DOE/ER/61116--2

DE93 006900

Technical Progress Report

Title: Oceanic CO_2 Measurements for the WOCE Hydrological Survey In the Pacific Ocean; Shipboard Alkalinity Analyses During 1991 and 1992

Principal Investigator: Charles D. Keeling

Period of Report: 1 February, 1992 through 31 October, 1992

Award No.: DOE DE-FG03-91ER61116

Address: Scripps Institution of Oceanography
University of California, San Diego
La Jolla, California 92093-0220

Summary of Progress

Over a period of several years the DOE Carbon Dioxide Science Team is contributing measurements of the carbon cycle in sea water on transects of the WOCE Hydrological Survey sponsored by the United States. As noted in our report of 6 December, 1991, our laboratory is contributing measurements of titration alkalinity of sea water to this effort.

During the first half of 1992, after our first field studies and before returning to sea, we carried out several modifications of a dual potentiometric sea-going titration system constructed in 1991 and first used on Leg 3 of the 1991 WOCE expedition from Tahiti to Hawaii. We replaced the Orion Ross combination pH electrodes previously in use in the titrator to Radiometer combination pH electrodes, which use silver/silver chloride reference electrodes with potassium chloride reference junctions. The Radiometer electrodes have proven to be more stable and reliable on the long term and also display a significantly faster response to pH change, speeding up typical titrations by about seven minutes (from 20 minutes to 13 minutes).

We also modified the temperature sensing of the titration system. Firstly, the temperature of the acid titrant, as measured by a surface probe on the Dosimat burette, was incorporated into the calculation of acid weight delivered. In 1991 this temperature was recorded but not used in the preliminary calculations. (These calculations have since been repeated taking into account the titrant temperature.) Secondly, we added surface probes to the sample syringes to take into account the measured temperatures when determining the weights of samples injected. It was necessary to change the operating procedure so that each

sample rested in the syringes for at least 10 minutes, a time sufficient to reach temperature equilibrium. Finally we erected a plastic cage around the system to reduce short term temperature fluctuations, and added shielding to the electrodes to reduce static electricity effects.

In the summer and early fall of 1992, we participated in the WOCE expedition, occupying Line P13 in the far western Pacific Ocean. The ship operations were supervised by NOAA's Pacific Marine Environmental Laboratory and carried out on the R/V John Vickers of the University of Southern California. Peter Guenther and Guy Emanuele of our group carried out alkalinity titrations at sea. They were assisted by personnel of Andrew Dickson's group, who were primarily responsible for the operation of a DOE SOMMA coulometric system to measure dissolved inorganic carbon (DIC) on the expedition. Mr. Guenther participated on Leg 1, from August 16 until September 15, Mr. Emanuele on Legs 1 and 2, from August 16 until October 21. Costs were shared, our grant paying for travel and other non-salary costs incurred by Dickson's group, since they were not funded for seagoing work. They, in turn, provided us assistance in analysis. (Another analyst was contributed for DIC measurements by Battelle NW. Thus, on both legs four CO_2 system analysts were on board, allowing the two systems to be operated around the clock and also allowing the analysts to do all the CO_2 sampling, including shore-based sampling.) The titration system could comfortably carry out 50 titrations per day, allowing one complete station of 36 Niskin samples plus extra surface samples and standards to be analyzed each day. The planned spacing for shipboard CO_2 stations was every third station or 1.5 deg. of latitude. Because of mechanical problems with the ship that led to a large reduction in the number of stations occupied, the spacing on Leg 2 was increased to every 2 deg. of latitude.

A total of 1636 titration analyses of alkalinity were made on the expedition. A total of 39 stations were sampled in profile, each nominally including 36 Niskin samples from surface to the bottom. Duplicate samples were routinely collected on these stations from two of the Niskin bottles. We attempted to collect a surface sample for shipboard analysis from all other stations occupied on the expedition. Forty-one out of a possible 45 stations were thus sampled. In total, 1256 Niskin bottles were sampled and analyzed, for both DIC on the coulometric system and alkalinity on the titration system. Even though the station density was curtailed from the original WOCE plan, the planned density of CO_2 system measurements was not greatly affected, aside from abandonment of all sampling

between 4 to 18 deg. south latitude.

Preliminary profiles of the data for each station were plotted immediately after completion of analyses at sea. These data display smooth changes in alkalinity with depth suggesting high precision in analysis. Work on finalizing the data is underway. This work includes resolving a problem involving a discrepancy between the two sides of the system, ranging from 0 to 6 microequiv./kg. We anticipate that the systematic use of standards and duplicate sea water samples on this expedition will allow us to correct the data to an accuracy approaching 1.5 microequiv./kg. When the equipment is returned to the laboratory in December we plan further to investigate the cause of the discrepancies. The electrodes themselves do not appear to be at fault.

Two types of reference materials were analyzed for alkalinity at sea, interspersed with the analyses of sea water samples. The first consisted of bicarbonate in sodium chloride solutions prepared in our laboratory and of the same type used by us for over five years previously. These solutions were bottled in one liter Pyrex glass bottles and were routinely analyzed five times each. The second type of reference material consisted of surface sea water samples (Certified Reference Material, Batch Number 13) prepared by Dr. Dickson's standards laboratory. These latter solutions, bottled in 500 ml Pyrex bottles, although they were designed primarily as DIC reference materials, were also routinely analyzed for alkalinity after having been analyzed for DIC with the coulometric system. In total we carried out 182 titrations in 38 bottles containing our standards and 84 titrations in 38 bottles of Dickson's standards.

A report will be prepared describing the results of both the 1991 and 1992 expeditions. A complete set of data will accompany a summary of the results.

END

DATE FILMED

3/12/93