centimeter (S.T.P.) quantities, and were measured with standard thermal conductivity equipment.

The most important general limitation on recycling indefinitely is reached when the material has spread and fills one entire section of the column. Thus, the separation of Fig. 3 could be continued until this point is reached; alternatively, the front of the peak to point *A* can be isolated, removed, and reinjected for a second passage. The separations reported here are typical, but optimum operating conditions for separation have not yet been systematically determined in any system. The technique has been used for 10- to 20-ml gas samples with the present equipment.

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Dolomitization: Observations on the Island of Bonaire, Netherlands Antilles

Abstract. *Evaporation of sea water and gypsum precipitation on south Bonaire produce dense brines having a high ratio of magnesium to calcium. Recent dolomite is a common replacement product in the associated carbonate sediments. A mass balance indicates that brine is being refluxed downward today, and the Pleistocene dolomite on north Bonaire could have been produced by similar reflux of brine.*

The problem of dolomitization of limestones [replacement of $CaCO_3$ by $CaMg(CO_3)_2$] has intrigued geologists for the last 100 years. Although many mechanisms have been proposed to explain dolomitization, no mechanism has yet been generally agreed upon. Observations which we recently made on the island of Bonaire in the Netherlands Antilles are consistent with the mechanism proposed to explain the dolomite found in the Permian Reef Complex (*1*).

In this proposed mechanism, the evaporation of sea water results in the precipitation of gypsum, which raises the ratio of magnesium to calcium of the water. The magnesium-rich water is capable of dolomitizing limestone and flows downward through the underlying sediments because it is more dense than fresh water or normal sea water. A similar mechanism has been proposed by Adams and Rhodes (*2*).

The south end of the island of Bonaire is a flat terrain close to sea level but isolated from the sea by a low coral rubble ridge. Exposed flats of soft, wet, Recent carbonate sediments cover about 34 m², and a number of hypersaline lakes are enclosed in the area by the coral rubble ridge. The sediments are composed of gypsum, aragonite, calcite, and dolomite. Most sediments from south Bonaire contain some dolomite, and some crusts are composed of as much as 95 percent of this mineral. Radiocarbon dating of two dolomite samples from these crusts gave ages of 1480 ± 140 and 2190 ± 150 years. The composition of the dolomite, determined by x-ray diffraction, ranges from $Mg_{46}Ca_{54}$ to $Mg_{44}Ca_{56}$. The ordering peaks 10·1, 10·5, and 20·1 of dolomite are visible on the x-ray powder pattern. The dolomite crystal size is about 2 microns, and replacement of shells demonstrates that at least some if not all of the dolomite was formed by replacing calcium carbonate.

Chemical analyses of the water in the hypersaline lakes and from pits in the Recent sediment indicate that the water has molar magnesium/calcium ratios which average about 30/1 compared with 5/1 in sea water. The results of a number of water analyses are plotted in Fig. 1. The logarithm of the chloride concentration is plotted against the logarithm of the concentration of the other ions. The data indicate that during evaporation of the original sea water, these waters have lost calcium carbonate and calcium sulfate, but there has been no detectable loss of magnesium. The water analyses are in general agreement with data of Usiglio (in Clarke, *3*) and confirm the gypsum solubility data of Posnjak (*4*) on gypsum.

Gypsum is a common mineral on the extensive flats of south Bonaire and is the predominant mineral in the sediments under the bottoms of the hypersaline lakes. On the other hand, the absence of halite and other late evaporite minerals in the sediments indicates

Table 1. Mass balance of Pekelmeer per unit area per year.

Source	g cm^{-2} year^{-1}					
	H_2O	Cl^-	$SO_4^=$	HCO_3^-	Mg^{++}	Ca^{++}
Sea water influx	85	1.6	0.23	0.012	.11	0.035
Rainfall	77					
Chemical precipitates	−0.015		−.07	−.005*		−.031
Evaporation	−150			−.005*		
Reflux	−12	−1.6	−.16	−.002	−.11	−.004

* $2HCO_3^- + Ca^{++} \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O\uparrow$.

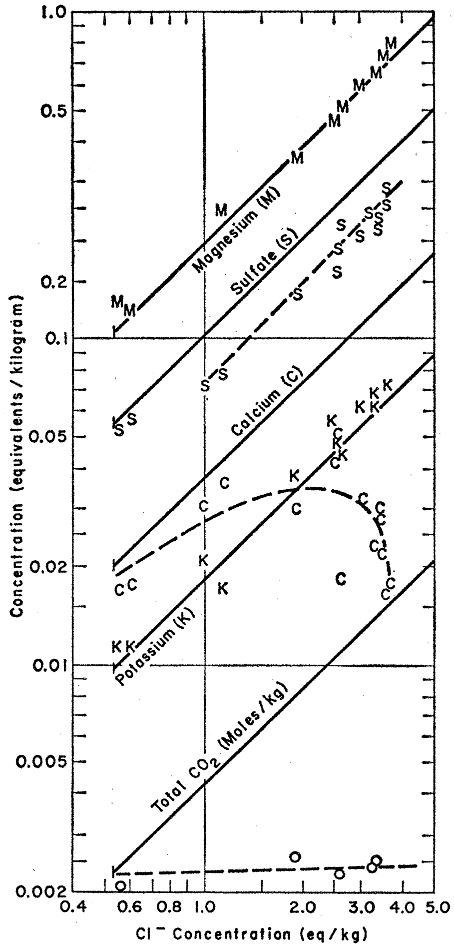

Fig. 1. Analysis of evaporite waters. Solid lines represent simple concentration of ions with evaporation. Dashed lines show the deviation of the actual concentrations from the solid lines.

that south Bonaire is not a closed evaporating pan.

We made detailed observations on the largest of the hypersaline lakes, the Pekelmeer. We located the major zone where sea water was seeping into the lake through the coral rubble ridge and measured the rate of influx. It was sufficient to account for the difference between the rate of evaporation from the lake estimated from the evaporative pan experiments on Curaçao and the rate of rainfall given by Westermann and Zonneveld (*5*). The absence of halite in the lake sediments and the fact that the lake water was only about seven times the concentration of sea water indicate that there must be a continuous loss of hypersaline water from the lake. The coral rubble ridge forms a natural dike around south Bonaire which does not allow surface loss of hypersaline water. We therefore must conclude the subsurface flow (reflux) takes place through the bottom of the lake. Reflux occurs because the density of the hypersaline water is higher than the density of the other waters present, and thus is related to evaporation. Because the interstitial water as well as the lake water is evaporating, reflux should be occurring from the entire area of south Bonaire. A mass balance of the water and the salts in the Pekelmeer allows us to estimate the rate of this reflux. The specific rates are given in Table 1.

We do not know the geometry of the refluxing waters beneath south Bonaire, nor were we able to examine the diagenesis produced by these magnesium-rich waters in traversing the older sediments. However, observations on north Bonaire suggest that Pleistocene limestones have been dolomitized by refluxing evaporite waters.

On the leeward side of north Bonaire are seaward-dipping Pleistocene or Pliocene carbonate rocks. The dip of the Pliocene-Pleistocene carbonate rocks is similar to the depositional dip of the lime sands being deposited today off the leeward coast of Bonaire, and petrographic comparison shows that the Recent sands and the Pliocene-Pleistocene rocks are very similar in sedimentary texture and fauna. We agree with Martin (*6*) and Schaub (*7*) that the dip is primary. The reconstruction of the Pliocene-Pleistocene topography of north Bonaire shown in Fig. 2 is based on the relationship between the Recent offshore sands and the Recent exposed carbonate flats. Thus, it is inferred that an area similar to south Bonaire existed above the Pliocene-Pleistocene rocks. Large dolomitized areas in the Pliocene-Pleistocene limestones cut across the bedding. The dolomite rhombs average 75 microns, and the composition determined by x-ray diffraction ranges from $Mg_{46}Ca_{54}$ to $Mg_{44}Ca_{56}$. The fact that dolomite is most abundant at the upward edge of the outcrop suggests downward movement of the dolomitizing water. The reflux of dolomitizing water from an area similar to south Bonaire would produce such a geometry in the underlying marine deposits.

The adequacy of the reflux mechanism observed on south Bonaire to explain the Pliocene-Pleistocene dolomites on north Bonaire is shown by the following calculation. The Pleistocene topography of north Bonaire could have had an evaporating surface of 10 km^2. A yearly net evaporation rate of 100 cm would evaporate a total of 10^{10} kg of sea water per year. This would supply 5 × 10^8 moles of magnesium ion per year. A rough estimate indicates that the inclined beds contain about 0.5 cubic kilometer (5 × 10^{14} cm^3) of dolomite. Therefore, the time required to form the estimated volume of dolomite is of the order of 10^5 years.

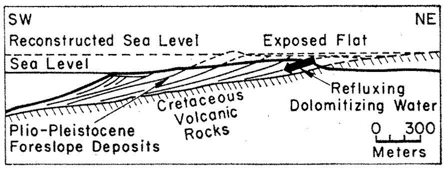

Fig. 2. Reconstruction of Pliocene-Pleistocene dolomitization.

Although these estimates do not prove that the inclined beds were dolomitized by the proposed mechanism, they indicate that the mechanism is adequate for the time available. We are not aware of any other mechanism of dolomitization that can explain qualitatively this amount and distribution of dolomite in about a million years. We believe that the conditions that occur on Bonaire may have existed many times in the past. The fine-grained Recent dolomites found on south Bonaire are similar to many ancient dolomites commonly interpreted as "primary" or "penecontemperaneous," and the Pliocene-Pleistocene dolomites from north Bonaire are very similar to the "secondary" or "replacement" dolomites found in older rocks.

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