

Supplementary Material

I. Controlling the mass bias introduced by sulfate in Si measurements by MC-ICP-MS

The cation-exchange purification technique used here does not remove anions (in our case, mostly Cl^- , SO_4^{2-} and to a lesser extent NO_3^-) from solutions. In this case, the addition of a known artificial matrix in excess in both the sample and standard solution can be used to dilute the natural concentration of the contaminant and to homogenize sample and standard matrices (doping method, Georg et al., 2006; Hughes et al., 2011). Indeed, dissimilar matrices will affect differently the plasma and ionization efficiency and will induce artificial bias in the delta measurements, invalidating the use of the standard-sample bracketing technique.

In our samples, Cl^- originating from seawater can be neglected compared to Cl^- added as HCl (Merck Suprapur) to dissolve the brucite; and as solutions were analyzed in a HCl matrix largely in excess (up to 0.5 mol L^{-1}) compared to natural Cl^- concentration. Similarly, the occurrence of NO_3^- in seawater was resolved by the use of HNO_3 (Merck Suprapur, 0.5 mol L^{-1}) as a solvent in both the samples and standards. For KEOPS-2 surface samples, sulfate concentrations measured by ionic chromatography after purification could be significant to generate a shift in isotopic measurements ($\text{SO}_4^{2-}/\text{Si}$ up to 20). Van den Boorn et al. (2009) has recently reported that the presence of sulfate in rock digestion solutions can induce a significant offset (up to +1.4 ‰) in silicon isotopic measurements when $\text{SO}_4^{2-}/\text{Si}$ ratios > 0.02 .

To test the effect of sulfate on silicon measurements, we doped 4 Diatomite purified solutions with variable amounts of H_2SO_4 (Merck, Suprapur) to yield solutions with $\text{SO}_4^{2-}/\text{Si}$ ratios ranging from 0 to 19. The sulfate-doped Diatomite solutions were then analyzed for silicon isotope composition using the sulfate-free standard-sample bracketing technique. These solutions were analyzed using the same configuration as for the KEOPS-2 samples and the procedure was replicated 6 times on separated MC-ICP-MS analytical sessions.

The results of the experiment show a clear positive relation between the silicon isotopic composition of Diatomite and $\text{SO}_4^{2-}/\text{Si}$ ratio of the solution (Fig. S1), with the increase of $\delta^{30}\text{Si}$ signatures becoming significant (+0.2 ‰) when $\text{SO}_4^{2-}/\text{Si}$ ratios > 8 . Moreover, we observe a degradation of the analytical reproducibility with increasing $\text{SO}_4^{2-}/\text{Si}$ ratios with standard deviations up to five times higher in the most sulfate-concentrated solution, suggesting a strong decline of the measurement quality.

Doping both standard and Diatomite solutions with H_2SO_4 (final concentration 1 mmol L^{-1}) would impose similar $\text{SO}_4^{2-}/\text{Si}$ ratios in the sample and the standard solutions and should prevent any matrix effect. Indeed, we observe that the doping procedure does not induce any bias on Diatomite reference material

measurements that have a $\delta^{30}\text{Si}$ signature similar to the published values ($1.27 \pm 0.06 \text{ ‰}$, $n = 50$; compared to $\delta^{30}\text{Si} = 1.26 \text{ ‰}$, Reynolds et al., 2007).

Thus, as proposed by Hughes et al. (2011) for river waters, samples and standards solutions used for seawater isotopic analyses must be doped with sulfate when their $\text{SO}_4^{2-}/\text{Si}$ ratios > 8 in order to control the sulfate matrix effect during MC-ICP-MS measurements. In our study, it concerned every surface samples where we used a preconcentration (MAGIC) volume $> 50 \text{ ml}$. However, to run the MC-ICP-MS in the same matrix conditions for all samples, we decided to apply this procedure for all KEOPS-2 seawater samples. Thus, after cationic exchange purification (Georg et al., 2006) and prior to MC-ICP-MS measurements, sulfuric acid (H_4SO_4 , Merck Suprapur) was added to both the standard and the samples in order to reach the same final SO_4^{2-} concentration (1 mmol L^{-1} , see Table S1).

II. Calculation of a mixed-layer deepening

The ML is subject to occasional deepening due to a variety of physical processes. Our goal here is to estimate the order of magnitude of a ML deepening that could correspond to the supply of DSi estimated from our sediment trap isotopic measurements (i.e. an increase of $7.39 \text{ } \mu\text{mol L}^{-1}$). Indeed, when the ML deepens, DSi from deeper waters is introduced to the surface. This DSi supply (or entrainment) depends therefore on three parameters: (i) the gradient of DSi concentration below the ML, (ii) the depth of the ML (H) and (iii) the depth of the deepening event (H' , see Fig. S2). The variation of the ML is closely linked to the change in DSi concentration and can be explained as follows:

$$\Delta H = \frac{(DSi_t - DSi_{t0}) \times H}{DSi_{\text{deep}} - DSi_t} \quad (1)$$

with ΔH , the change of ML depth; DSi_t and DSi_{t0} , the concentration of silicic acid in the ML before and after the mixing event respectively; and DSi_{deep} , the concentration of silicic acid below the ML.

We assume that the ML is well-homogenized with a DSi_{t0} of $9.53 \text{ } \mu\text{mol L}^{-1}$ and we neglect the inverse process of “detrainment” when the water column stratifies again after the mixing event. The DSi_{deep} corresponds to the averaged WW DSi concentration estimated from the Plateau stations ($32.87 \text{ } \mu\text{mol L}^{-1}$) and the supply of DSi is estimated either from a Rayleigh model ($DSi_t - DSi_{t0} = 2.3 \text{ } \mu\text{mol L}^{-1}$) or from a steady state model ($DSi_t - DSi_{t0} = 7.39 \text{ } \mu\text{mol L}^{-1}$). Therefore, the estimated deepening of the ML is $+ 8.75 \text{ m}$ or $+ 37 \text{ m}$ in when we consider respectively a closed system or an open system.

References

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Hughes, H. J., Delvigne, C., Korntheuer, M., De Jong, J., André, L., D. Cardinal, D.: Controlling the mass bias introduced by anionic and organic matrices in silicon isotopic measurements, *Journal of Analytical Atomic Spectrometry*, 26, 1892-1896, 2011.

Reynolds, B. C., Aggarwal, J., André, L., Baxter, D., Beucher, C., Brzezinski, M. A., Engström, E., Georg, R. B., Land, M., Leng, M. J., Opfergelt, S., Rodushkin, I., Sloane, H. J., van den Boorn, S. H. J. M., Vroon, P. Z., Cardinal, D.: An inter-laboratory comparison of Si isotope reference materials, *Journal of Analytical Atomic Spectrometry*, 22, 561-568, doi:10.1039/b616755a, 2007.

Van den Boorn, S. H. J. M., Vroon, P. Z., Van Bergen, M. J.: Sulfur-induced offsets in MC-ICP-MS silicon-isotope measurements, *Journal of Analytical Atomic Spectrometry*, 24, 1111-1114, 2009.

Tables

Table S1: Running concentrations for isotopic analysis of seawater sample

	Si	HCl	HNO₃	H₂SO₄	Mg
Concentrations	2-2.5 ppm	0.5 mol L ⁻¹	0.5 mol L ⁻¹	1 mmol L ⁻¹	2-2.5 ppm

Table S2: Silicic Acid, biogenic silica concentrations and $\delta^{30}\text{Si}$ of DSi and BSi for all KEOPS-2 samples. * refers to particles collected using Niskin bottles only and ** refers to particles collected with Niskin bottles and in-situ pumps.

Table S3: Neptune+ MC-ICP-MS operating conditions

Resolution	Medium
Forward Power	1200 W
Accelerating Voltage	10 kV
Plasma Mode	Dry Plasma
Cool Gas Flow Rate	16 L min ⁻¹
Auxiliary Gas Flow Rate	1.1-1.4 L min ⁻¹
Sample Gas Flow Rate	0.9-1 L min ⁻¹
Cones Type	Nickel X-Skimmer cone + Standard Ni-Sample cone
Desolvator	Apex (ESI)
Nebulizer	PFA microcentric nebuliser 100 µL min ⁻¹
Running Concentrations	Si = 2-2.5 ppm, Mg = 2-2.5 ppm
Sensitivity	3-4 V ppm ⁻¹
Blank Level	< 1% signal
³⁰ Si Interference	< 30 mV (usually 10-15 mV)

Table S4: Central values of DSi concentrations (µmol L⁻¹) and δ³⁰Si_{DSi} signatures (‰) for different water masses across the Kerguelen Plateau region (ML: Mixed Layer; WW: Winter Water; UCDW: Upper Circumpolar Deep Water; LCDW: Lower Circumpolar Deep Water; AABW: Anatarctic Bottom Water). Except for the WW, median and interquartile range represent the "central values" and dispersion for the water masses. Since they displayed the strongest gradient of values, the WW Si-properties were defined using the threshold salinity method (see text for further details).

Station	CTD #	ML			WW			UCDW			LCDW			AABW	
		[H ₄ SiO ₄] ($\mu\text{mol L}^{-1}$)	$\delta^{30}\text{Si}_{\text{DSI}}$ (‰)	[H ₄ SiO ₄] ($\mu\text{mol L}^{-1}$)	$\delta^{30}\text{Si}_{\text{DSI}}$ (‰)	[H ₄ SiO ₄] ($\mu\text{mol L}^{-1}$)	$\delta^{30}\text{Si}_{\text{DSI}}$ (‰)	[H ₄ SiO ₄] ($\mu\text{mol L}^{-1}$)	$\delta^{30}\text{Si}_{\text{DSI}}$ (‰)	[H ₄ SiO ₄] ($\mu\text{mol L}^{-1}$)	$\delta^{30}\text{Si}_{\text{DSI}}$ (‰)	[H ₄ SiO ₄] ($\mu\text{mol L}^{-1}$)	$\delta^{30}\text{Si}_{\text{DSI}}$ (‰)		
A3-1	4	23.38 ± 3.23	1.97 ± 0.09	31.55 ± 2.21	1.76 ± 0.05	70.39 ± 0.00	1.38 ± 0.00								
TNS08	8	19.00 ± 1.82	2.24 ± 0.10	26.80 ± 1.88	1.93 ± 0.05	72.46 ± 4.61	1.22 ± 0.05								
TNS06	10	16.56 ± 0.11	2.41 ± 0.00	31.31 ± 2.19	1.71 ± 0.05	73.26 ± 5.39	1.28 ± 0.02	92.17 ± 3.79	1.00 ± 0.05						
TNS01	15	8.96 ± 0.50	2.26 ± 0.07	13.40 ± 0.94	2.23 ± 0.11	57.49 ± 8.23	1.35 ± 0.04	89.20 ± 8.39	1.01 ± 0.01						
R2	17	12.94 ± 0.07	2.24 ± 0.09	21.74 ± 1.52	1.92 ± 0.05	66.18 ± 15.18	1.23 ± 0.08	90.91 ± 16.85	1.10 ± 0.07						
E1	27	16.25 ± 1.06	2.21 ± 0.18	28.88 ± 2.02	1.84 ± 0.06	76.46 ± 5.24	1.22 ± 0.11	94.72 ± 6.34	1.08 ± 0.10						
TEW1	35	13.93 ± 3.73	2.19 ± 0.22												
TEW3	38	19.90 ± 7.94	2.16 ± 0.34	24.74 ± 1.73	1.86 ± 0.05	75.14 ± 0.00	1.41 ± 0.02								
E2	43	18.03 ± 2.66	2.28 ± 0.20	20.32 ± 1.42	1.99 ± 0.05	73.80 ± 2.30	1.21 ± 0.14	75.24 ± 0.00	0.93 ± 0.04						
TEW8	47	9.20 ± 2.24	2.47 ± 0.03	20.62 ± 1.44	2.08 ± 0.05	66.67 ± 9.20	1.40 ± 0.06	133.84 ± 0.00	1.07 ± 0.00						
E3	50	17.85 ± 2.90	2.16 ± 0.14	28.88 ± 2.02	1.92 ± 0.05	78.85 ± 4.75	1.24 ± 0.06	82.52 ± 0.00	1.09 ± 0.03						
FL	63	8.70 ± 1.17	2.53 ± 0.16	14.42 ± 1.01	2.12 ± 0.07	70.70 ± 7.11	1.26 ± 0.01	101.94 ± 0.00	1.04 ± 0.04		135.36 ± 0.00	1.13 ± 0.03			
E4W	81	22.53 ± 5.11	2.07 ± 0.01	36.71 ± 2.57	1.67 ± 0.05	76.46 ± 5.00	1.25 ± 0.07	101.94 ± 0.00	1.01 ± 0.03						
E4E	94	15.42 ± 7.46	2.36 ± 0.26	22.68 ± 1.59	2.14 ± 0.05	78.28 ± 3.58	1.20 ± 0.05	90.61 ± 2.72	1.10 ± 0.08						
A3-2	107	19.71 ± 0.31	2.10 ± 0.04	31.90 ± 2.23	1.69 ± 0.05	71.66 ± 8.56	1.39 ± 0.05								
E5	114	12.94 ± 2.11	2.44 ± 0.11	22.75 ± 1.59	2.12 ± 0.05	86.31 ± 13.67	1.21 ± 0.13	112.72 ± 0.00	1.11 ± 0.04						

Figure captions

Figure S1: Effect of sulfate (expressed as $\text{SO}_4^{2-}/\text{Si}$ ratios) on silicon isotope measurements ($\Delta\delta^{30}\text{Si}$ = offset in $\delta^{30}\text{Si}$ of sulfate-doped Diatomite relative to pure standard). Error bars represent 1sd. Black dashed and red dotted lines are the + 1 sd and + 2 sd from the initial (non-doped) value, respectively.

Figure S2: Schematic representation of entrainment and its impact on DSi concentration in the mixed layer. Grey dotted line and dark strait line correspond to the conditions before and after the mixing event, respectively.

Figure S3: $\delta^{29}\text{Si}$ versus $\delta^{30}\text{Si}$ of samples measured by Neptune+ MC-ICP-MS in dry plasma mode. DSi samples are in blue, surface BSi samples (collected using nuclepore membrane filtration) are in green, and deep BSi samples (collected with in situ pumps) are in black. Error bars represent the average standard deviation of duplicates (± 1 sd) and the line shows the theoretical kinetic fractionation law between ^{29}Si and ^{30}Si ($y = 0.51x$, as calculated following Young et al., 2002).

Figure S4: All KEOPS-2 (black diamonds) and KEOPS-1 (grey crosses) silicic acid $\delta^{30}\text{Si}$ plotted against the silicic acid concentration.

Figure S5: Potential temperature – salinity (θ -S) diagram for all KEOPS-2 stations.

Figures

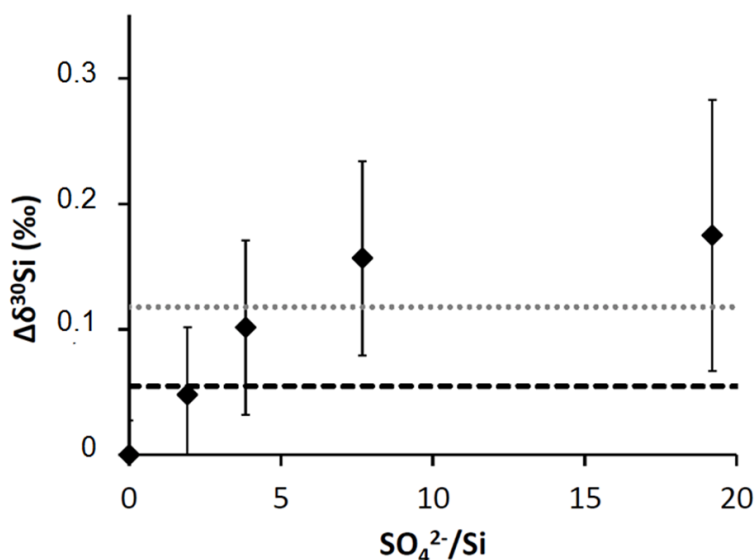


Figure S1

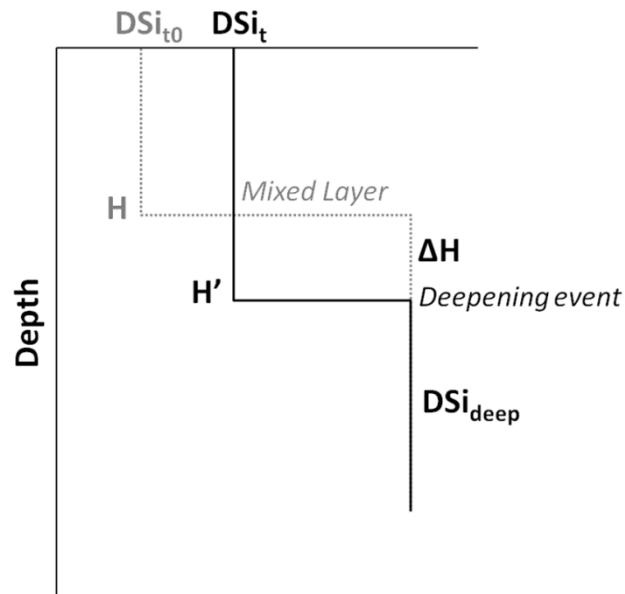


Figure S2

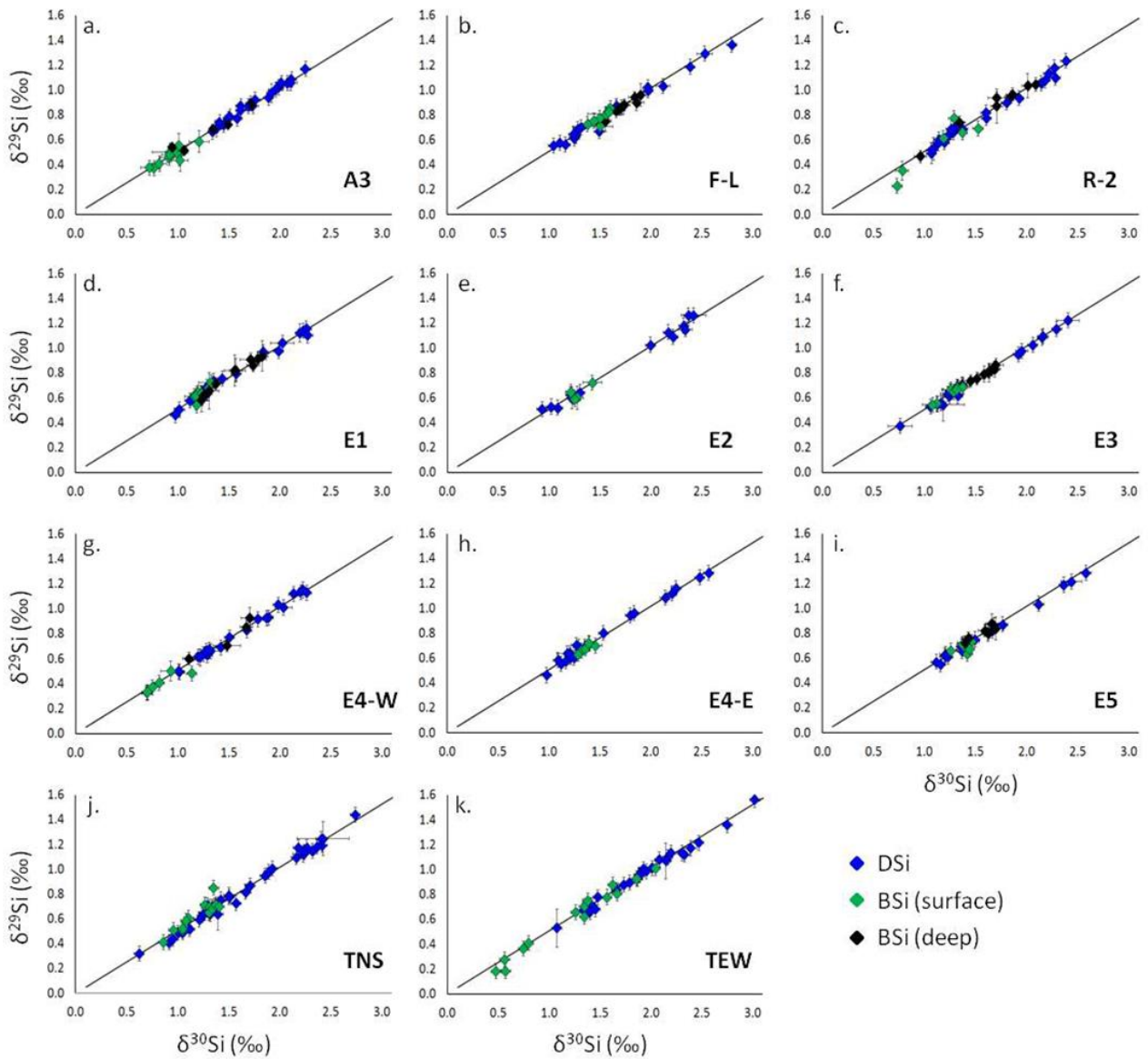


Figure S3

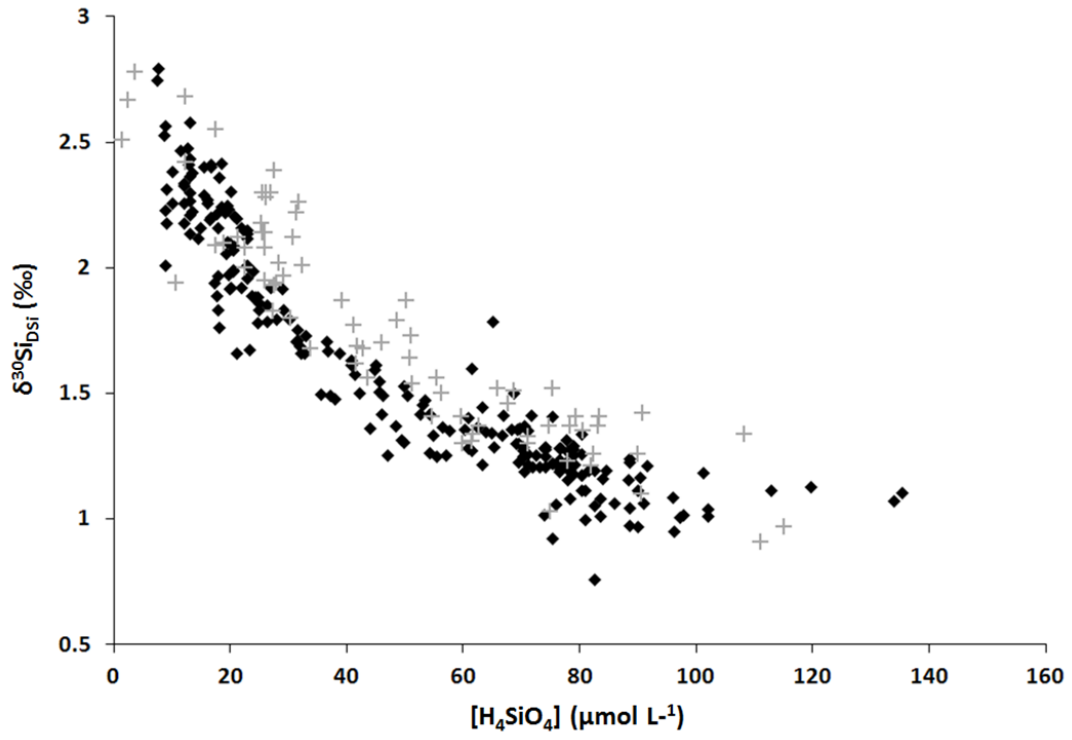


Figure S4

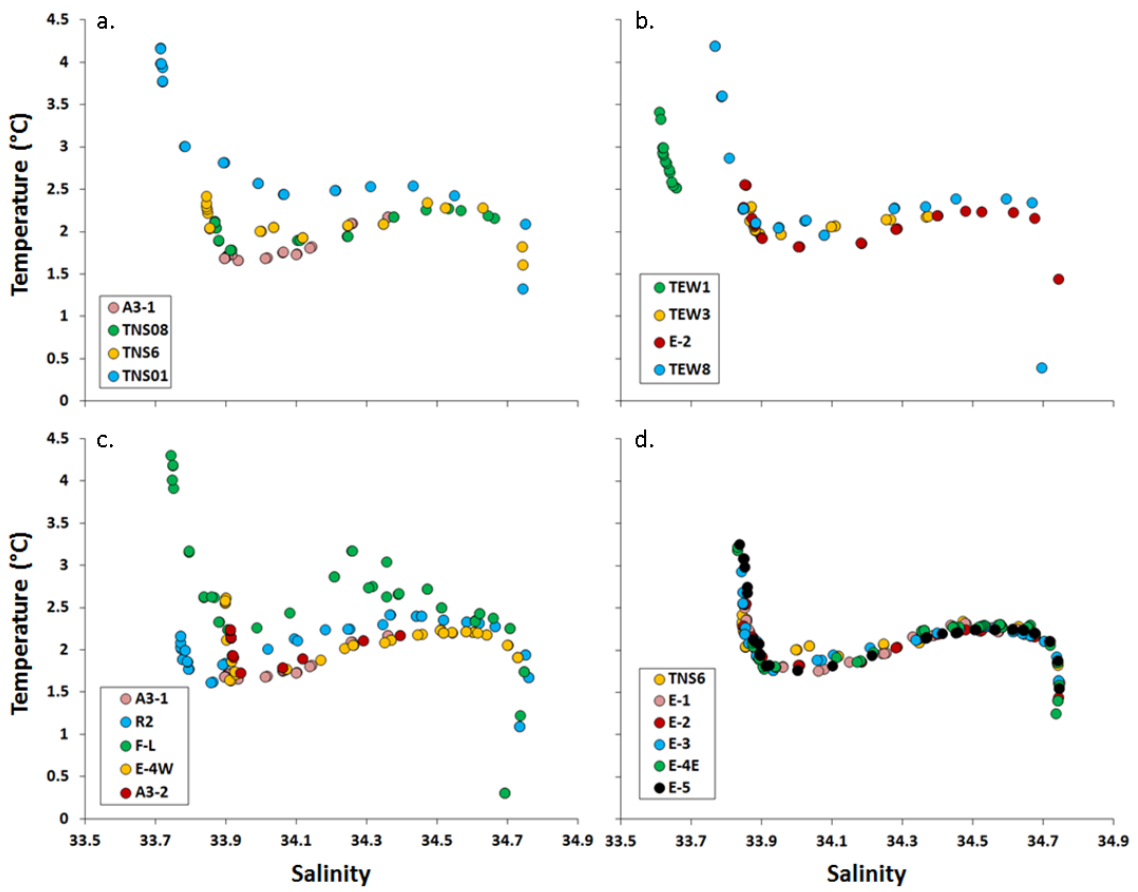


Figure S5