Seawater carbonate chemistry (TA, DIC, pH) measured on water bottle samples during POLARSTERN cruise PS94 (ARK-XXIX/3)

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Dataset: PS94_Seawater_Carbonate_Chemistry

Ancillary parameters in dataset

Physical parameters (salinity, temperature, theta, oxygen) have been published on PANGAEA [*Rabe et al.*, 2016].

Nutrients (nitrate, phosphate, silicate) have been published on PANGAEA [*van Ooijen et al.*, 2016].

Seawater carbonate chemistry

Seawater samples for total dissolved inorganic carbon (DIC, TCO_2, C_T), total alkalinity (TA, A_T), and pH (total scale, 25°C, pressure 0) were taken from the Niskin bottles mounted to the CTD rosette at depths throughout the water column, but with a bias towards the upper water column.

DIC and TA were determined on all seawater and ice core melt samples. Both DIC and TA are measured in parallel with a VINDTA 3C instrument (MARIANDA, Kiel). The accuracy is set by internationally recognized and widely used certified reference material (CRM), batch 144, obtained from Prof. A. Dickson at Scripps Institute of Oceanography (USA). DIC is the sum of all dissolved inorganic carbon species and is determined by a precise coulometric method [*Dickson et al.*, 2007]. For every coulometric cell that was used in the coulometer, at least two CRMs were measured in duplicate at the beginning and the end of the analyses, where differences in the measurements infer the precision of the instrument. The TA measurements were made by

potentiometric titration with a strong acid (HCl) as a titrant. The acid consumption up to the second endpoint is equivalent to the titration/total alkalinity. The system uses a highly precise Metrohm Titrino for adding acid, a pH electrode and a reference electrode. The measurement temperature for both DIC and alkalinity was 25°C. Analyses were usually carried out immediately after sampling from the CTD and upon complete melt of the ice core sections. In a very few cases, samples had to be stored prior to analysis and where fixed with mercuric chloride solution and were stored in the dark. A total of 57 stations were sampled for DIC and TA totaling about 1100 samples. The precision for DIC and TA was determined from the in-bottle CRM duplicate analyses to be better than 2 μmol/kg. The accuracy was checked against frequent analysis of CRMs.

A total of 54 stations were sampled for seawater pH using borosilicate bottles (250 mL), having tight plastic screw caps, and were rinsed with at least one bottle volume and filled to the rim. All samples were thermostated to 25°C at least 30 min prior to analysis directly after sampling. Seawater pH was determined spectrophotometrically [*Clayton and Byrne*, 1993] using the sulfonephthalein indicator m-Cresol Purple (mCP). Purified mCP [*Liu et al.*, 2011] was purchased from the laboratory of Robert H. Byrne, University of South Florida, USA. The indicator solution (0.2 mM) was prepared by dissolving pre-weighed mCP indicator in 0.5 L filtered seawater (0.20 μm) of about salinity 34. The indicator was adjusted to a pH in the same range as the samples, approximately ± 0.2 pH units, by adding a small volume of concentrated HCl or NaOH. Before running a set of samples, the pH of the indicator was measured using a 0.02 cm cuvette. The measurements were performed on board within hours of sampling. The shipboard setup is based on the absorption ratios of the indicator at wavelengths 434 nm, 578 nm, and 730 nm (background correction) using a 1-cm flow cuvette and a diode array spectrophotometer (Agilent 8453). Each run consists of the three main steps; i) rinsing of tubing and cuvette with sample (15 mL) ii) sample blank (25 mL) and iii) sample run (20 mL) including indicator (0.5 mL). The sample is pumped and mixed using a Kloehn V6 syringe pump (Norgren) with a zero-dead volume syringe. Sample temperature is measured directly after the cuvette. The magnitude of the perturbation of seawater pH caused by the addition of indicator solution is calculated and corrected for using the method described in *Chierici et al.* [1999]. The instrument setup is controlled by a PC running a LabView program [*Fransson et al.*, 2011]. The pH values are corrected to 25°C on the total scale. The overall precision from duplicate sample analysis was better than ±0.001 pH units. The accuracy is mainly set by the accuracy of the physico-chemical characterizations of the indicator with respect to temperature dependence and the determination of the equilibrium constants of the indicator, as well as the purity of the indicator [*Liu et al.*, 2011]. The accuracy was checked against Certified Reference Material for total alkalinity and total dissolved inorganic carbon, indicating that it should be well below 0.01 pH units.

References

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