

DESCRIPTIVE TEXT
SEA WATER INORGANIC CARBON DATABASE
for the CARBON DIOXIDE INFORMATION AND ANALYSIS CENTER (CDIAC)
prepared by the CARBON DIOXIDE RESEARCH GROUP (CDRG)
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I. GENERAL DESCRIPTION

The database consists of tables presenting oceanic inorganic carbon analyses of the Carbon Dioxide Research Group (CDRG) at Scripps Institution of Oceanography (SIO), La Jolla, CA, USA, along with auxiliary oceanographic data. Data are shore-based analyses of aliquots of sea water from bottles ("grab samples") collected at sea from Niskin bottle casts. The CDRG has measured dissolved inorganic carbon (database abbreviation: "DIC"), also known as total carbon or total CO₂, titration (total alkalinity (database abbreviation: "ALK"), and the ¹³C/¹²C isotopic ratio of the carbon comprising DIC (database abbreviation: C13). The tables include salinity and inorganic nutrients measured at SIO on aliquots from the same sample bottles. The database also includes sample identification information and shipboard-derived data on salinity, in situ temperature, inorganic nutrients, and oxygen. For descriptions of the CDRG analytical methodology see Guenther et al. [1994] and Appendix A of Gruber et al. [1997]. The database is derived from a more complex Master Database maintained at SIO.

II. NOTES ON STRUCTURE OF THE DATABASE TABLES

A. GENERAL COMMENTS

The database is a set of tables, each line containing 236 characters. The tables are sorted by oceanographic cruise and, within the section of the table for each cruise, by date and depth. See the accompanying list for the identification of each cruise corresponding to each abbreviation. Also see the accompanying description of the database format.

The alphabetic prefix on the bottle number indicates a type of sample bottle. "P" represents a 1 liter borosilicate glass bottle, "Q" a 1 liter vitreous quartz bottle, "S" a 500 ml borosilicate glass bottle with a metal "bail" stopper closure, and "R" a 500 ml borosilicate glass bottle with a Rodaviss stopper closure. Additional one-time prefixes are "H" for 250 ml "HOT" program glass bottles (HAWI cruise, 12-1997), and "N" for 500 ml NOAA program glass bottles (NOAA cruise, 04-1992).

B. REPLICATE DATA

Most CDRG inorganic carbon measurements were made in duplicate. Two glass sample bottles normally were filled consecutively with sea water from a single Niskin bottle. Single measurements for DIC, ALK, and C13 were usually performed on each of the samples. Sometimes, for example on samples from the Indomed cruise (database abbreviation: "INDO"), duplicate DIC analyses were performed on each bottle, therefore four CDRG measurements corresponding to a single Niskin bottle. There are also cases where two or more alkalinity titrations were performed on each bottle

(often, one or more of these titrations has been given a flag indicating rejection).

The database lists the CDRG sample bottle number in columns 142-147, along with the number of its bottle pair in columns 149-154. The identical information (e.g. station number, Niskin number, latitude) is not repeated on additional lines with replicate analysis data.

C. FLAGS

CDRG measurements of the three inorganic carbon parameters (DIC, ALK, and C13) in the CDRG Master Database have been quality assured to identify data affected by analytical problems and outlier data. Flags have been inserted adjacent to suspect data in the CDRG Master Database, and appear as well in the CDIAC database outputs. The flags are three-digit numbers and are defined in an accompanying document.

III. STATUS OF CALIBRATION OF INORGANIC CARBON ANALYSIS RESULTS

A. DISSOLVED INORGANIC CARBON (DATABASE ABBREVIATION: "DIC")

Results are reported in micromoles of carbon per kilogram of sea water. The DIC in a gravimetrically-determined aliquot of sea water is converted quantitatively to CO₂ gas, the gas then measured non-destructively in a manometer. Calibration through 1999 depended upon measurements made using a constant-volume mercury manometer (CMM, database abbreviation: "M"). Determinations of the volume of the sample chamber of the CMM were made by measuring known amounts of CO₂ from a set of seven glass plenums whose volumes were calibrated by weighing them filled with mercury. Designated sample chamber volumes between 2 October 1978 and 30 March 1985 are reported by Keeling et al. [1986] and from 1 April 1985 to 19 November 1999 by Keeling et al. [2002]. The calibration applies not only to the CMM but also to two constant-volume manometers for which the pressure in the sample chamber was determined by a quartz spiral pressure sensor. The first device, called XR38 (named for the sensor, manufactured by Ruska Instrument Corporation, database abbreviation of the manometer: "S"), was used from March 1983 to April 1992. The second device, called "electronic constant-volume manometer" (ECM, database abbreviation: "E"), was used thereafter.

The sample chamber of the ECM is partly made of glass, but also partly a compartment of a metallic differential pressure gauge manufactured by Ruska Instrument Corporation. The gas pressure exerted on a second compartment of the pressure gauge, separated from the first compartment by a diaphragm, is made equal to the sample pressure by supplying pressure from a Ruska DDR6000 quartz spiral manometer, configured as a pressure delivery source. This quartz spiral is mechanically immobile, held in place by an opposing electromagnetic field from which the pressure is accurately calculated. The position of the diaphragm in the differential pressure transducer is additionally detected electrically to very high precision.

Calibrations of the XR38 and the ECM were linked to calibrations of the CMM by repeatedly measuring a set of secondary standard samples on both instruments. A special calibration of the ECM in April 2000 using plenums has confirmed the relative

calibration of the two instruments, with a standard deviation of one part in 2700 [Keeling et al., 2002].

Beginning on 25 January 2000, the volume of the sample chamber of the ECM has been calibrated directly by using plenums, whose volumes were calibrated by weighing them filled with water, and which were filled with pure CO₂ gas to pressures determined precisely by a gas-lubricated piston pressure gage (Ruska Instrument Corporation, model 2465-754, with low range piston). The volume of the ECM chamber, so determined from January 2000 to January 2001, is reported in Keeling et al. [2002]. Calibration after January 2001 has not been finally reported; thus all data for this most recent period are provisional. Calibration of DIC in the database is identical to that used to certify for DIC the sea water Certified Reference Materials (CRMs) prepared and distributed by A. G. Dickson of SIO.

B. TOTAL ALKALINITY (DATABASE ABBREVIATION: "ALK")

Results are reported in micromoles of hydrogen ion equivalent per kilogram of sea water. An aliquot of sea water is titrated with strong acid and the resulting titration curve evaluated using a non-linear least squares fit, as described in Standard Operating Procedure No. 3 in [DOE, 1994]. Through April 1998, titrations were made on one of three CDRG closed-cell titration systems (Gravimetric No. 1, database abbreviation: "G1"; Gravimetric No. 2, database abbreviation: "G2"; or Volumetric, database abbreviation: "V"). Normalities of hydrochloric acid (HCl) titrants were calibrated by titrating solutions of sodium carbonate, using the same titration procedures as for sea water. The CDRG calibration of the closed-cell system (G2) was tested by comparing results for 19 batches of CRMs, including a total of 210 CDRG titrations between September 1994 and April 1998, to values certified in the laboratory of A. G. Dickson at SIO [Dickson et al., 2002]. CDRG measurements of the ALK of CRMs have not been published or reported. The average difference found was 0.06 umol/kg, CDRG higher, with a standard deviation of the set of differences of 1.66 umol/kg. Since earlier data received no such test and since there were unresolved inconsistencies in calibration throughout the data set, all closed-cell ALK results reported in the database are provisional, with errors possibly exceeding 10 umol/kg, unless or until final calibrations can be completed.

Beginning in January 1999, ALK was measured in the laboratory of A. G. Dickson at SIO, using an open-cell titration system (database abbreviation: "OC"). Calibration is dependent upon coulometric titration of the concentration of HCl titrants in the same laboratory. This method and its calibration are identical to those used to certify sea water Certified Reference Materials (CRMs) for total alkalinity [ibid].

C. ¹³C/¹²C STABLE CARBON ISOTOPIC RATIO OF THE DIC (DATABASE ABBREVIATION: "C13")

The reduced isotopic ratio, $\delta^{13}\text{C}$, is defined as the relative variation in ¹³C/¹²C isotopic ratio from that of the carbonate standard Pee Dee Belemnite ("PDB") given by the formula:

$$\delta^{13}\text{C} = (R/R_s - 1) * 1000$$

where R denotes the $^{13}\text{C}/^{12}\text{C}$ of the sample, and R_s the $^{13}\text{C}/^{12}\text{C}$ of the standard, assigned as 0.0112372. The $\delta^{13}\text{C}$ is expressed in parts per thousand (per mil) difference from the PDB standard (symbol, ‰ PDB).

The CO_2 gas sample that was measured manometrically for the DIC analysis is subsequently introduced into a dual-inlet mass spectrometer (DIMS) to measure $\delta^{13}\text{C}$. Calibration depends upon mass spectrometric measurements of National Bureau of Standards (NBS) carbon isotope standards, and in addition upon secondary standards run on the DIMS for daily stability checks. Analyses made at the Centre for Isotope Research, University of Groningen, the Netherlands (CIO) from 1978 until early 1992 [Roeloffzen, 1993] are still subject to calibration adjustments, although the data have been reported and interpreted in a number of published research articles. The data set is currently being re-evaluated by Dr. Harro Meijer of CIO. The Roeloffzen version of this data set is being submitted here, with the understanding that Dr. Meijer's future efforts may produce an updated version. Analyses made at SIO from 1992 to July 2000 on a VG Prism DIMS of Martin Wahlen [Bollenbacher et al. and Guenther et al., 2002] received direct calibrations with NBS carbon isotope standards in 1994 and 1997. Daily measurements are referenced to these standardizations by measurement of a set of secondary standards. Since 1 September 2000, $\delta^{13}\text{C}$ measurements have been made on a Micromass Optima DIMS by the CDRG. These measurements have also been referenced to the 1997 NBS calibration through the daily measurement of secondary standards. Since 1997, the $\delta^{13}\text{C}$ data may be subject to small adjustments because there have been no additional NBS calibrations. They should be considered preliminary.

Comparable data from CIO and SIO during the period 1989-1994 have revealed no measurable difference in calibrations of the two systems with respect to samples derived from sea water [Bollenbacher et al., 2002].

IV. REFERENCES

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