**Report on alkalinity measurements on S4P (Feb – Apr, 2011)**

**Method**

Total alkalinity measurements were made using an open-cell, two-stage, potentiometric titration procedure similar to that used to certify reference materials for total alkalinity (see Dickson *et al.*, 2003), except that samples were not weighed into the titration vessel. Samples of volume 92.085 ± 0.021 ml were prepared using a volumetric pipette and a system of relay valves and air pumps, controlled by a laptop using LabVIEW 2010. The temperature of the samples at time of dispensing was taken automatically by a computer using a Measurement Specialties 4600 thermometer, to convert this volume to mass for analysis.

The analytical procedure was as follows:

1. An aliquot of seawater was dispensed into the titration vessel (a jacketed glass beaker, temperature controlled to ±0.02 °C at about 20.0 °C), a stirrer bar added, and the temperature probe and burette tip inserted in the solution.
2. The solution was then acidified to a pH of about 3.6 with a single aliquot of the

titration acid, stirred vigorously, while bubbling air through for 5 minutes to remove CO2 from the sample.

1. The titration was then started using 0.04 mL increments of the titration acid taking the sample to a pH of about 3.0. Data from the pH range 3.5–3.0 were used in a non-linear least squares process that corrects for the reactions with sulfate and fluoride ions to estimate the total alkalinity of the sample—see Dickson *et al.* (2003) for more details.

The equipment used for this is listed in Table 1.

**Table 1: Listing of equipment used for alkalinity titrations for S4P**

250-cm3 capacity glass jacketed beaker

Thermostat bath (Thermo Scientific RTE7)

Magnetic stirrer and stir bar

Calibrated thermometer probes ± 0.01 °C for cell temperature and acid temperature

Agilent 34970A Data Acquisition/Switch Unit

Custom high-impedance voltage amplifier

Ross-Orion combination pH electrode (model 1802)

Metrohm Dosimat® model 765 burette with calibrated 5 mL burette unit

The hydrochloric acid used for the titration was made up in bulk and then stored in

1 L Pyrex bottles with greased ground-glass stoppers. The acid strength was approximately 0.100 mol kg–1, and it was made up in a 0.6 mol kg–1 sodium chloride background so as to approximate the ionic strength of seawater. Selected bottles of the acid are then analyzed coulometrically (Dickson *et al.*, 2003) to assign a concentration to the batch.

**Quality Control and Calibration of Reported Results**

The at-sea repeatability of the method was estimated by analyzing duplicate samples, collected on each cast. These results were used to estimate a standard deviation using the standard expression (Dickson *et al.*, 2007 – SOP 23). The repeatability was 0.99 µmol kg-1, based on 288 pairs of analyses. In addition, analyses were made of the alkalinity of CO2 reference material 256 times through out the cruise and at most stations.

**Figure 1.** Plot of the deviations of analyses of reference materials (Batch 106) from the certified values (Δ = measured value – certified value).

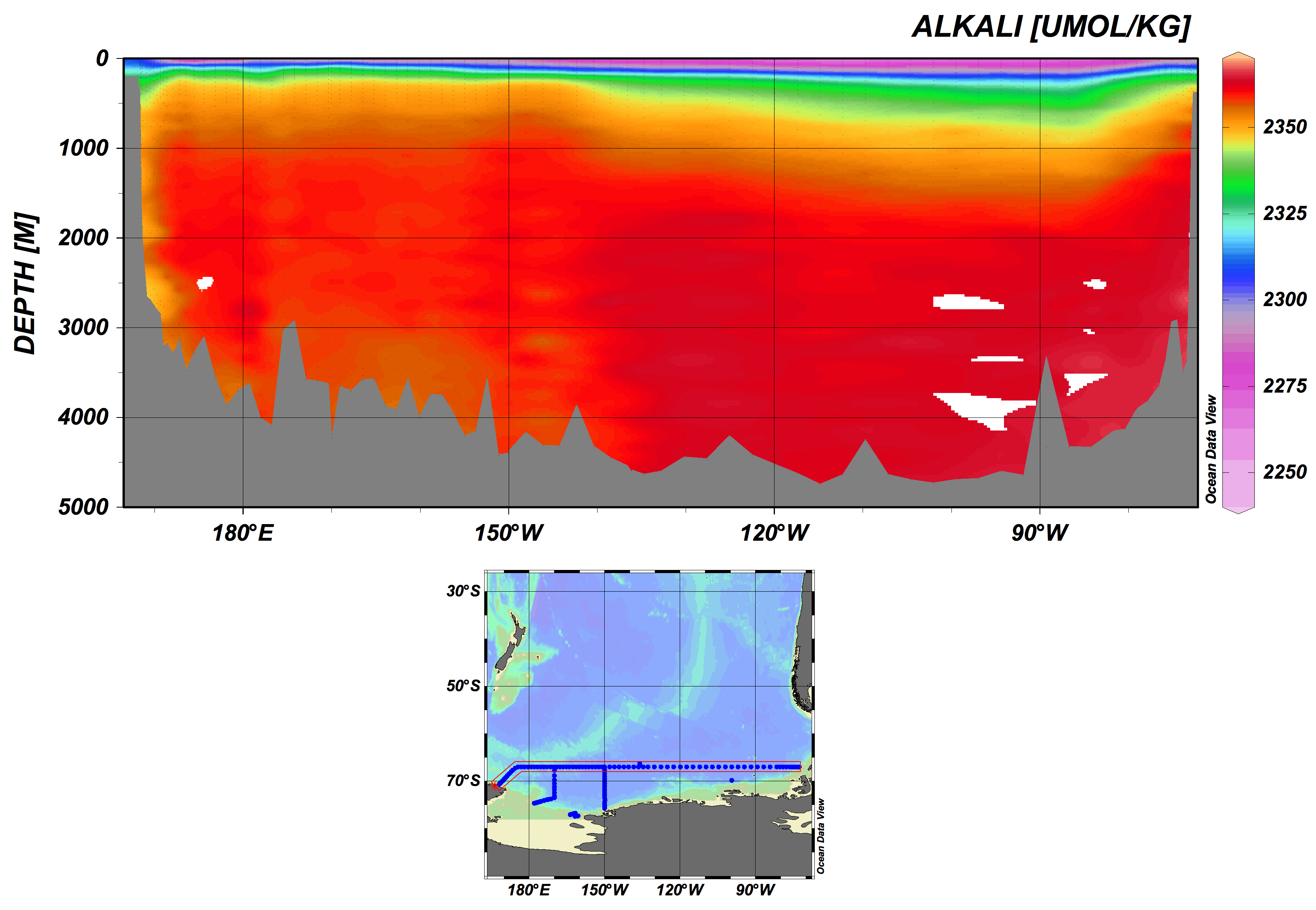
An examination of Figure 1 suggests two nearly horizontal linear trends, with the change occurring between April 2nd and 4th when the Electrode, Agilent and Acid Dosimat were all replaced during a break. Therefore a decision was made to treat the cruise data as two separate groups, and adjust the groups to correct for the error in the reference materials.

For the period 2/22-4/2 the average value for CRMs Batch 106 was found to be 2217.97 ± 1.37 µmol kg–1. The alkalinity sample data for this period (Station 2 – 102) was adjusted multiplicatively by 1.000772 to account for the difference of the reference material mean from the certified value. For the period 4/4-4/20 (Station 105-140) the measured average value was found to be 2217.22 ± 1.20 µmol kg–1 and the alkalinity results were adjusted by 1.001108.

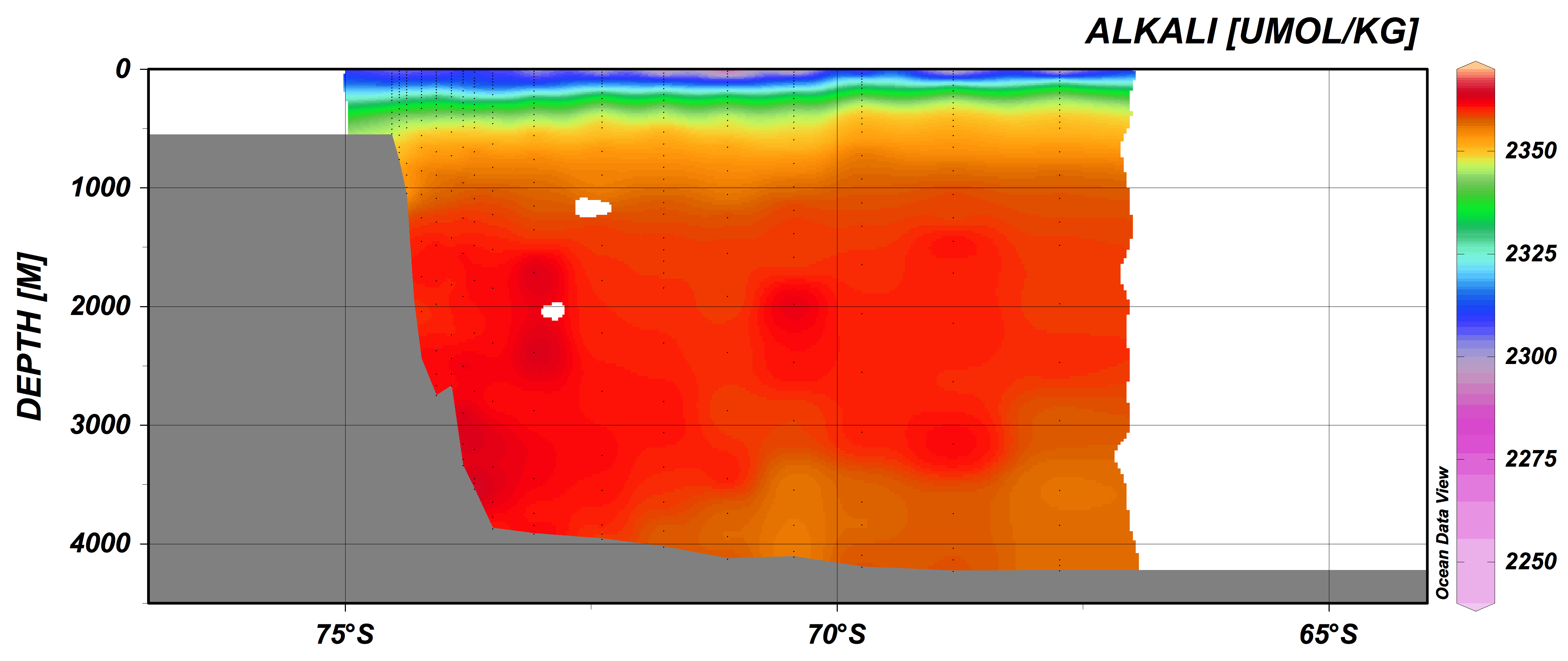
All alkalinity values were then multiplied by 1.0002143 to adjust for the dilution due to the addition of saturated mercury (II) chloride solution to each sample.

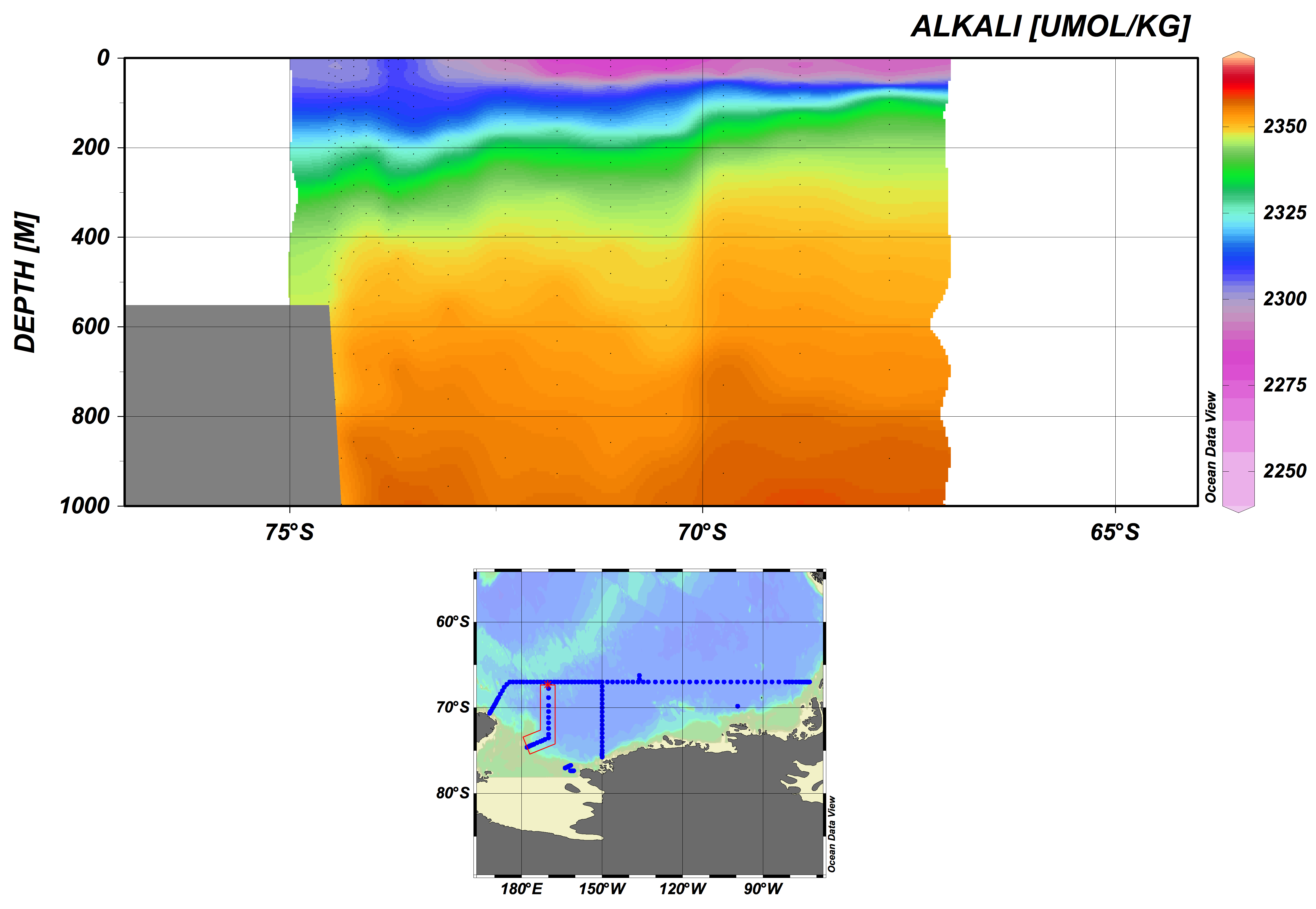
Once the at-sea alkalinity measurements had been adjusted in this fashion, they were salinity normalized to a salinity of 35 and the resulting values plotted in Ocean Data View (ODV) to help identify any questionable data.

A. Section 1 Horizontal Transect along latitude 67S

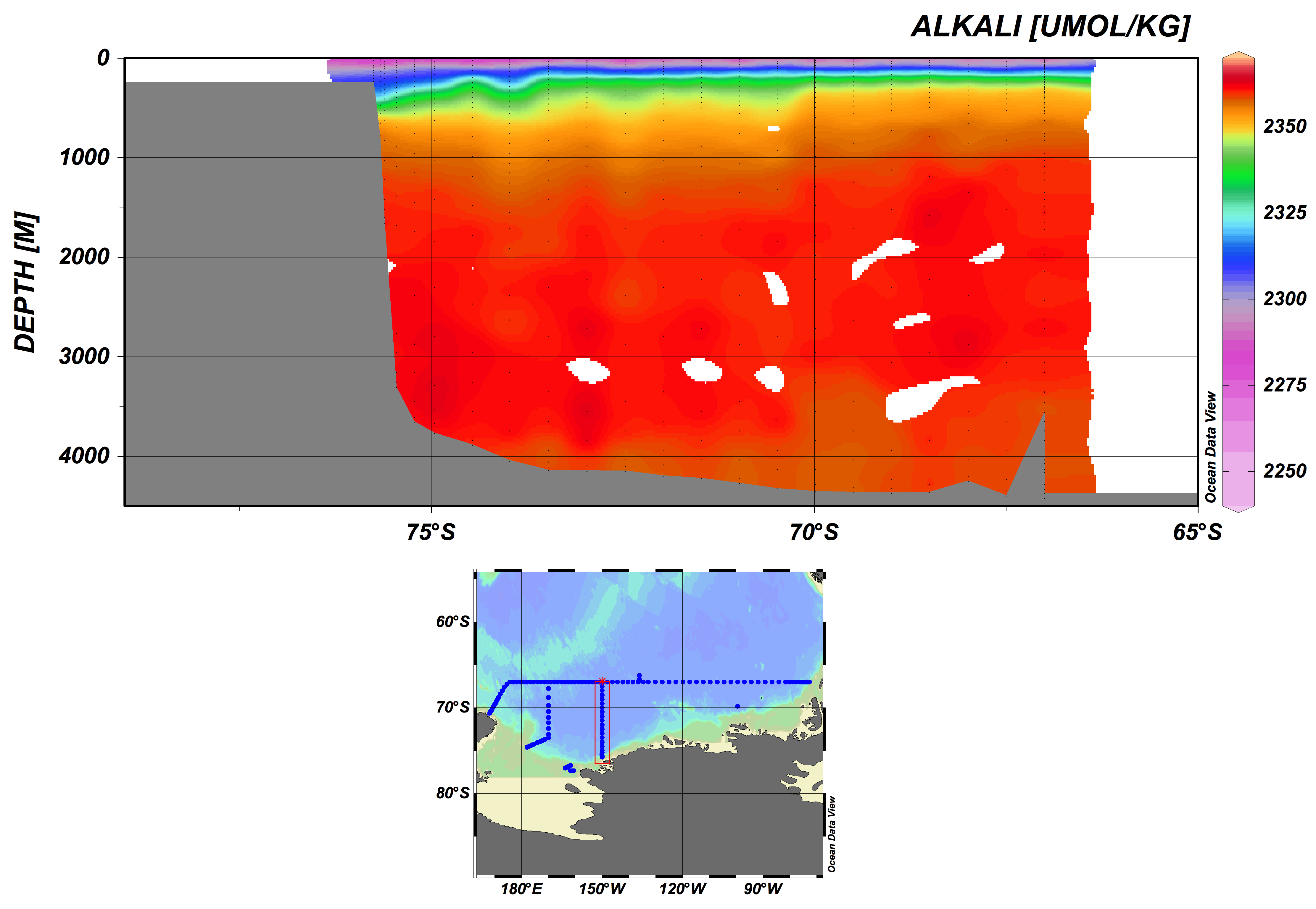


B. Section 2 Vertical Transect along longitude 170W





C. Section 3 Vertical Transect along longitude 150W



**Figure 2. A, B, C** Final corrected data for Alkalinity on S4P plotted in ODV.

**References**

Dickson, A. G., Afghan, J. D. & Anderson, G. C., 2003. Reference materials for oceanic

CO2 analysis: A method for the certification of total alkalinity. *Marine Chemistry* 80,

185–197.

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO2 measurements. PICES Special Publication 3, 191 pp.