

acid-water system (8). Although this study revealed that the anhydrous acid was the stable crystallizing phase in water concentrations up to 5 percent by weight at 50°C, no attempts were made to exploit this information in the growth of large single crystals.

We have been unable to grow good single crystals of oxalic acid dihydrate from pure water solution despite careful attention to detail and rigorous control of temperature and temperature-programming. Seed crystals were prepared in conventional fashion by evaporation of water solvent, then planted in the larger growth chambers and grown by temperature drops not in excess of 0.015°C per day. Experiments were conducted at temperatures near 30°C and near 55°C, but there was no obvious advantage in either temperature region. The crystal shown in Fig. 4 is typical of the specimens we obtained. Polycrystalline growth and inclusions of mother liquor are characteristic of such crystals.

Seed crystals which were prepared by solvent evaporation from solutions in acetone-water mixtures, then grown further from water solution by temperature-programming (linear temperature drop of 0.015°C per day in the temperature range from 42° to 35°C), gave single crystal specimens of greatly improved quality. The crystal at the right in Fig. 5 is typical. Resting on the basal plane in the photograph, the crystal shows the predominance of {001}, {101}, and {110} forms in habit.

From the standpoint of optical clarity, freedom from mother liquor inclusions, and well-developed habit, the best single crystals of oxalic acid dihydrate were grown from solution in acetone-water mixtures by the temperature-dropping technique. Seeds were prepared in a solvent consisting of 75 percent acetone and 25 percent water, with the temperature being in the range from 35° to 30°C. Single crystals of the dihydrate were then grown from solutions in (i) 75 percent acetone and 25 percent water, and (ii) 93 percent acetone and 7 percent water; the latter was prepared by dissolving the dihydrate acid in essentially anhydrous acetone. Resultant typical crystals are shown in Fig. 5. The crystal in the center was grown from the solution with the higher water content; the one at the left, at the lower water concentration.

The three crystals in Fig. 5 are oriented identically with {001} parallel to

the surface on which they are placed and [010] in the plane of the picture. Prismatic habit is characteristic of crystals grown from acetone-water mixtures. Growth on {110} is most rapid, with an observable difference in the growth rate on these surfaces in different acetone-water mixtures. The prismatic habit in both cases is defined by {001}, {110}, and {101}. The crystal grown from water solution (Fig. 5, right) shows more rapid growth on {001} and {101}, and again the {001}, {110}, and {101} forms predominate.

The crystals of oxalic acid dihydrate grown from acetone-water mixture are considered to be the best in quality of any produced in this investigation. Portions of several specimens were analyzed by a precise coulometric titration for acidic hydrogen (9) to give a stoichiometric composition on this basis of 99.985 percent (standard deviation, 0.001 percent). Flame photometric analyses for lithium and sodium and spectrographic analyses for other alkali, alkaline-earth, and heavy metals indicated the presence of the following impurities: lithium, less than 1 part per million; sodium, 38 to 40 ppm; potassium, less than 1 ppm; rubidium, less than 1 ppm; magnesium, less than 1 ppm; iron, less than 1 ppm; and silicon, less than 1 ppm. Other elements were not detected. The sodium content,

accounting for approximately two-thirds of the deviation from stoichiometric composition as based on the titration for acidic hydrogen, does not differ significantly from that contained in the starting material. No explanation of this indicated retention of sodium is apparent at the present time.

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Clay- and Carbonate-Accumulation Rates in Three South Atlantic Deep-Sea Cores

Abstract. *Three South Atlantic deep sea cores have been dated by the carbon-14 technique, and rates of accumulation of clay and calcium carbonate have been determined. The highest eupelagic clay rates for the Atlantic found to date are in the Argentine Basin, and the lowest are on the Mid-Atlantic Ridge.*

The rates of accumulation of both clay and calcium carbonate components of deep-sea sediments have been determined for a large number of locations in the north and equatorial Atlantic by the method of radiocarbon dating and paleontologic correlation (1). Although a few radiocarbon dates exist for the sediments around Antarctica, the sediments in the South Atlantic have not been dated by the radiocarbon technique.

This report includes rates of accumulation for three cores raised by the Lamont Geological Observatory, one from the Argentine Basin (V15-142), one

from the Mid-Atlantic Ridge (V16-36), and one from the Walvis Ridge (V12-66). The last two are high carbonate cores (about 90 percent CaCO_3), and the usual method of carbon-14 assay of the carbonate was followed. The Argentine Basin sediments are all very low in calcium carbonate but significantly high in organic carbon (about 0.8 percent) so that dates were obtained on the organic matter. There may be some uncertainty about the amount of fossil carbon represented. Because of the homogeneous appearance of these cores down their lengths, the density and calcium carbonate content determined on

Table 1. Rates of accumulation of the South Atlantic deep-sea sediments in three LGO cores.

Yale No.	Sample depth (cm)	Mid-point	Age (yr)	Depth difference	Age difference	Accumulation rate per 1000 yr			
						Total (cm)	Total (g/cm ²)	CaCO ₃ (g/cm ²)	Clay (g/cm ²)
		Core V15-142, 44° 33.7' S, 51° 32' W, 5885 m, Argentine Basin*							
	0	0	>0						
Y 1344	23-35	29	10,200±400	29	<10,200	>2.8	>2.7	~0	>2.7
Y 1345	35-50	42.5	12,200±300	13.5	2,000	6.8	6.6	~0	6.6
		Core V16-36, 19° 22.5' S, 11° 26.5' W, 3329 m, Mid-Atlantic Ridge†							
	0	0	>0						
Y 1346	2-8	5	5,940±120	5	<5,940	>1.9	>1.3	>1.25	>0.05
Y 1347	23-29	26	19,700±350	21	13,760	0.66	0.47	0.45	0.02
Y 1348	61-71	66	30,100±800	40	10,400	0.38	0.26	0.25	0.01
		Core V12-66, 22° 59' S, 07° 01' E, 2759 m, Walvis Ridge‡							
Y 1341	0-5	2.5	4,320±160						
Y 1342	20-27	23.5	10,310±100	21	5,990	3.5	2.52	2.39	0.13
Y 1343	100-107	103.5	37,000±2,000	80	26,690	3.0	2.16	2.05	0.11

* Very low in calcium carbonate; salt free, water free, uncompressed density is 0.97 g/cm³ (20- to 21-cm interval). † Top of core has 96 percent CaCO₃; salt free, water free, uncompressed density is 0.69 g/cm³ (38- to 41-cm interval). ‡ Top of core has 95.1 percent CaCO₃; salt free, water free, uncompressed density taken as 0.72 g/cm³.

any segment of a core was used for the entire length sampled of that core.

The results are presented in Table 1.

Although the rates of clay accumulation in the Argentine Basin core are the highest of the three southern Atlantic cores studied, they are not much higher than some rates in the northwestern Atlantic (1). The clay-accumulation rate at Walvis Ridge is as low as the lowest figures found for the north and equatorial Atlantic.

The lowest clay-accumulation rates found to date in the Atlantic Ocean by the method of radiocarbon dating are

those in V16-36. An average rate of about 0.03 g/cm² per 1000 years is one-tenth the average rates for the Mid-Atlantic and eastern Atlantic areas at the equator and north.

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Electrolytic Conductance of Sea Water: Effect of Calcium Carbonate Dissolution

Abstract. *Calcium carbonate dissolution in the presence of excess carbon dioxide increased the specific conductance of sea water by approximately 6×10^{-5} ohm⁻¹cm⁻¹ per millimole of carbonate dissolved. The observed conductance increase can be explained by the partial equivalent conductance of calcium bicarbonate and by the hindrance effect of uncharged carbon dioxide dissolved in sea water.*

Oceanographers use the electrical conductance of sea water to estimate its density and salinity. In order to understand how certain factors may alter the conductance, we previously studied the partial equivalent conductances of electrolytes in sea water (1) and the effect of carbon dioxide on the

electrolytic conductance of sea water (2). Since calcium carbonate precipitation and dissolution are active processes occurring in the oceans, the effect of calcium carbonate dissolution on the conductance of sea water is of interest.

For this experiment, 200-ml samples

of sea water with a chlorinity of 19.7 parts per thousand and a carbonate alkalinity of 2.55 meq/liter were mixed with 1 gram of oolite (aragonite). In order to facilitate the dissolution of the carbonate, the mixtures were equilibrated with varying amounts of carbon dioxide gas for 5 days. A temperature-compensated inductive (electrodeless) conductivity and salinity meter, a-c, 10 kcy/sec oscillation (3), was used to measure the relative conductances of the samples at room temperature (23°C). Concurrently, the pH and alkalinity were determined. The amount of dissolution of calcium carbonate was calculated from the increase in alkalinity. The conductance of the sea water sample without any addition of carbon dioxide gas was arbitrarily taken as 1.0000.

Figure 1 shows the changes in pH and electrical conductance with calcium carbonate dissolved. The pH decreased from nearly 8 to 6. The conductance increased about 0.12 percent per millimole of calcium carbonate dissolved.

In the presence of excess carbon dioxide (carbonic acid) the carbonate ion resulting from the dissolution of calcium carbonate crystal reacts with carbon dioxide to form bicarbonate ion. Thus, the observed conductance increase is due to the addition of calcium bicarbonate to sea water.

The partial equivalent conductance of calcium bicarbonate in sea water is not reported, but it can be estimated from earlier data (1). For sea water with a chlorinity of 19.4 parts per thousand at 23°C, values of 90 ohm⁻¹cm² per equivalent for sodium chloride, 78 for calcium chloride, and 47 for sodium bicarbonate were obtained.

From these values, the calculated partial equivalent conductance of calcium bicarbonate in sea water is 35 ohm⁻¹cm² per equivalent. The dissolution of one millimole of calcium carbonate crystal into dissolved calcium bicarbonate, therefore, should increase the specific conductance by 7×10^{-5} ohm⁻¹cm⁻¹. Since the specific conductance of the sea water was about 0.05 ohm⁻¹cm⁻¹, the dissolution of one millimole of calcium carbonate should change the conductance by about 0.14 percent (Fig. 1).

In addition, in the presence of excess carbon dioxide, the carbonate ion present initially will transform into bicarbonate ion. Sodium carbonate and