

**INTERGOVERNMENTAL OCEANOGRAPHIC COMMISSION**  
(of UNESCO)

**CO<sub>2</sub> DISPOSAL IN THE OCEANS**

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Although much experimentation is currently taking place internationally on the possibility of disposing of CO<sub>2</sub> in the oceans, there is concern that this matter is not being addressed yet at the Intergovernmental level. Clearly the prospect of large scale environmental modification made possible by such disposal or by large scale experimentation on such disposal should be a matter for intergovernmental concern, and the IOC is an appropriate forum in which to discuss the issue and its implications. Accordingly, the Executive Secretary has invited Peter Brewer of the Monterey Bay Aquarium Research Institute (MBARI) to address the IOC-EC on the subject. Background to the issue is provided in the attached paper by Peter Brewer on Direct Experiments on the Ocean Disposal of Fossil Fuel CO<sub>2</sub> (*Science* 284, 943-945, 1999). The Executive Council will be asked to approve a Resolution requesting the IOC Executive Secretary to take the matter up with the Subsidiary Body for Scientific and Technological Advice (SBSTA) to the UN Framework Convention on Climate Change (UNFCCC) prior to the next Conference of the Parties of the UNFCCC, so that the question of the experimentation needed for any consideration of CO<sub>2</sub> disposal in the ocean can be brought to the attention of the Parties at their COP-VI meeting later this year.

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**SCIENCE**

**Direct Experiments on the  
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# Direct Experiments on the Ocean Disposal of Fossil Fuel CO<sub>2</sub>

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Field experiments were conducted to test ideas for fossil fuel carbon dioxide ocean disposal as a solid hydrate at depths ranging from 349 to 3627 meters and from 8° to 1.6°C. Hydrate formed instantly from the gas phase at 349 meters but then decomposed rapidly in ambient seawater. At 3627 meters, the seawater-carbon dioxide interface rose rapidly because of massive hydrate formation, forcing spillover of the liquid carbon dioxide from the container. A strong barrier between the liquid carbon dioxide and interaction with the sediments was observed. A pool of liquid carbon dioxide on the sea floor would expand in volume more than four times, forming hydrate, which will dissolve.

One possibility for the disposal of fossil fuel CO<sub>2</sub>, in order to forego atmospheric emissions and the concomitant enhancement of the atmospheric greenhouse effect, is to place it in the deep ocean (1). Fossil fuel CO<sub>2</sub> in the atmosphere is already passively absorbed by the ocean, in the amount of some 2 GT of carbon per year (2). The invading wave of atmospheric CO<sub>2</sub> has already dramatically altered the chemistry of surface seawater worldwide (3), and over much of the ocean this tracer field has now penetrated to a depth of >1 km.

We conducted a set of deep-sea experiments on the direct injection of CO<sub>2</sub> in both the liquid and gas phase into seawater under various pressure and temperature conditions (4, 5). The experiments were carried out to extend laboratory pressure vessel studies (6) to real world conditions and to begin evaluating the various models proposed for disposal of fossil fuel CO<sub>2</sub> in seawater. The advantages of ocean experiments lie in their fidelity as tests for industrial processes, their incorporation of the fluid dynamics and reactions of the open release, and the ability to study marine biological responses and sediment geochemical interactions.

Two key features make deep ocean disposal attractive. First, because of the large size of the ocean and the geochemical buffer provided by the alkalinity of seawater,  $[(\Delta PCO_2 / PCO_2) / (\Delta TCO_2 / TCO_2)] \approx 10$  ( $P$  = pressure and  $T$  = temperature), and the carbonate sediments, little disposed material will return to the atmosphere (7). Second, CO<sub>2</sub> can react with water at low temperature and

high pressure to form a solid hydrate (8), which might sequester CO<sub>2</sub> from the geochemical cycle. Much uncertainty surrounds the process. Although pure CO<sub>2</sub> hydrate is denser than seawater and will sink, in practice occluded gas and liquid can make globules rise (6). Formation of hydrate is exothermic, and the release of heat and rejection of salt may generate local instabilities that strongly affect the system.

We carried out a series of five experiments off the coast of central California. At an appropriate temperature and pressure (Fig. 1), CO<sub>2</sub> in excess of that required to saturate the surrounding seawater may exist as a gas and will react to form a hydrate. In an experiment conducted at a depth of 349 m and at 8°C, we released CO<sub>2</sub> into an inverted glass beaker. A mass of bright, white hydrate with occluded gas formed immediately along with a bubble of excess gas at the top of the beaker (Fig. 2). Compression of the mass of hydrate and gas bubbles as the vehicle descended below 349 m caused flakes of hydrate to fall into the ambient seawater outside the beaker, where they appeared to dissolve in seconds (9).

We released about 50 ml of liquid CO<sub>2</sub> (10) at a depth of 430 m into an inverted beaker. The liquid mass became coated with a thin hydrate film, but the ensemble was strongly buoyant because of density differences between liquid CO<sub>2</sub> and seawater. When the CO<sub>2</sub> mass was released, it broke down into smaller globules that rose rapidly. It was possible to fly the 3000-kg vehicle upward at a rate equal to the rise rate of the released CO<sub>2</sub> (18 to 20 m/min) and to maintain visual contact with the plume as it passed through the liquid-gas phase boundary. Estimation of the ascent rate of a CO<sub>2</sub> release within the hydrate-forming region has been the object of much study (6) and is an essential goal of large CO<sub>2</sub> release experiments

being planned (11). Visual contact was lost shortly after the gas-phase boundary was crossed.

The method of injection caused changes in the surface area of the hydrate formed and in its dissolution rate. At a depth of 905 m we created, by vigorously injecting liquid CO<sub>2</sub> through a narrow-bore tube, a mass of flocculant hydrate (Fig. 3), completely filling the inverted 2-liter beaker. The hydrate remained trapped and buoyant. The apparatus was left moored in place; 17 days later, all the hydrate had disappeared either by dissolution in the beaker or by sinking into the surrounding water. The result of a much slower release of liquid CO<sub>2</sub> at this depth into a 1-liter reaction chamber was that a two-layer CO<sub>2</sub>-water system, stable for the several hours of observation, was formed. Even mechanical mixing back and forth across the interface did not create a hydrate mass; thus, energetic water-CO<sub>2</sub> mixing is required to promote large-scale hydrate formation.

At 2°C and at depths greater than about 2600 m, liquid CO<sub>2</sub> is denser (12) than seawater (Fig. 4). We placed a frame containing a 4-liter beaker and a glass tube (diameter, 30 × 17.5 cm) on the ocean floor at a depth of 3627 m and a temperature of 1.6°C. In this region the liquid CO<sub>2</sub> should be significantly denser than the local seawater and less dense than the hydrate. Liquid CO<sub>2</sub> in the beaker was exposed only to seawater, whereas the CO<sub>2</sub> in the open tube was exposed to seawater

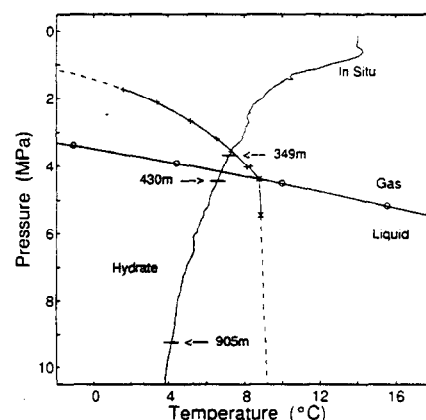


Fig. 1. A typical ocean water column temperature-pressure profile (solid line) for the experimental area off Monterey Bay, California, with the phase boundaries for the gas-liquid transition of CO<sub>2</sub> (○) and CO<sub>2</sub> hydrate formation (+), the gas-seawater hydrate boundary (×), liquid CO<sub>2</sub>-seawater hydrate boundary (□) overlaid for reference. The quadruple point, where all four phases coexist, is indicated (\*). Shaded region is the area where CO<sub>2</sub> hydrate is stable if a sufficient amount of CO<sub>2</sub> is present. Depths for four of the five releases are indicated: experiment 1 at 349 m, experiment 2 at 430 m, and experiments 3 and 4 at 905 m. At this latitude and in this depth interval, 1 MPa is approximately equivalent to 99 m.

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ter on the upper surface and to sediment on the lower surface. The surrounding sediment was also used for free-release studies.

The beaker was filled (10) about half full with  $\text{CO}_2$ , which was expelled slowly from a small-bore tube. Initially, the individual drops did not coalesce; instead they appeared as of a pile of translucent marble-sized spheres. When they did coalesce, the surface of the  $\text{CO}_2$  phase had a strongly curved and lobate shape. A significant increase in volume was soon observed. About 100 min after the initial release, the  $\text{CO}_2$  phase volume had increased to fill the beaker. As the volume continued to increase, the liquid  $\text{CO}_2$  overflowed onto the sea floor (Fig. 5). Fifteen similar overflow events occurred over the next 80 min (13). Some hydrate was formed at the bottom of the beaker early in the experiment. Its translucence and optical properties, closely similar to the liquid phase, made it difficult to determine the amount and exact position of the solid-liquid interface.

About 1.8 liters of liquid  $\text{CO}_2$  was also delivered into the larger tube (volume, about 7 liters) and exposed to the sea floor at one end. Again, the individual drops eventually

coalesced into a larger mass and the volume increased steadily to cause overflow after 283 min. Motions at the surface were easily observed, with schlieren in the overlying seawater, presumably from the dissolution of  $\text{CO}_2$ , the release of heat, and the rejection of salt by the hydrate-formation process.

The  $\text{CO}_2$  that spilled onto the sea floor did not penetrate or appear to react with the sediment in any way. It was highly mobile and, because the experimental site was on a slight slope, much of the material rolled out of view. Sediment particles did not stick to its surface as it moved. We excavated a small hole in the sediment in an attempt to contain the material. However, the density of the  $\text{CO}_2$  globules was only slightly greater than that of the surrounding seawater and passing eddies easily disturbed the liquid. The strong surface tension of the  $\text{CO}_2$  resulted in disappearance of the entire blob as a unit. Freely released  $\text{CO}_2$  was so mobile that it was difficult to determine whether volume changes were occurring. In addition, the presumed presence of a hydrate skin did not impede movement of the  $\text{CO}_2$  globules on the sea floor (14).

Reaction of 1 mol of  $\text{CO}_2$  with 5.75 mol of water to produce hydrate should yield an increase in volume of about a factor of 3 under these conditions; we observed a volume increase much larger than this, perhaps as much as a factor of 4 to 7. Thus, it appears that a metastable phase with a large number of vacancies and trapped brine formed in the first few hours, displacing the remaining liquid  $\text{CO}_2$  upward and forcing overflow. Attempts to model this process

have been published (15, 16). Had our experiment been sited much deeper, a floating skin of hydrate probably would have formed over the denser liquid  $\text{CO}_2$ . We calculate that this would occur at a depth of more than 4500 m. We were not able to observe the complete cycle of massive hydrate formation and dissolution. A thruster failure after 13 hours forced us to terminate the experiment. When we lifted the experimental frame, a block of ~7 liters of hydrate, formed in the open-ended tube, slid out and stood as a column on the sea floor. The near equivalence of the index of refraction of hydrate and seawater made visualization difficult.

These experiments imply that liquid  $\text{CO}_2$  on the sea floor, in the depth range 2700 to 4500 m, would quickly react with water, form hydrate, and swell to many times its original size. A rough approximation of rates based on these observations (17) suggests that the rate of hydrate formation was about 1.2 liters/hour. If we assume formation of a  $\text{CO}_2 \cdot 6\text{H}_2\text{O}$  hydrate, then the rate of water incorporation is about 0.94 liter/hour. This reaction is strongly exothermic [271 kJ/(kg of water)] (18); thus, the upper interface is releasing considerable heat and rejected brine.

Ideas of "permanent" disposal of  $\text{CO}_2$  as a hydrate on the sea floor probably are not realistic, although quite long residence times may very well be possible—first in the hydrate phase and later because of the long ocean circulation time scales. The necessity for equality of chemical potential in all three phases as a condition for hydrate stability [ $\mu_{\text{aq}} = \mu_{\text{CO}_2} = \mu_{\text{clath}}$ ] has long been known (19), but background ocean  $\text{CO}_2$  levels are far from saturation. Ocean disposal of  $\text{CO}_2$  remains attractive for the basic reasons of enormous reservoir size, the ability of the carbonate sediments to restore buffer capacity, the long circulation times of the ocean, and a

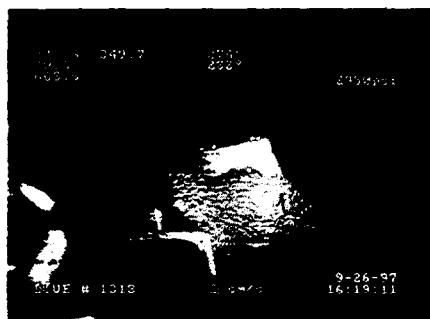


Fig. 2. Image of  $\text{CO}_2$  hydrate formation from the gas phase at a 349-m depth,  $T = 8^\circ\text{C}$ , showing white hydrate rind on the bubble skin. Image overlay shows depth in meters (top left) and date time (bottom right).



Fig. 3. Mass of flocculant  $\text{CO}_2$  hydrate created at a 905-m depth,  $T = 4^\circ\text{C}$ , by vigorous injection of liquid  $\text{CO}_2$  through a small-bore tube. The pure hydrate density is greater than that of seawater but at the time of formation in this manner occluded liquid  $\text{CO}_2$  and trapped water warmed by the heat of formation create a buoyant mass.

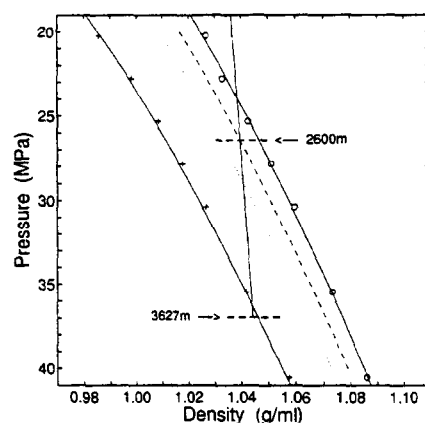


Fig. 4. Pressure-density curves of liquid  $\text{CO}_2$  at various temperatures overlaid on the pressure-density profile for our experimental region. The curves for  $0^\circ\text{C}$  (o) and  $10^\circ\text{C}$  (+) were fit to experimental data; the curves for  $4^\circ\text{C}$  (---) and  $2^\circ\text{C}$  (---) were obtained by linear interpolation. In practice the neutrally buoyant point is reached at about 26.50 MPa (2600 m). Our controlled release took place at 36.95 MPa (3627 m) and the ambient temperature was  $1.6^\circ\text{C}$ .



Fig. 5. Overflow of liquid  $\text{CO}_2$  from the 4-liter beaker onto the sea floor at a 3650-m depth. A mass of transparent hydrate ( $\text{CO}_2 \cdot 5.75\text{H}_2\text{O}$ ), formed at the upper interface, sank to the bottom of the beaker and pushed out the remaining liquid  $\text{CO}_2$ . Ejected liquid  $\text{CO}_2$  was highly mobile and did not appear to penetrate, or interact with, the sediments.

favorable equilibrium with the atmospheric reservoir. Formation of a hydrate is but one component of the ocean disposal process, and it can have a dramatic effect.

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- For injections at depths of <1000 m we used the R/V *Point Lobos* and ROV *Ventana*. The 3627-m experiment was carried out using the R/V *Western Flyer* and the ROV *Tiburon*. The R/V *Western Flyer* is a 35.7-m SWATH (small waterplane area twin hull) ship with a center "moon pool" for ROV deployment. *Tiburon* is a 4000-m capable ROV attached to the mother ship by an armored steel cable with both copper power conductors and single-mode optical fibers for communication and control. Six 3.7-kW electric thrusters supply thrust. The vertical ascent speed is 100 feet/min (30.48 m/min). The experiments were imaged by the vehicle cameras and data were recorded on videotape. The *Ventana* observations were made with a Sony DXC-3000 three-chip camera, and the *Tiburon* made observations with two Panasonic VW E5550 three-chip cameras, with data recorded in digital beta format. Ocean temperature, pressure, and conductivity were sensed continually by a CTD package (Falmouth Scientific) attached to either vehicle within 2 m of the experimental chambers.
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- Liquid CO<sub>2</sub> injections were carried out by expulsion from a reservoir by a piston, activated on command from the vehicle control room. For the shallow releases a small volume (~500 ml) steel cylinder was used. For the 3627-m experiment about 9 liters of liquid CO<sub>2</sub> was contained in a commercial accumulator (Parker A4N0578D1) installed horizontally in the tool sled frame. The accumulator was connected to a set of valves and fittings, which permitted loading of the cylinder with liquid CO<sub>2</sub> from standard gas cylinders before the dive. Procedurally, after the first filling, an accumulator gauge pressure of about 600 pounds per square inch (psi) was observed, with the piston set at maximum accumulator capacity. The gas delivery cylinder was then warmed (to compensate for expansion cooling on CO<sub>2</sub> transfer), and the accumulator was packed in ice to lower the temperature of the contained CO<sub>2</sub>. A second filling was carried out, and the ice was removed. The filled accumulator was vented to about 750 psi as it warmed to room temperature to prevent overpressure. The system was configured to permit open contact between seawater and the ocean side of the accumulator piston. As the vehicle dived, and pressure increased, the decrease in volume of the contained liquid CO<sub>2</sub> was compensated for by active piston motion to maintain pressure equality. Camera inspection of the pressure gauge during the dive showed the expected drop in accumulator pressure as the pressure-temperature boundary for liquid CO<sub>2</sub> was approached (in practice at a depth of about 400 m), and the differential pressure across the piston dropped effectively to zero. A system check was carried out by opening the quarter-turn CO<sub>2</sub> release valve at several depths during deployment, thereby venting small amounts of liquid CO<sub>2</sub>.
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- The total volume of the glass tube was ~7.22 liters (diameter, 30 × 17.5 cm) and the initial volume of liquid CO<sub>2</sub> was 1.8 liters. It is possible to calculate the minimum rate of water incorporation, assuming that the rate of filling [(7.2 liters - 1.8 liters)/4.5 hours = 1.2 liters/hour] was equivalent to hydrate formation, hydrate density was 1.1 kg/liter, and water accounted for 71% of the mass of the hydrate (CO<sub>2</sub>·6H<sub>2</sub>O): rate = 1.2 liters/hour × 1.1 kg/liter × 0.71 = 0.94 kg/hour. The actual rate is somewhat faster as some CO<sub>2</sub> is incorporated into the hydrate.
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