-0.36	50.12	0.05	32.00	8.83	8.19	29.51	-0.08	1.61	0.99	0.96	0.56	
07-Oct-09	17				16.06	13.35	12.71	6.38				32.19	8.95	8.20	29.85		1.61	1.01	0.97	0.58	
07-Oct-09	17				16.02							31.85					1.61				
09-Oct-09	19		20.01		16.05	13.21	12.73	6.23	-0.37	50.03		31.79	8.43	8.07	30.26	-0.09	1.60	1.00	0.96	0.56	
09-Oct-09	19					13.26	12.73					32.03	8.59	8.07			1.61	1.00	0.96		
11-Oct-09	21					13.45			-0.30	50.45	0.20	31.77	8.57	8.28	30.12	-0.09	1.60	0.99	0.96	0.55	
11-Oct-09	21					13.36						31.82	8.75	8.12	29.54		1.58	0.98	0.96	0.55	
12-Oct-09	22		20.32		16.09			6.34	-0.48	50.36		31.99	8.66		30.14	-0.12	1.59		0.98	0.53	
12-Oct-09	22				15.97			6.41				8.83			30.32				0.96	0.54	
		Expected Value	20.00	0.00	16.00	13.50	13.00	6.35		50.00	0.00	32.00	8.70	8.10	30.30		1.60	1.02	0.99	0.56	
		Average Measurement	-0.10	20.08	0.06	16.02	13.30	12.85	6.25	-0.35	50.16	0.12	31.94	8.60	8.05	29.89	-0.10	1.59	1.01	0.98	0.56
		<i>n</i>	10	15	6	31	24	24	29	13	17	6	34	23	24	31	14	34	23	28	31
		StDev	0.02	0.13	0.09	0.07	0.12	0.13	0.08	0.06	0.19	0.06	0.13	0.14	0.09	0.25	0.01	0.02	0.02	0.02	
		Diff (Avg - Expected)		0.08	0.06	0.02	-0.20	-0.15	-0.10		0.16	0.12	-0.06	-0.10	-0.05	-0.41		-0.01	-0.01	-0.01	0.00
		Max	-0.08	20.32	0.11	16.13	13.49	13.07	6.49	-0.27	50.58	0.20	32.19	8.95	8.28	30.41	-0.07	1.62	1.06	1.02	0.61
		Min	-0.13	19.81	-0.12	15.88	13.06	12.65	6.12	-0.48	49.90	0.05	31.51	8.38	7.88	29.51	-0.12	1.56	0.98	0.94	0.53
		Slope	0.000	0.009	-0.005	-0.001	-0.002	-0.020	0.002	-0.003	0.013	0.002	-0.001	0.005	0.005	0.000	0.002	-0.002	-0.002	-0.001	
		R2	0.002	0.211	0.089	0.011	0.010	0.667	0.030	0.155	0.177	0.067	0.001	0.063	0.110	0.000	0.037	0.308	0.243	0.418	0.136

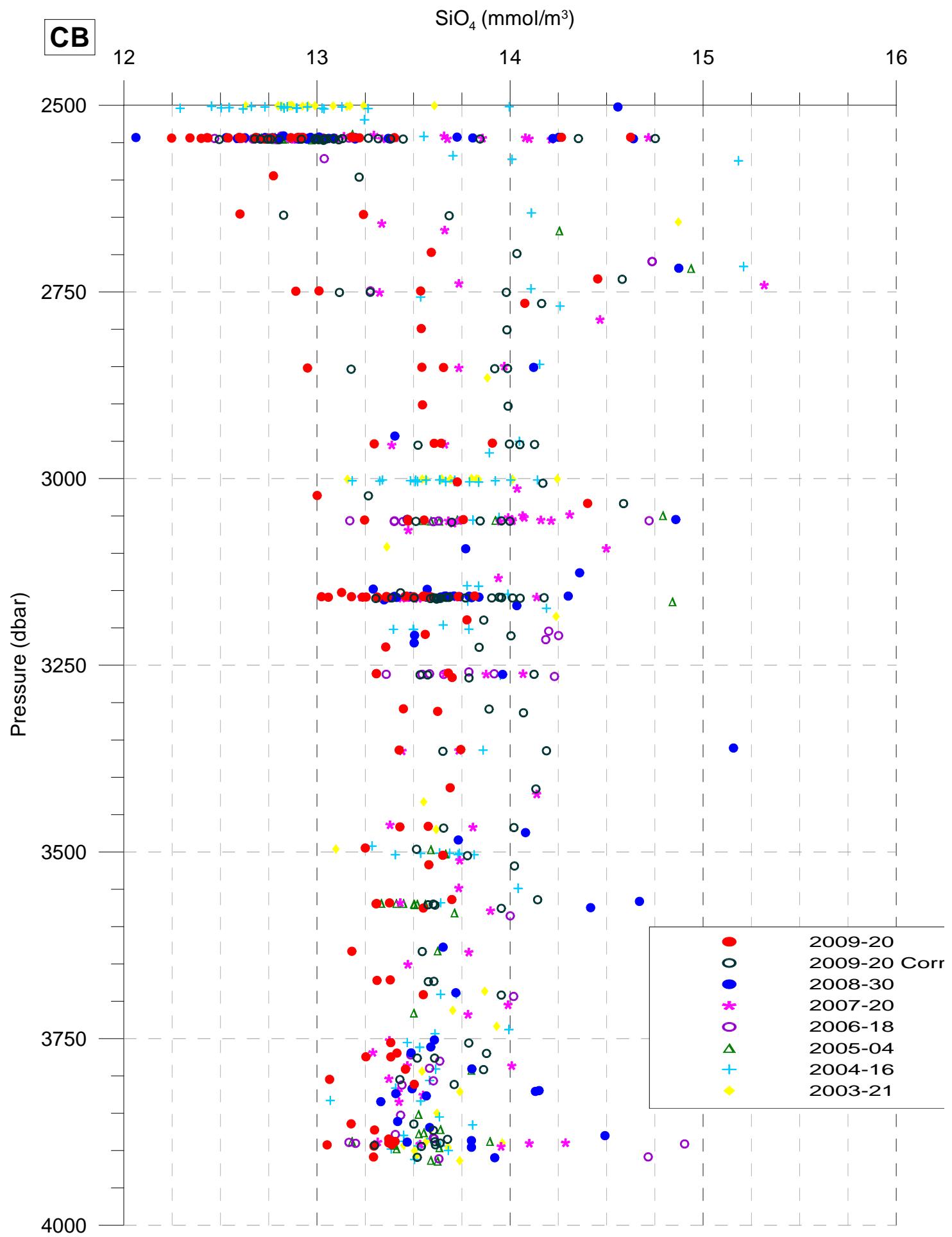
Appendix Figure A7



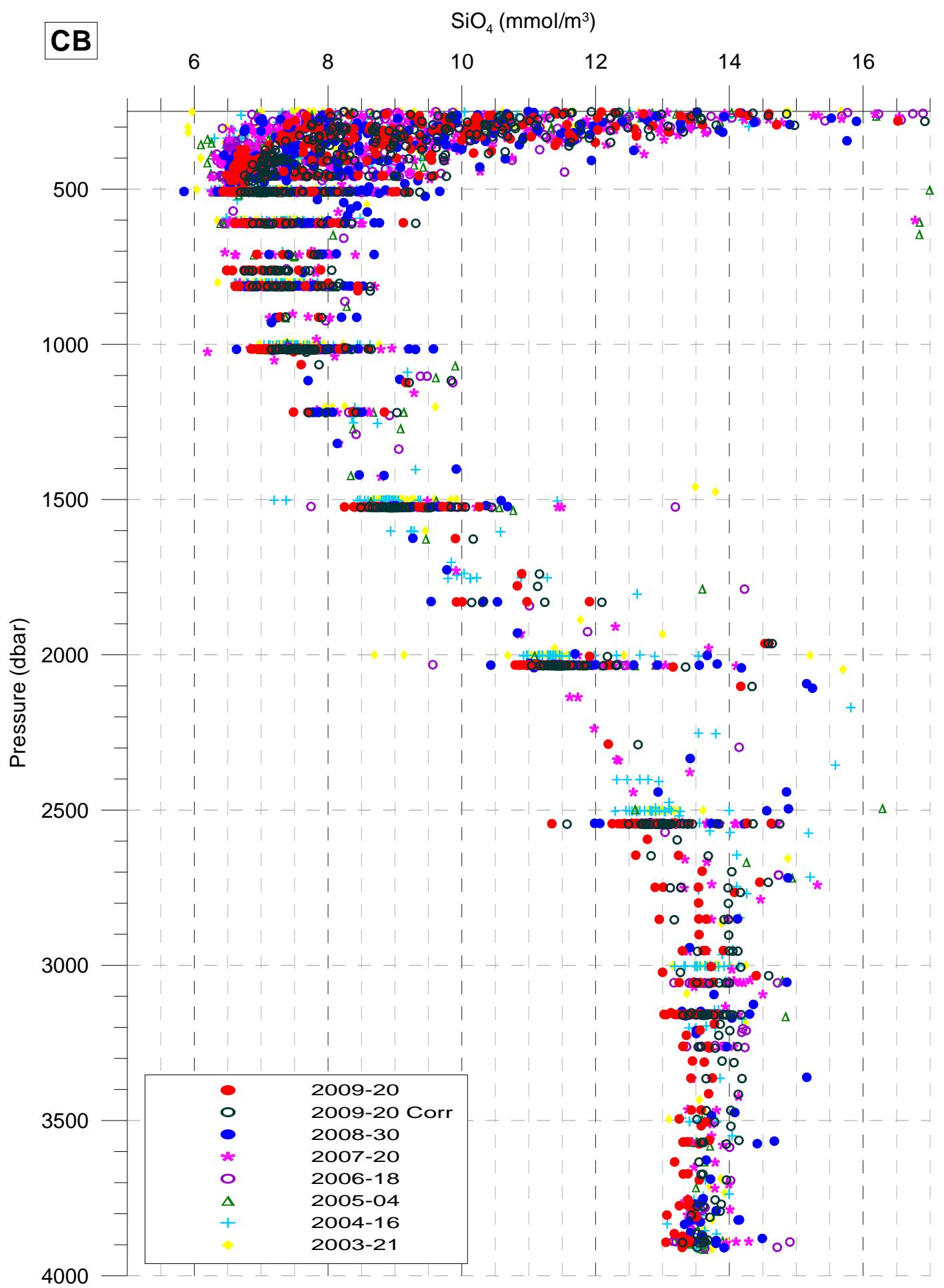
Appendix Figure A8



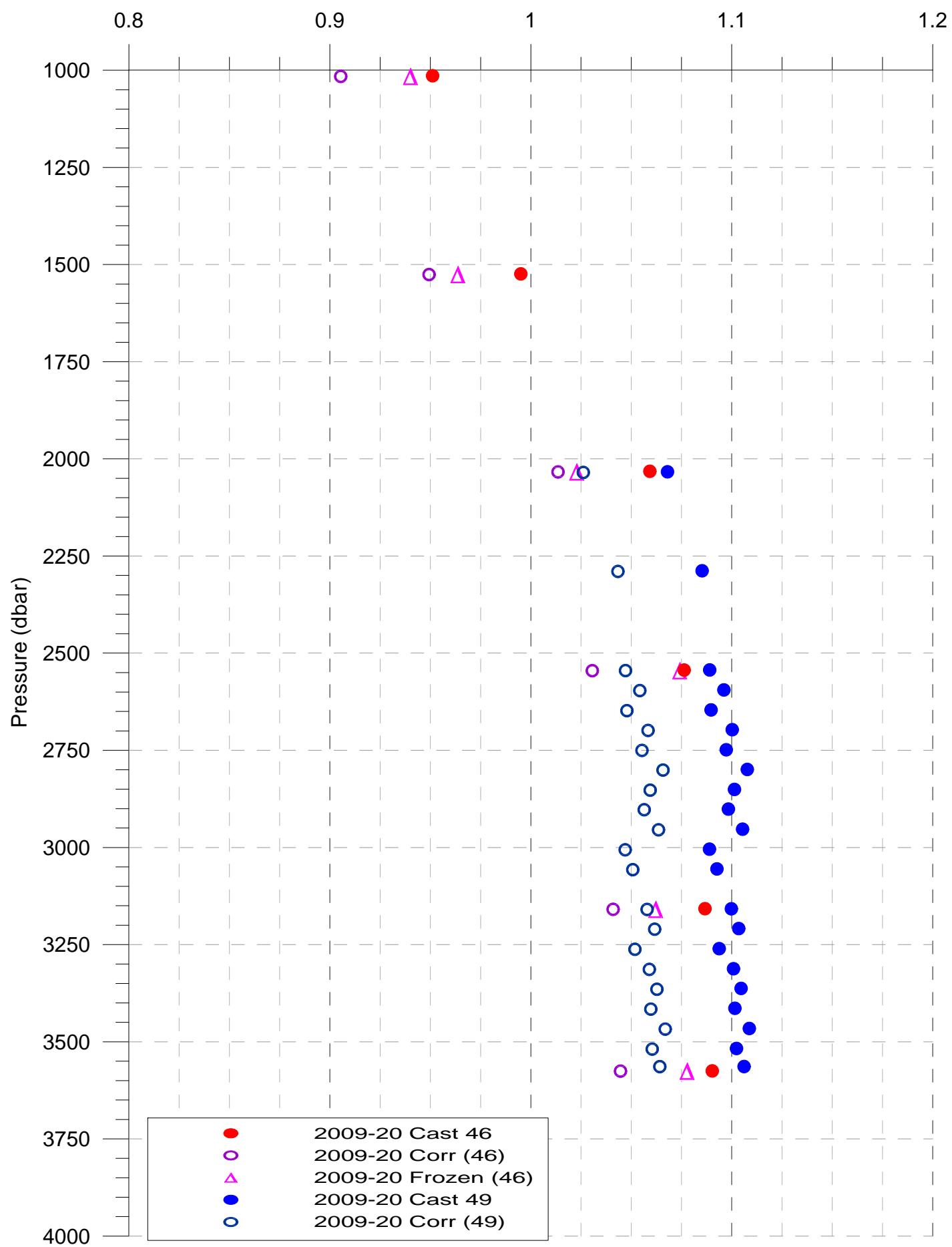
Appendix Figure A9

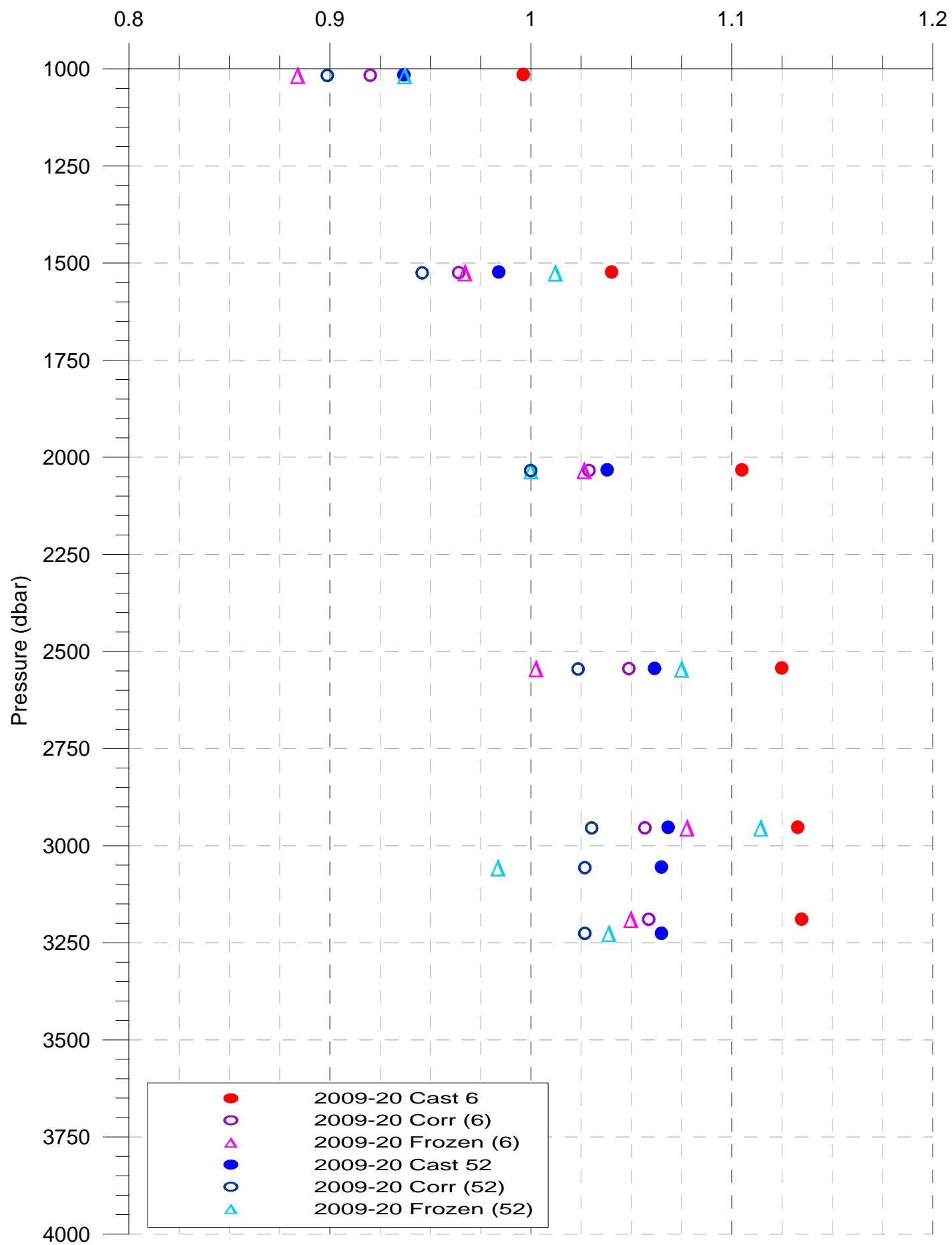


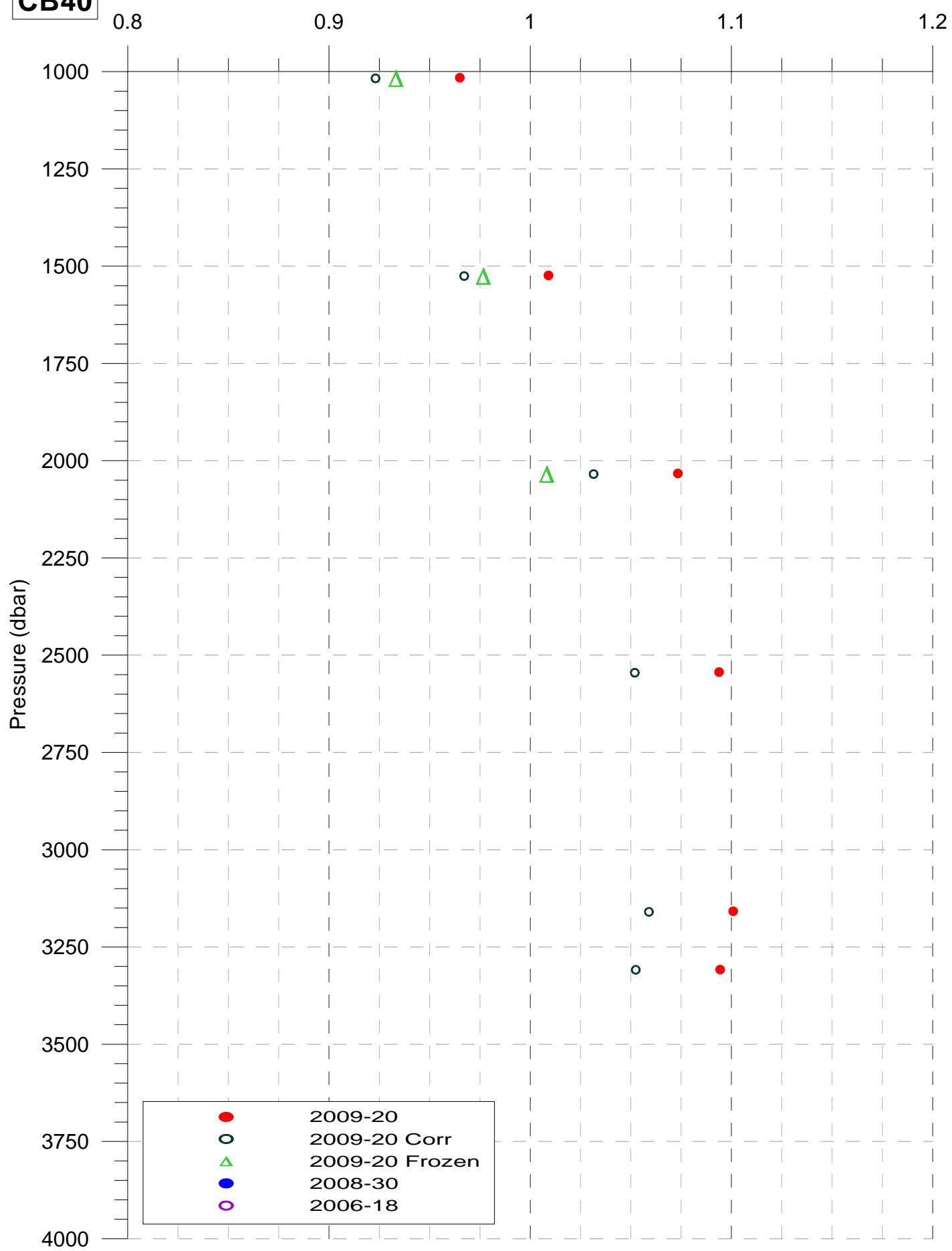
Appendix Figure A10

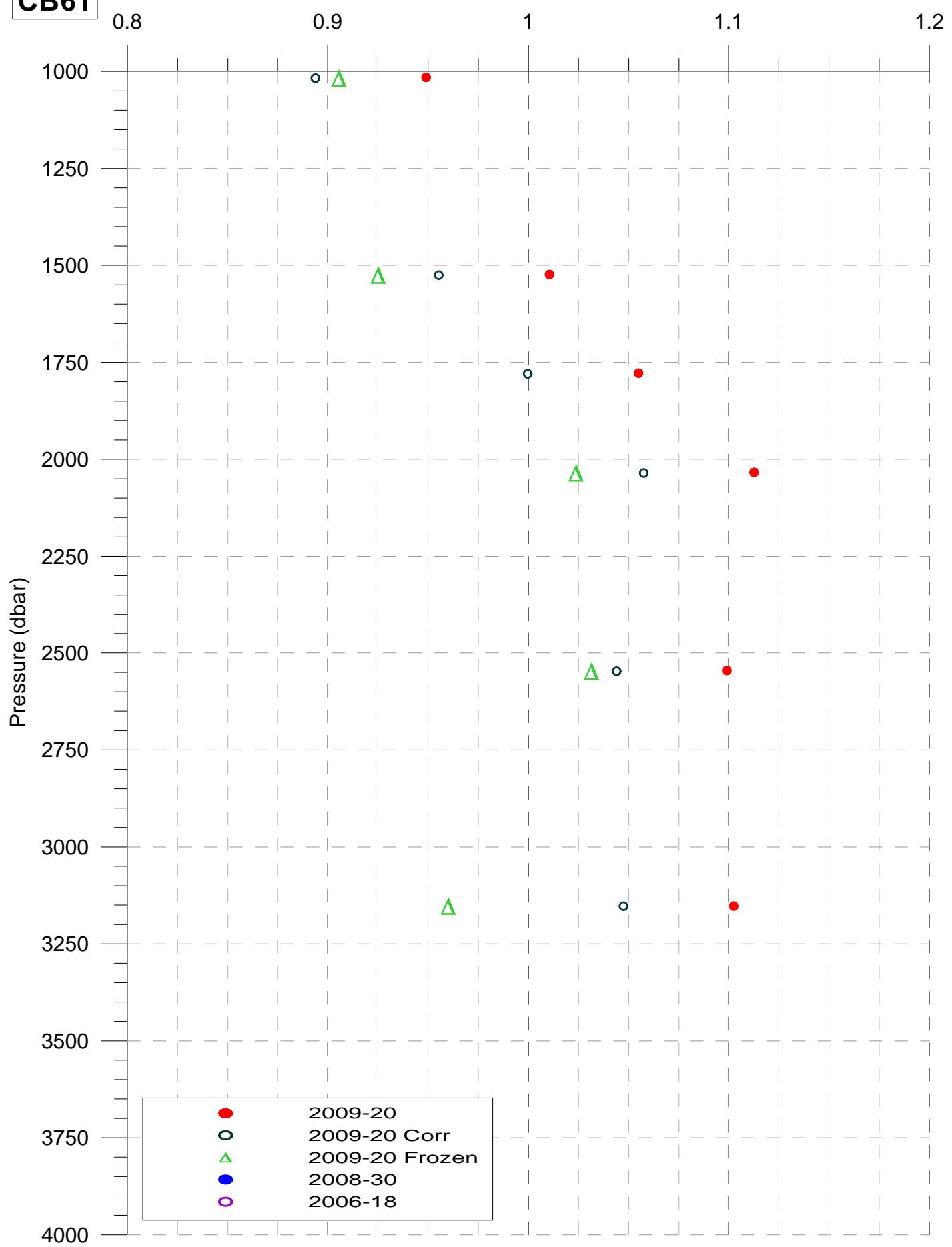


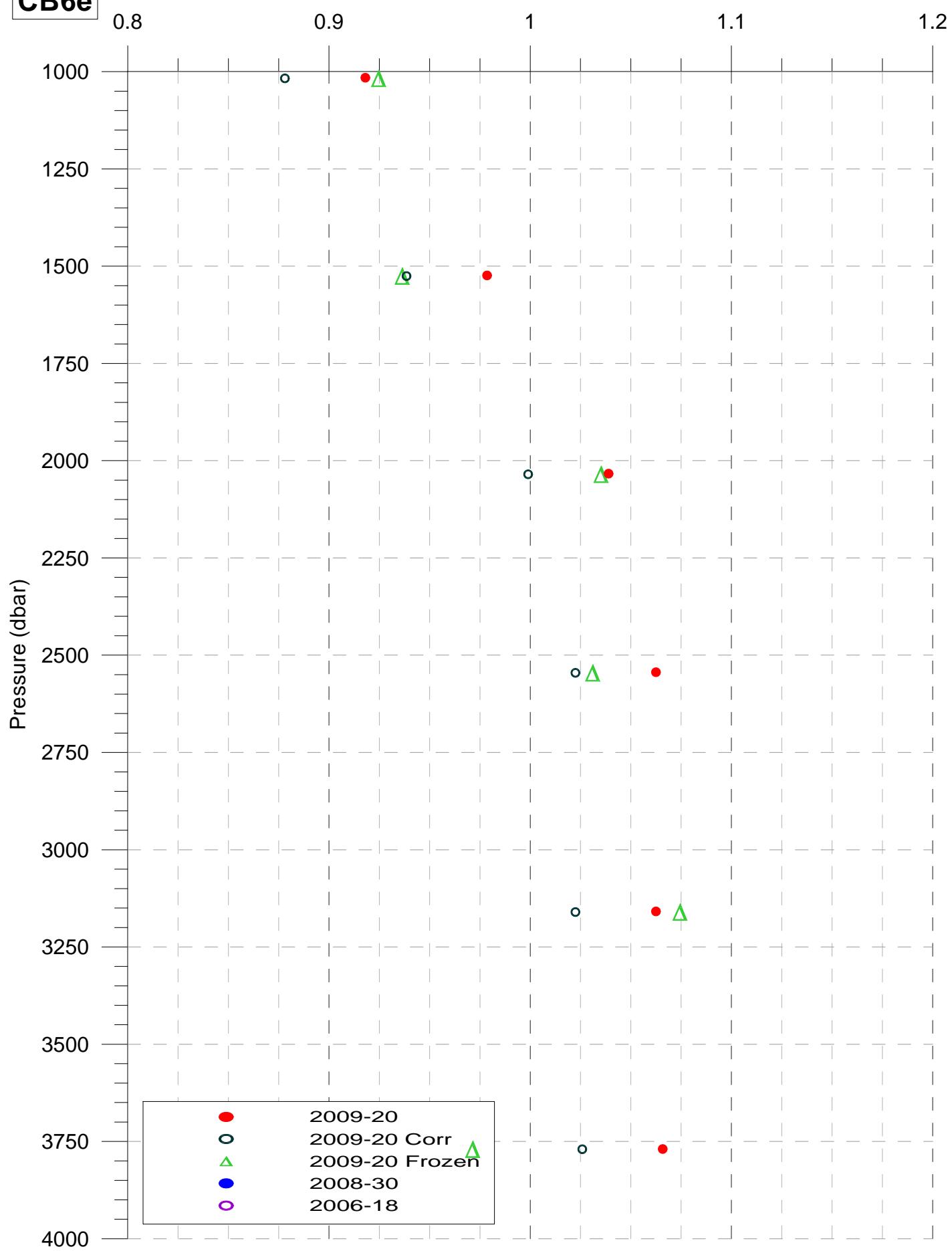
Appendix Figure A11

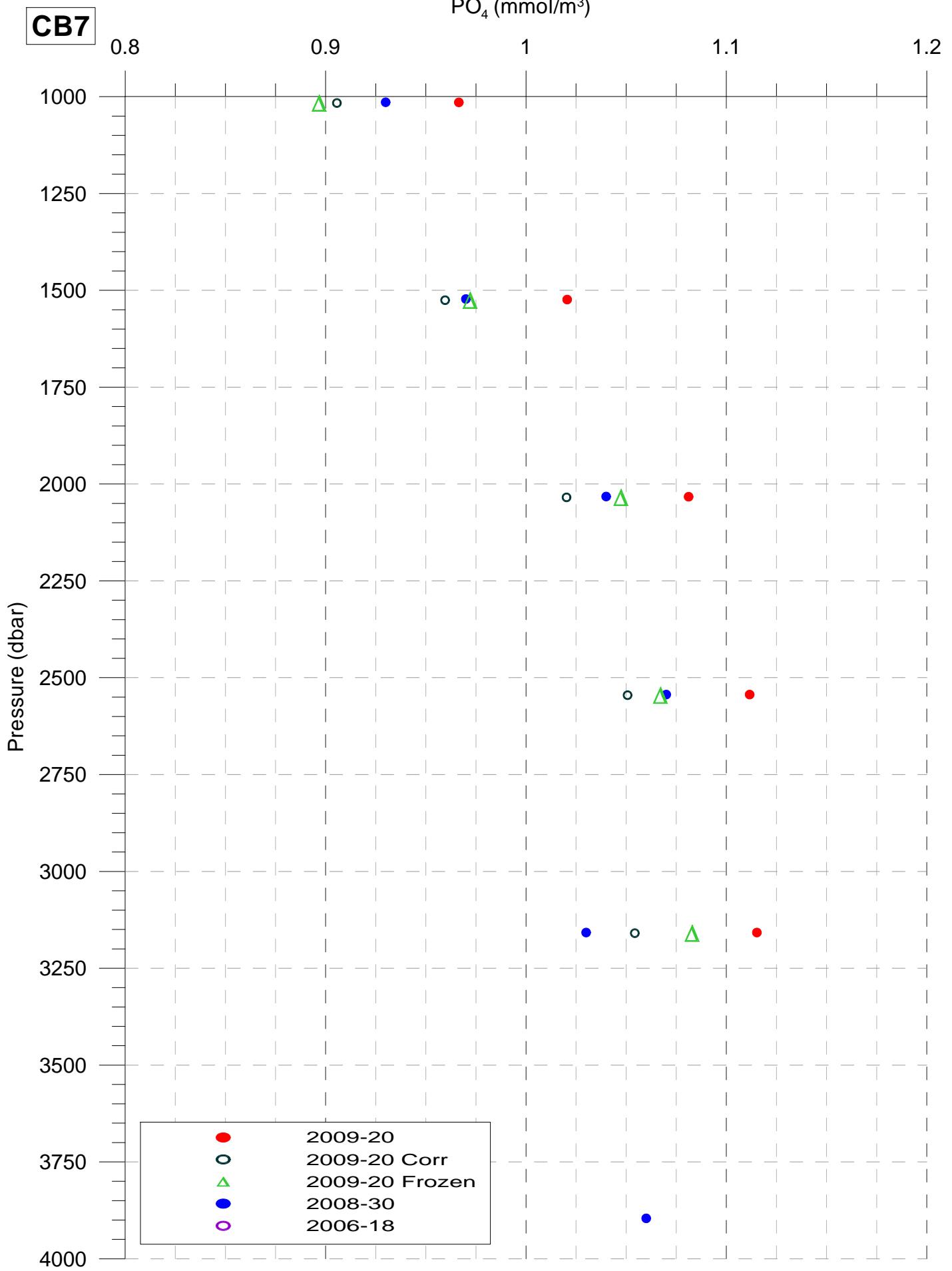
CB21 Cast 46 & 49 $\text{PO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A12**

CB22 Cast 6 & 52PO₄ (mmol/m³)**Appendix Figure A13**

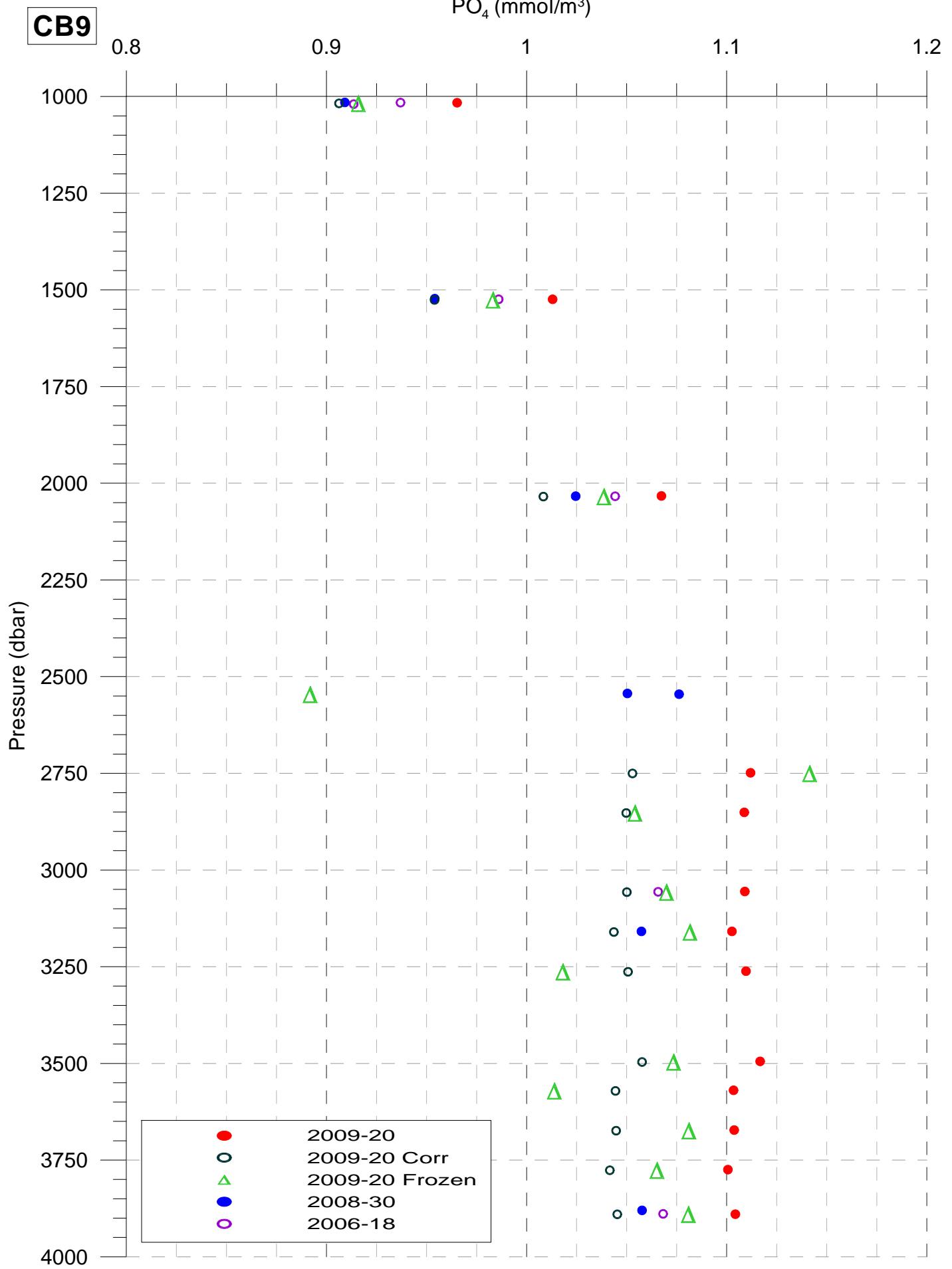
CB40 $\text{PO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A14**

CB61 $\text{PO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A15**

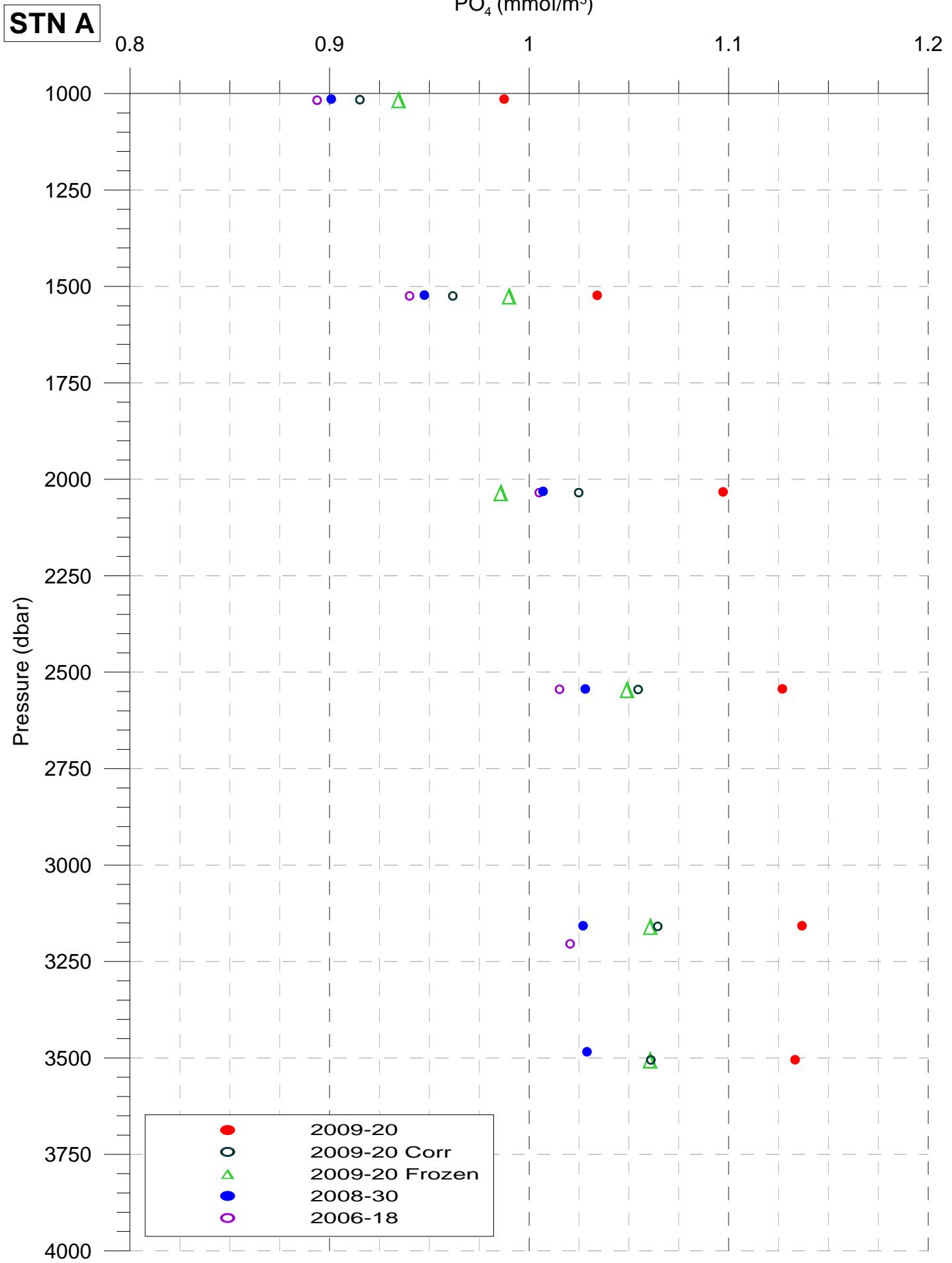
CB6e $\text{PO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A16**



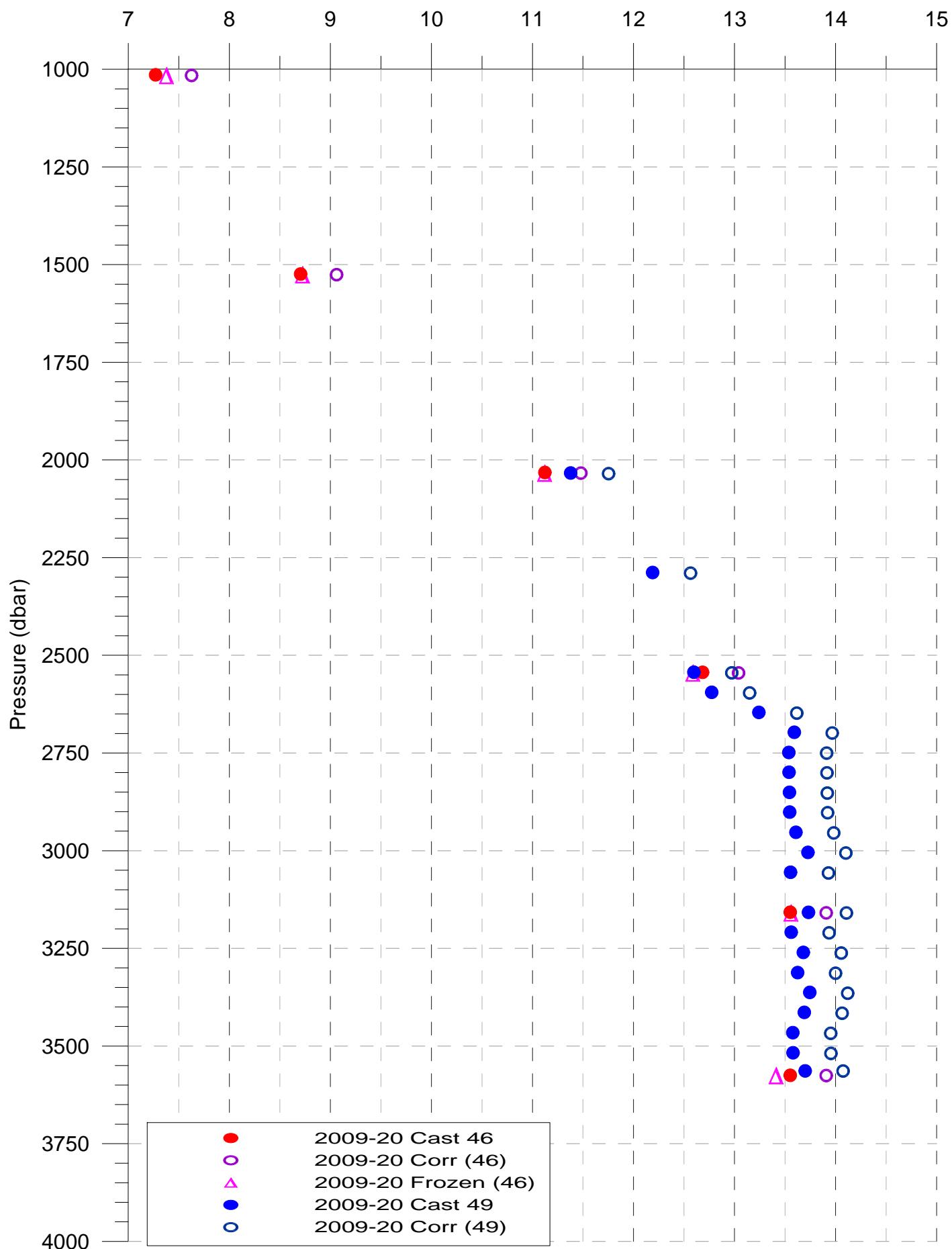
Appendix Figure A17



Appendix Figure A18

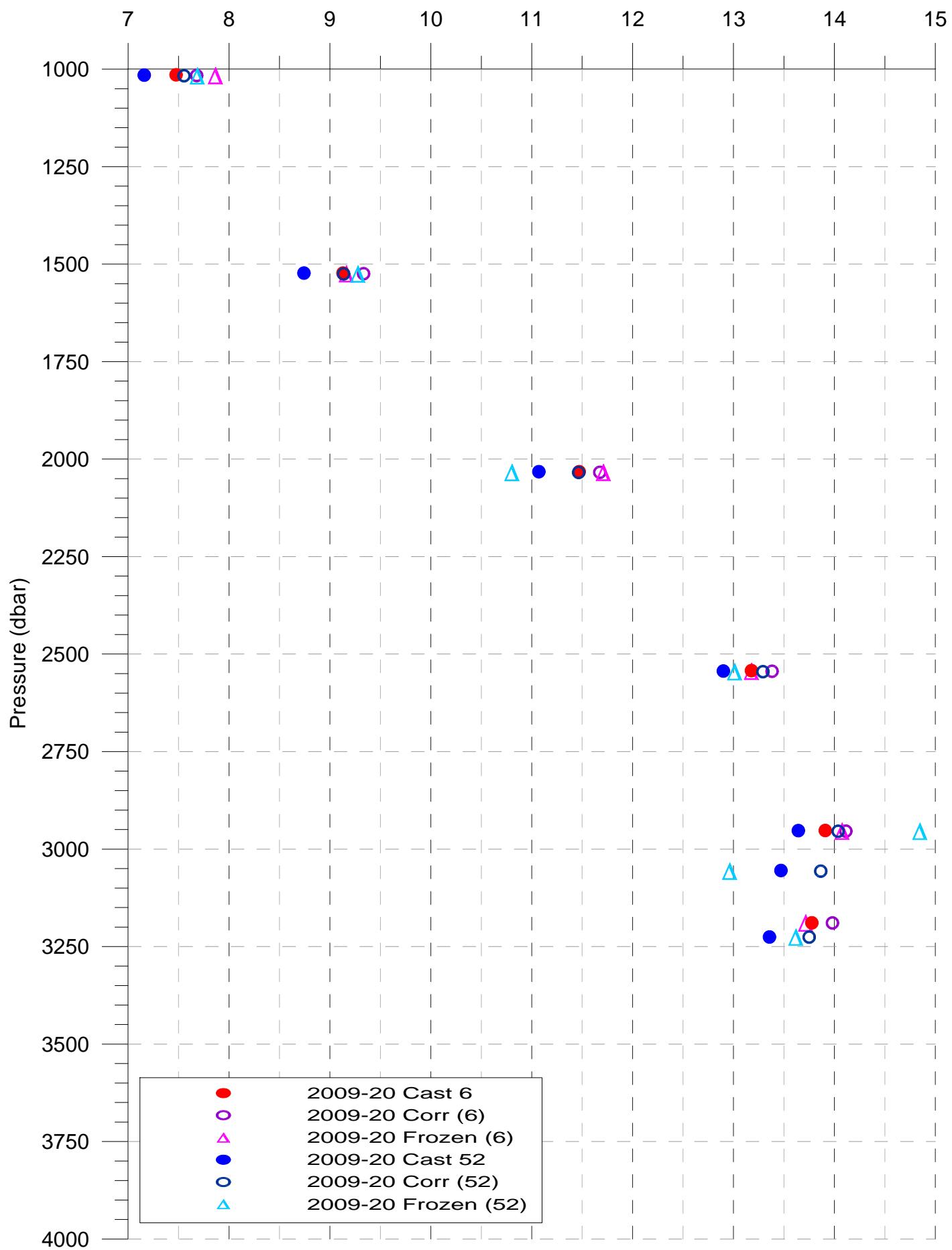


Appendix Figure A19

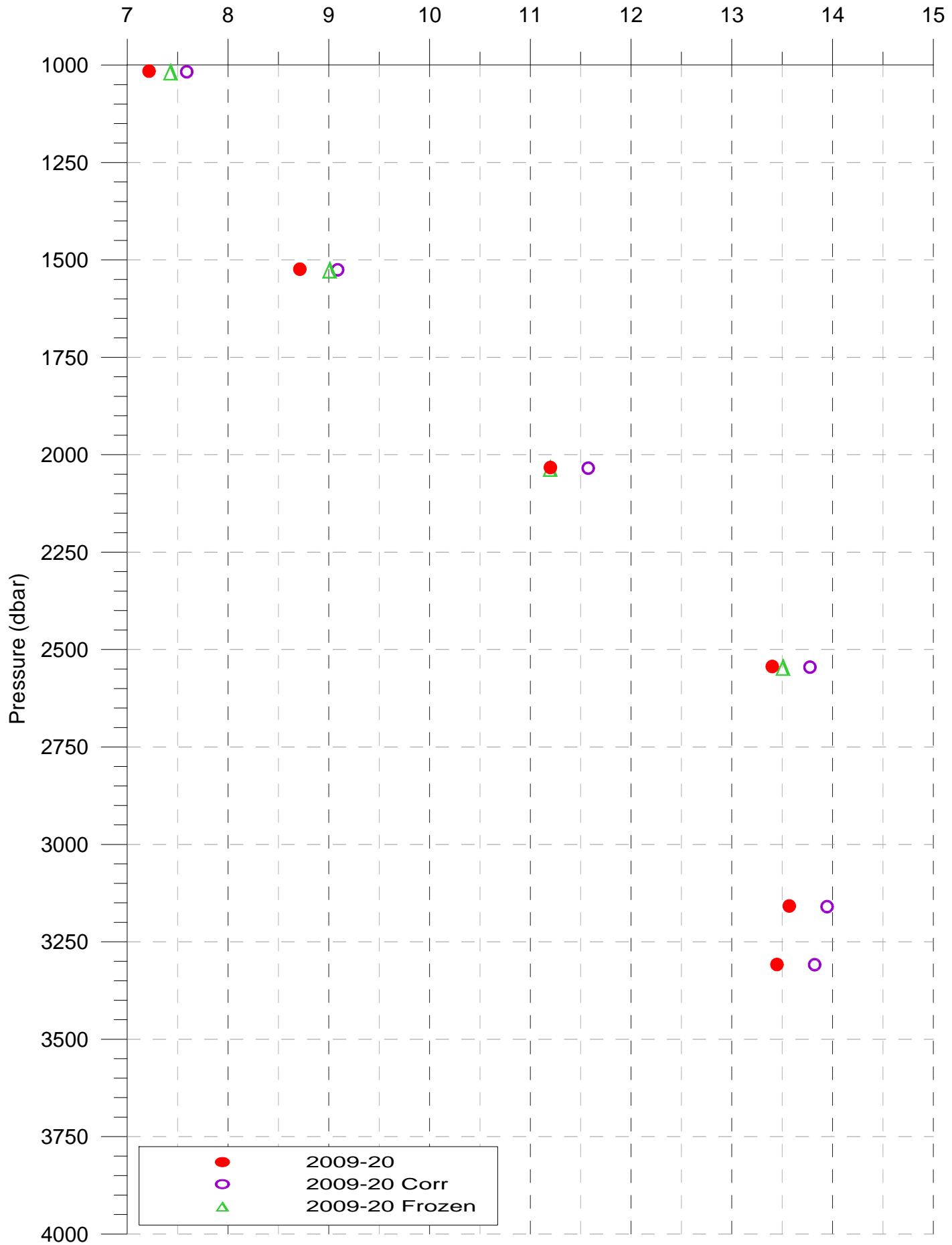
CB21 Cast 46 & 49 $\text{SiO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A20**

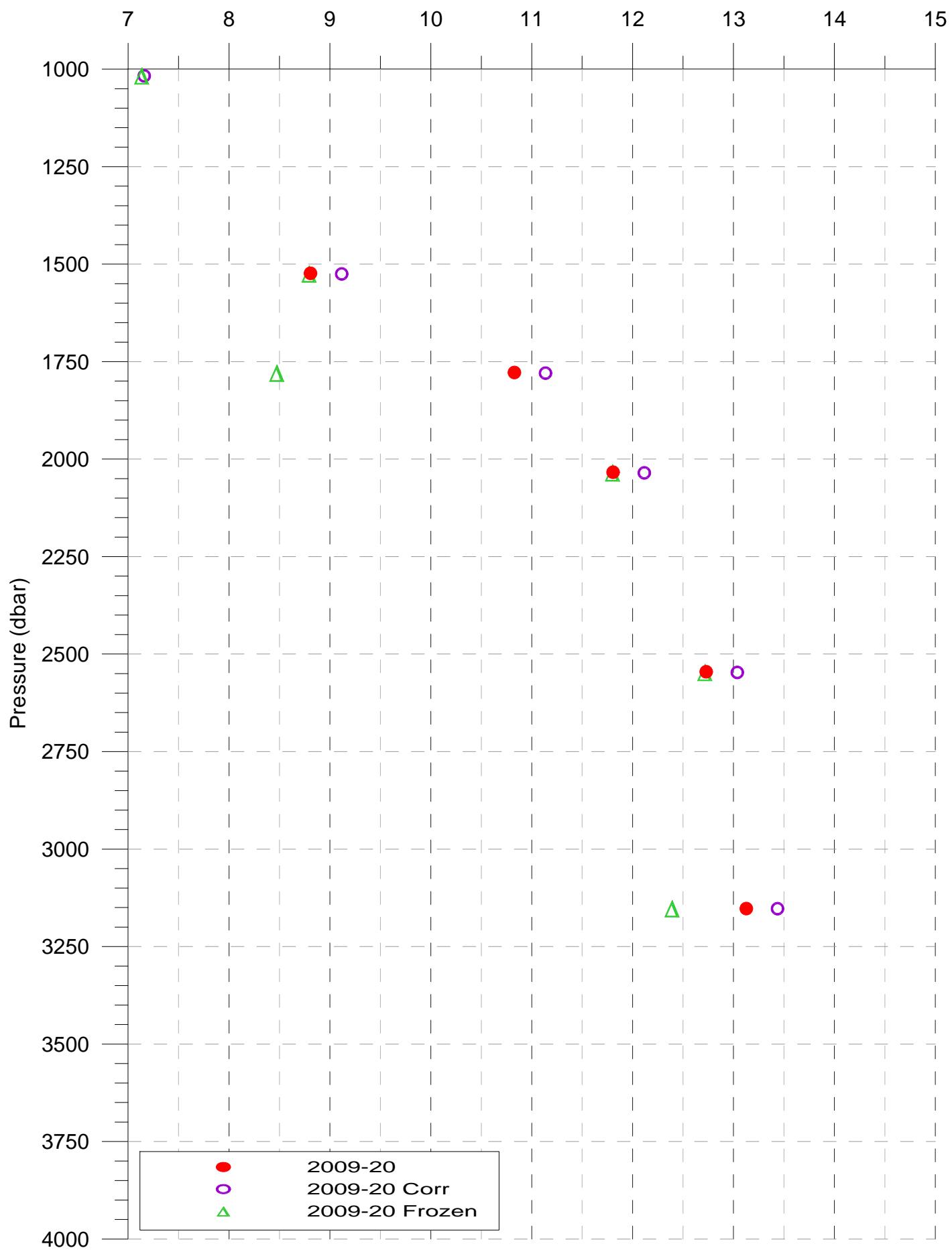
CB22 Cast 6 & 52

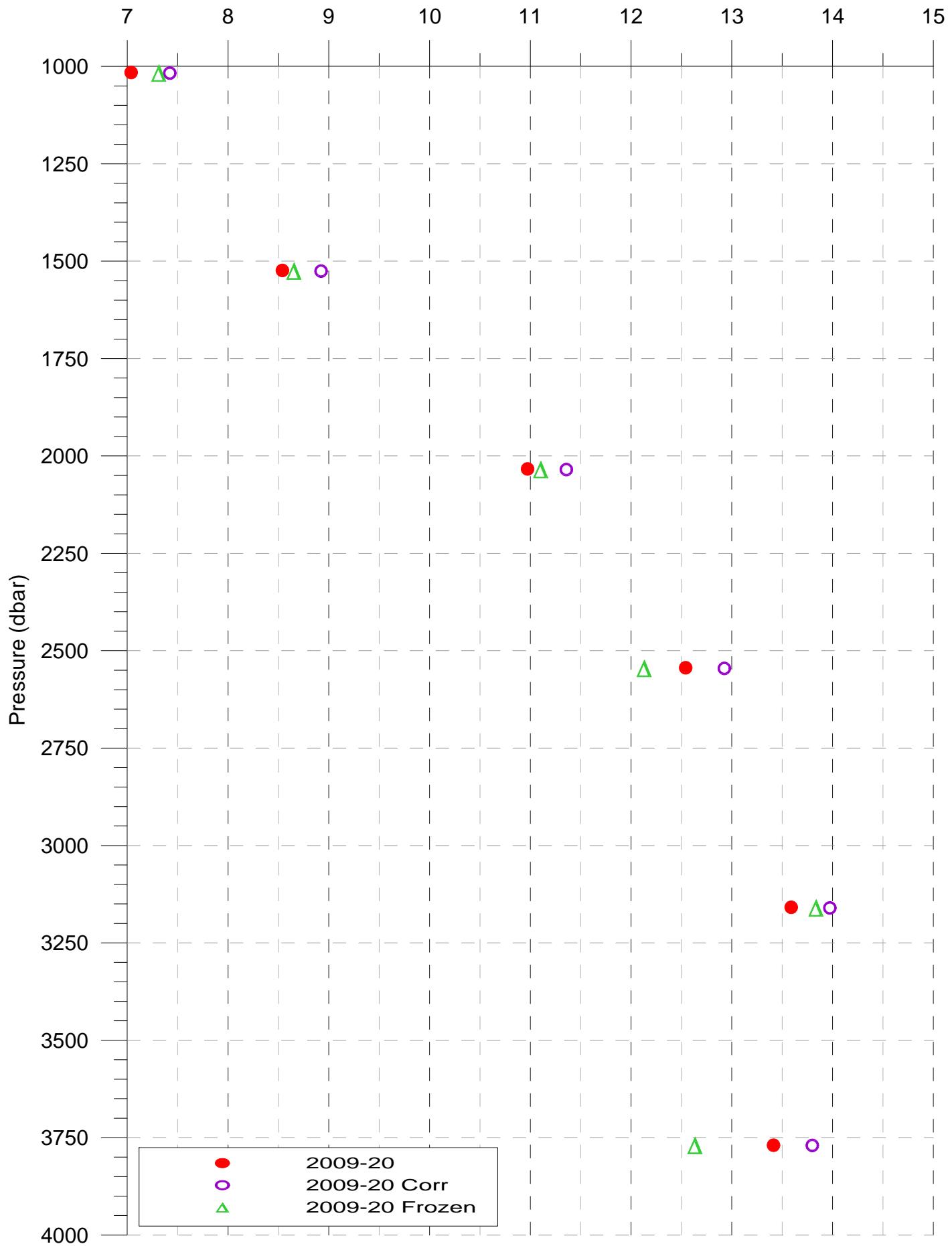
SiO_4 (mmol/m³)

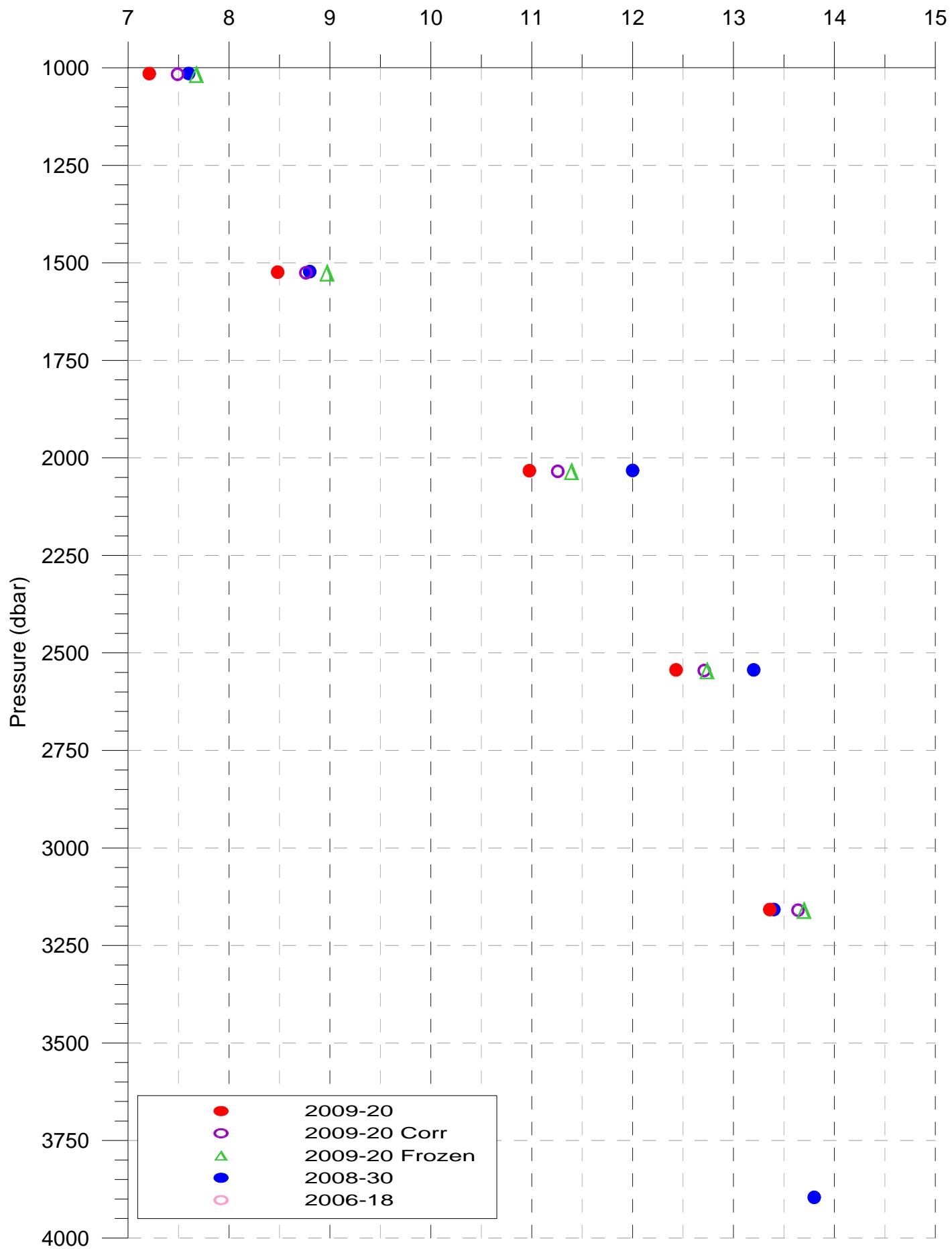


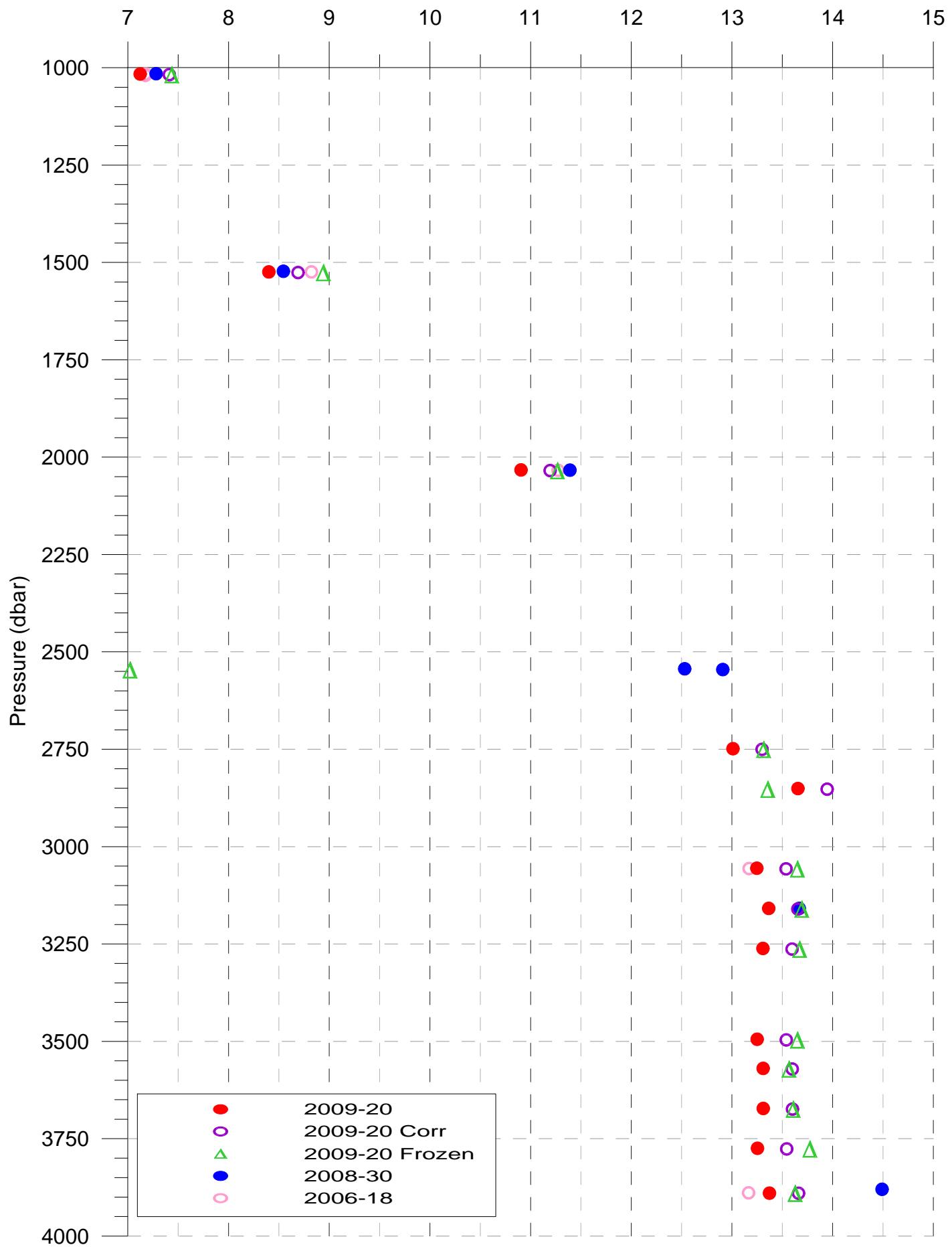
Appendix Figure A21

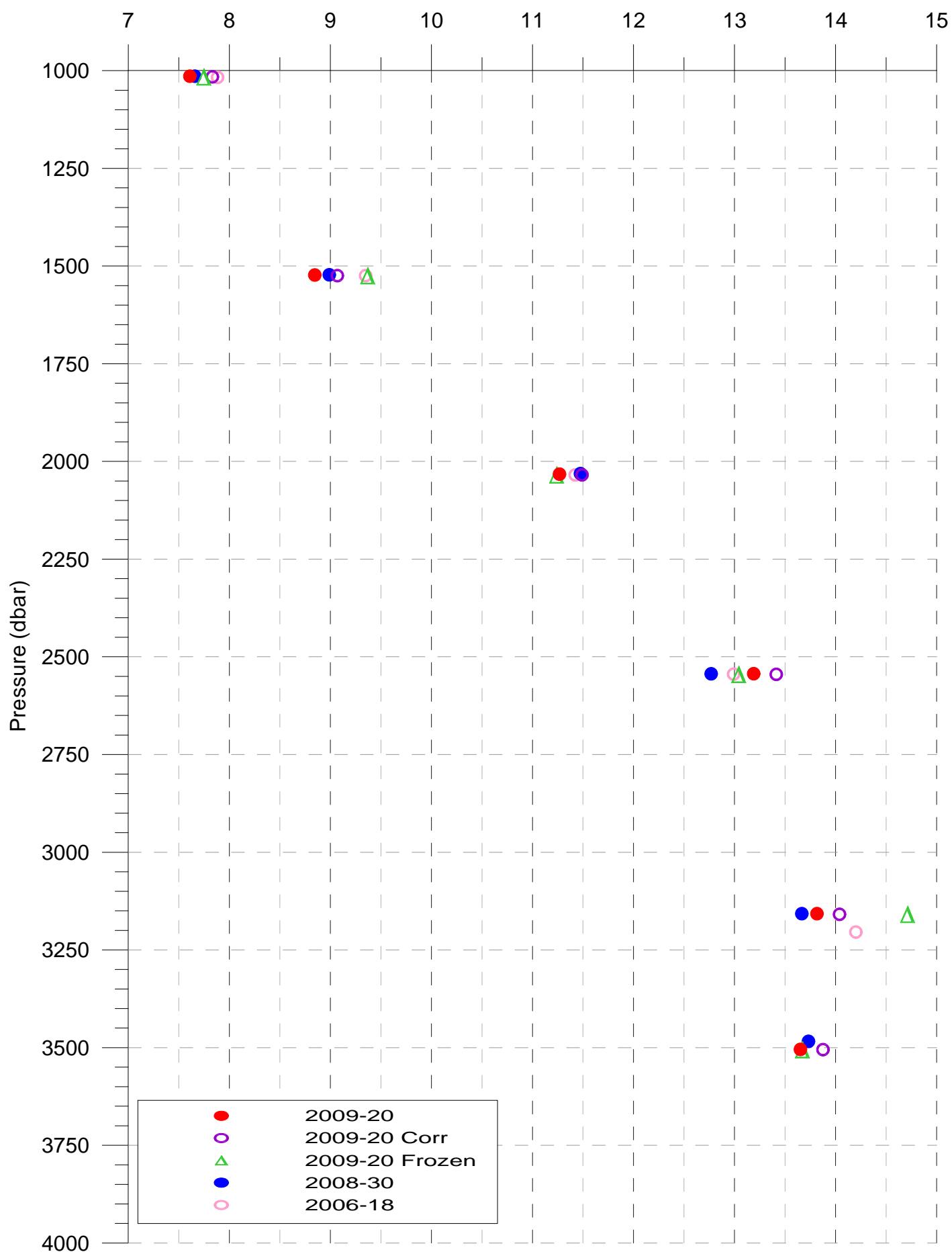
CB40 $\text{SiO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A22**

CB61 $\text{SiO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A23**

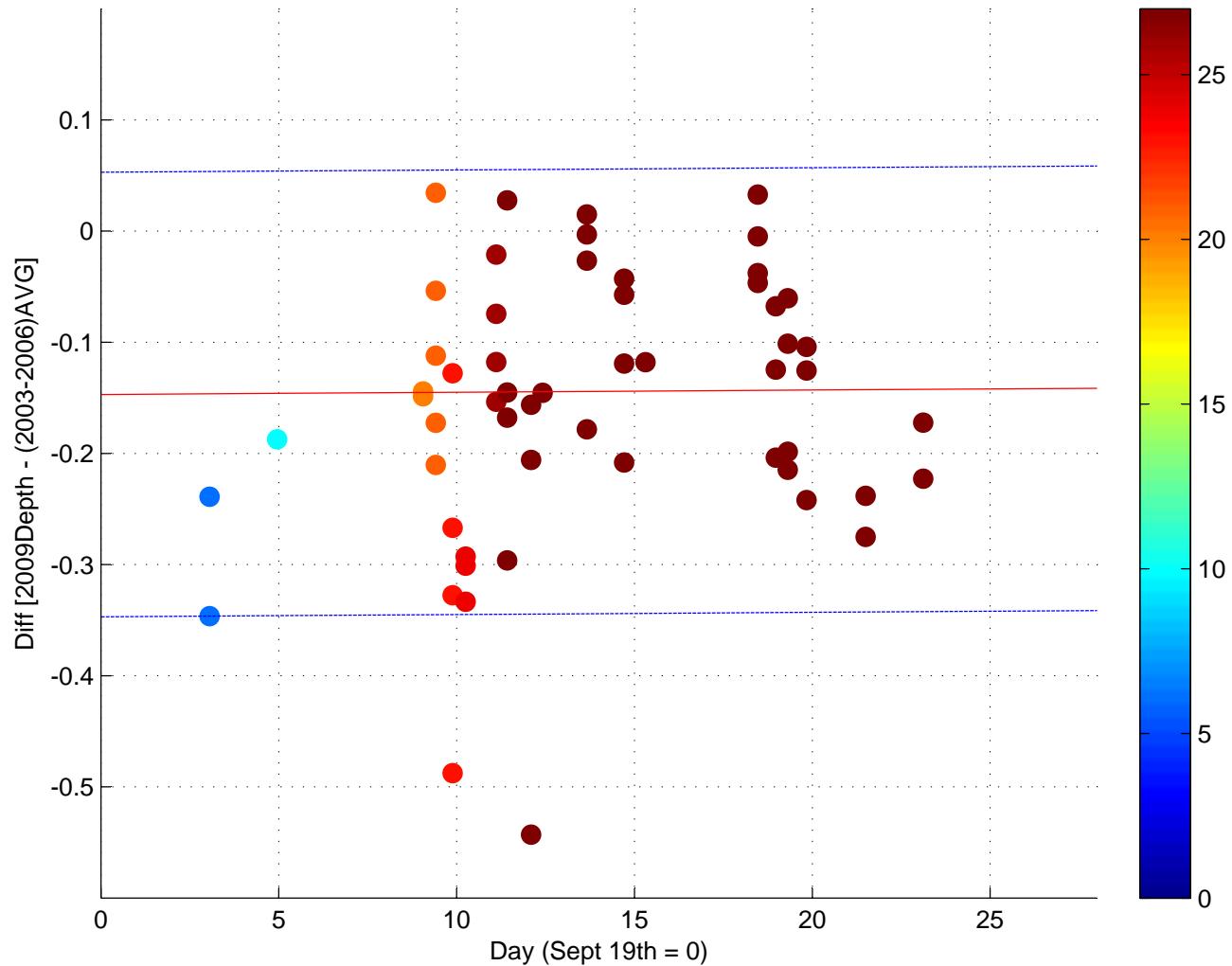
CB6e $\text{SiO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A24**

CB7 $\text{SiO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A25**

CB9 $\text{SiO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A26**

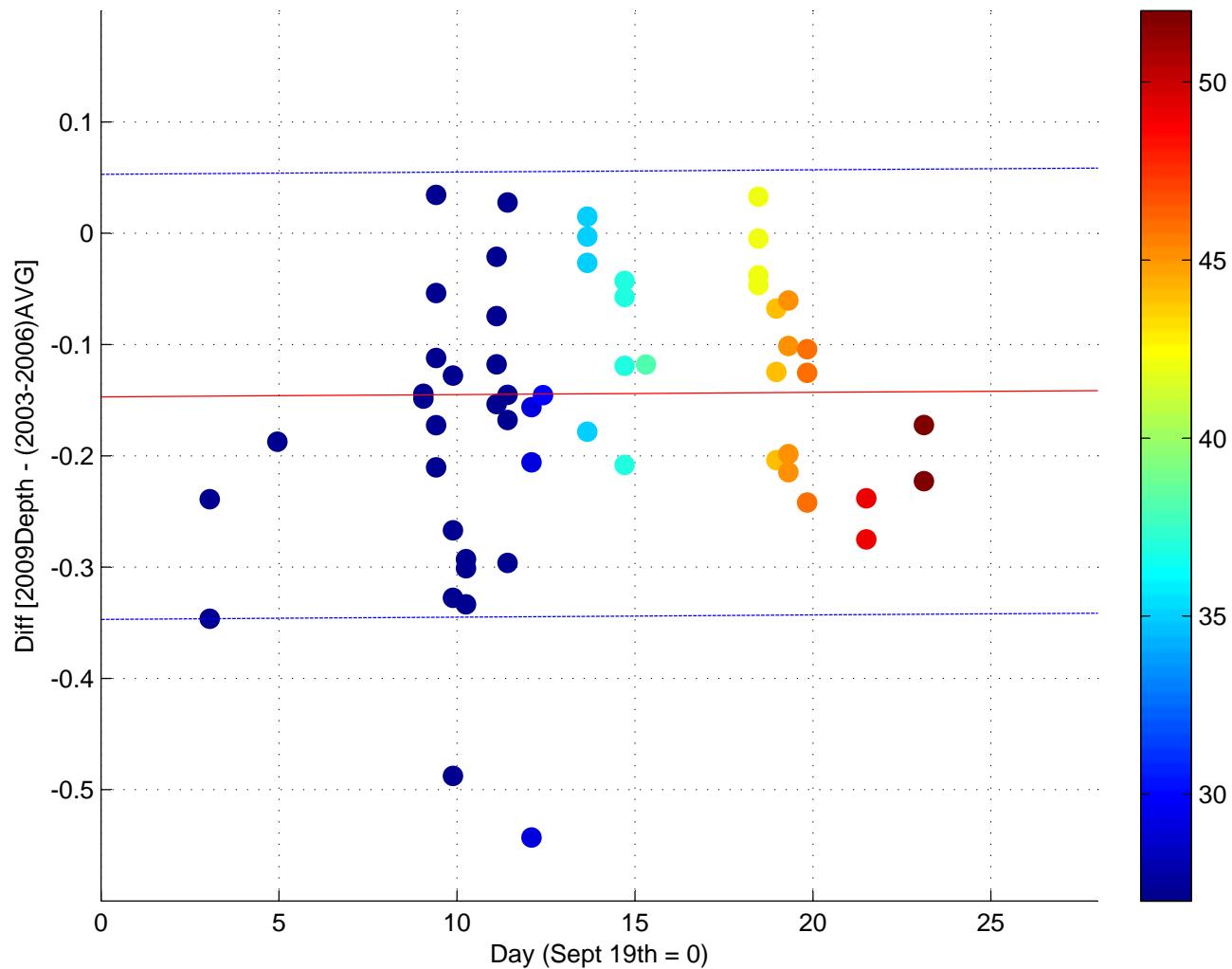
STN A $\text{SiO}_4 \text{ (mmol/m}^3\text{)}$ **Appendix Figure A27**

2009-20 NO₃ Diff vs Date Run, colour coded by Cast Number (0-27)



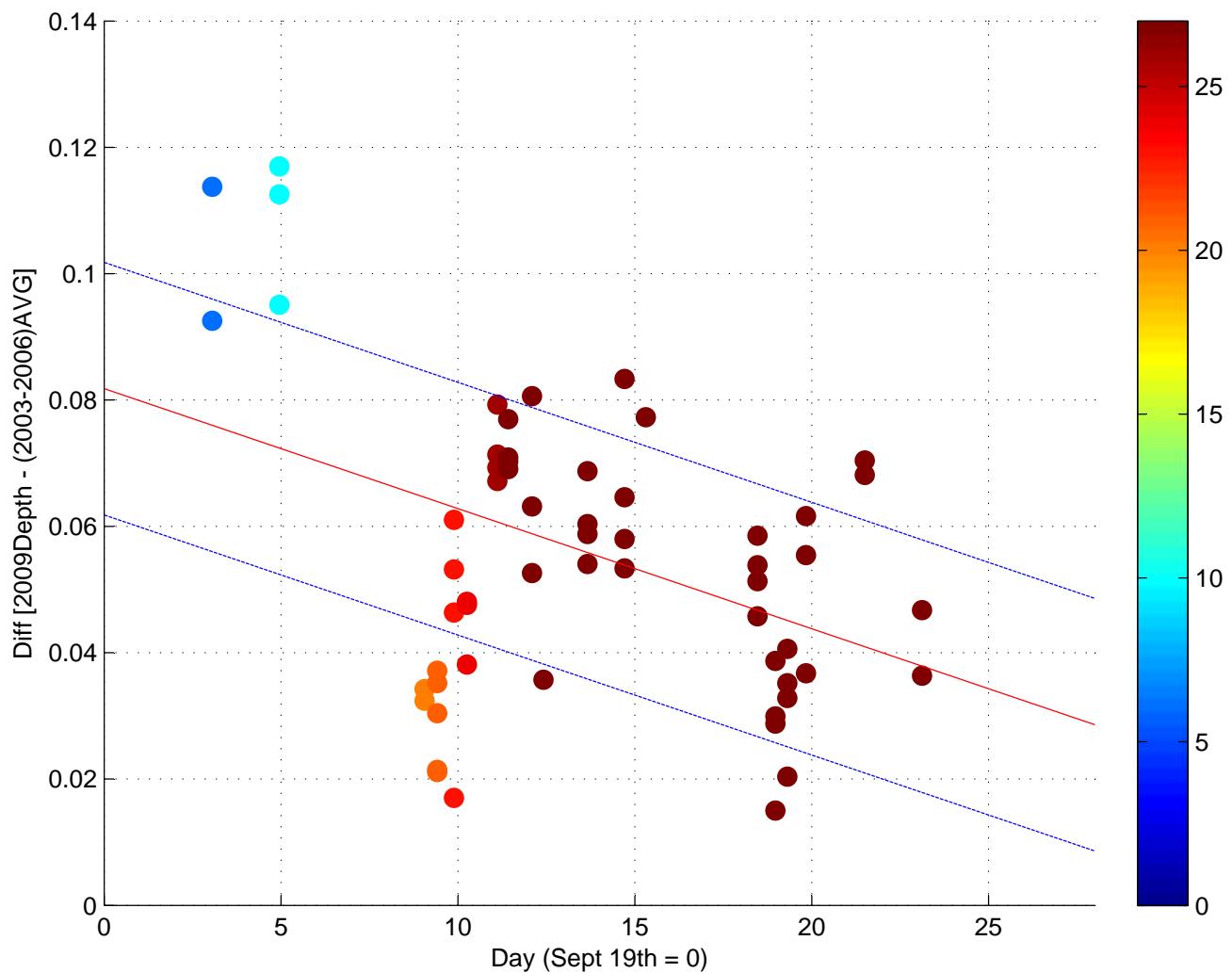
Appendix Figure A28

2009-20 NO₃ Diff vs Date Run, colour coded by Cast Number (27-52)



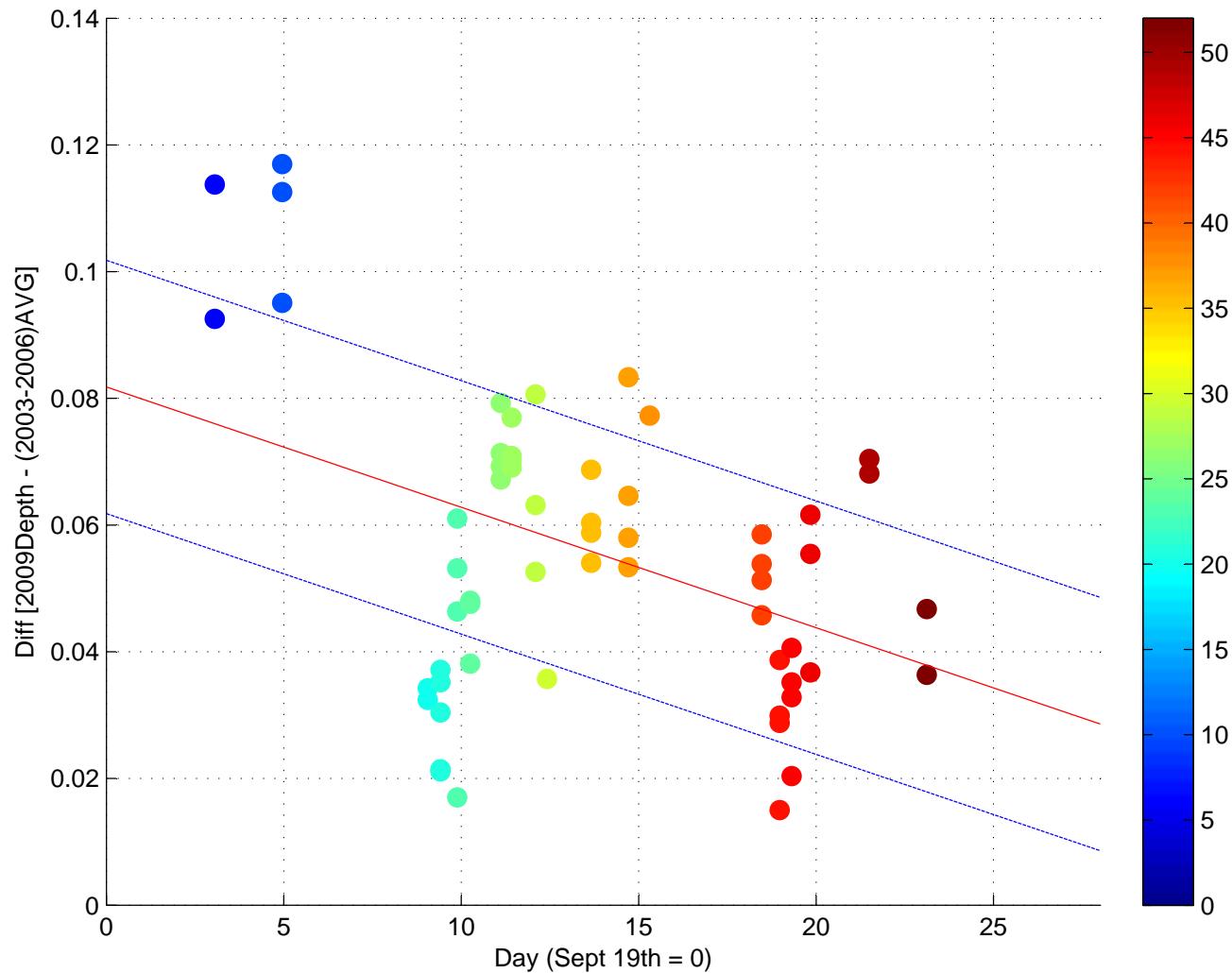
Appendix Figure A29

2009-20 PO4 Diff vs Date Run, colour coded by Cast Number (0-27)



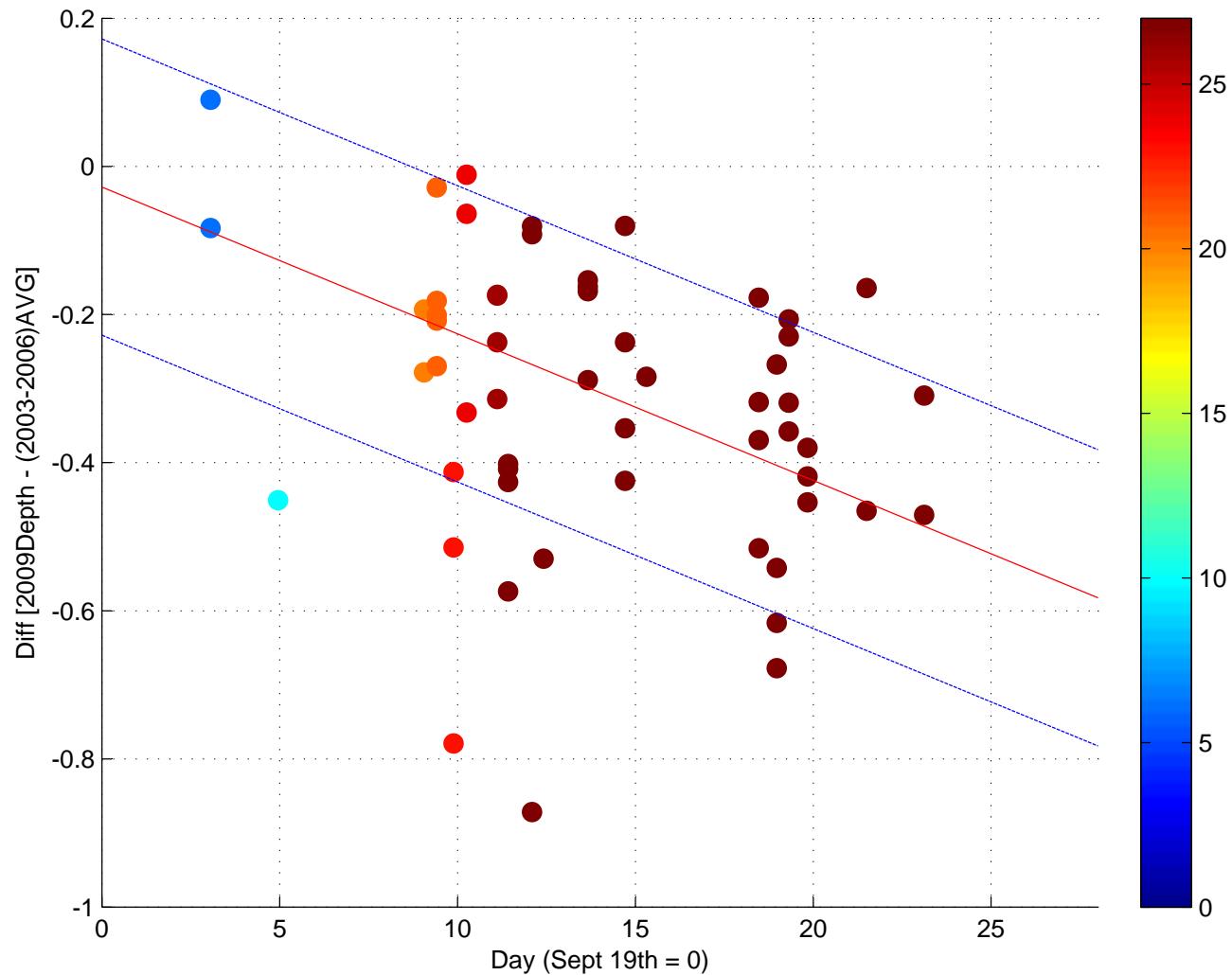
Appendix Figure A30

2009-20 PO4 Diff vs Date Run, colour coded by Cast Number (27-52)



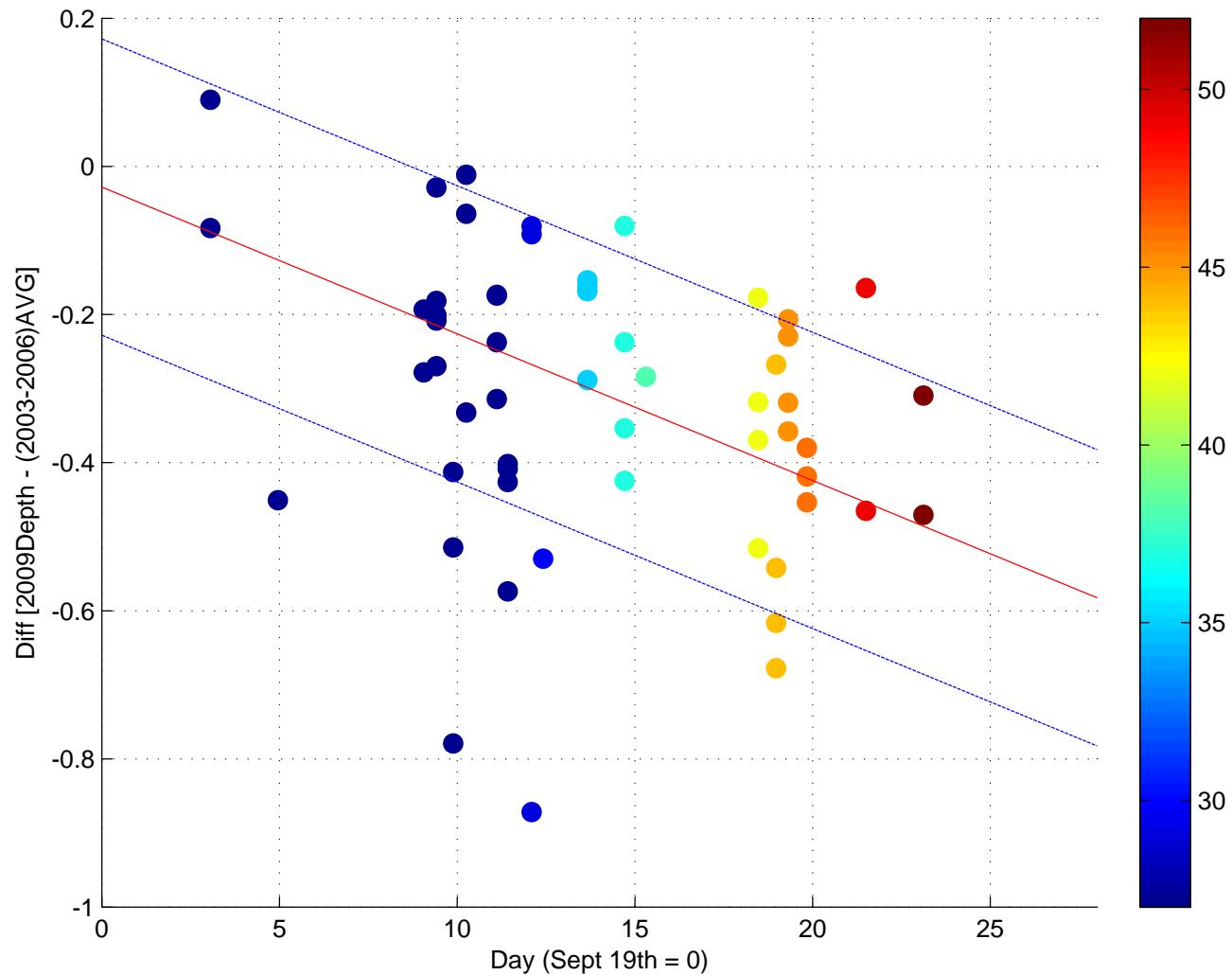
Appendix Figure A31

2009-20 SiO₄ Diff vs Date Run, colour coded by Cast Number (0-27)



Appendix Figure A32

2009-20 SiO₄ Diff vs Date Run, colour coded by Cast Number (27-52)



Appendix Figure A33