# Oxygen Loss in Biosphere 2

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Oxygen concentrations have dropped sharply in the air of "Biosphere 2," an enclosed experimental ecosystem located in southern Arizona. Biosphere 2 is a 3.15-acre airtight structure roofed in glass and underlain by an impermeable liner. It houses an artificial ecosystem containing soil, air, water, flora, and fauna and was built primarily as an apparatus for the experimental investigation of biogeochemical cycles, whole ecosystems, and life-support systems for space habitation [see Nelson et al., 1993].

O_2 in Biosphere 2 decreased during the first 16 months of closure from the ambient 21% to 14%, enough to cause health problems in the human occupants. We present evidence that the O_2 loss is caused by microbial respiration of the excessive amount of organic matter incorporated into the experiment's soils and furthermore, that the respired CO_2 is reacting with the structure's concrete to form calcium carbonate.

Oxygen and Carbon Budgets for Biosphere 2

Biosphere 2's soils are rich in organic matter. The topsoil was manufactured from a mix of 70% clay loam obtained locally, 15% commercial compost, and 15% commercial peat (volume proportions). In addition, plant growth is limited by the fact that only about 45% of ambient light penetrates the glass cover. Therefore, an obvious hypothesis for the O_2 loss is that photosynthesis (that is, addition of biomass) has not kept up with respiration (that is, microbial oxidation of soil organic matter). Thus, the O_2 would have been consumed by the reaction:

$$O_2 + CH_2O \rightarrow CO_2 + H_2O \qquad (1)$$
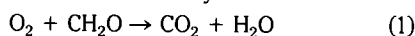
where CH_2O approximately represents soil organic matter.

Because one mole of CO_2 is produced for each mole of O_2 consumed, this hypothesis predicts that the same number of CO_2 molecules should have appeared in the air as the number of O_2 molecules removed from the air.

As can be seen in Figure 1, the increase of CO_2 in the air is less than 0.5%. However, an important CO_2 sink in Biosphere 2 is the chemical scrubber similar to those used on submarines, which has taken up an amount of CO_2 equivalent to 1.5%, so that the total increase of CO_2 would be 2%. This is still much less than the O_2 decrease of 8%, so this hypothesis fails. In other words, the amount of evolved CO_2 is not nearly as

much as would be expected if the O_2 loss were attributable to respiration alone.

Instead, some nonrespiratory process must be consuming O_2, or alternatively, respiration must be occurring in conjunction with an unidentified process that captures CO_2. Table 1 quantifies these two options.

We discuss four observations: abnormally high levels of $CaCO_3$ in Biosphere 2 concrete, a ^{13}C deficit in new vegetation, seasonal changes in the rate of O_2 or CO_2 loss, and a soil gas O_2 and CO_2 concentration profile.

Excess $CaCO_3$ in Biosphere 2 Concrete

CO_2 from the air commonly reacts with calcium hydroxide in cast concrete in the carbonation reaction:

$$CO_{2(aq)} + Ca(OH)_{2\ (s)} + \rightarrow CaCO_{3\ (s)} + H_2O_{(aq)} \qquad (2)$$
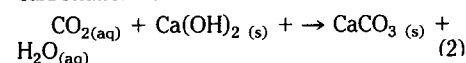
To test the hypothesis that carbonation is a significant sink for CO_2 in Biosphere 2, on June 7, 1993, we took twelve cores of concrete from representative locations in Bio-
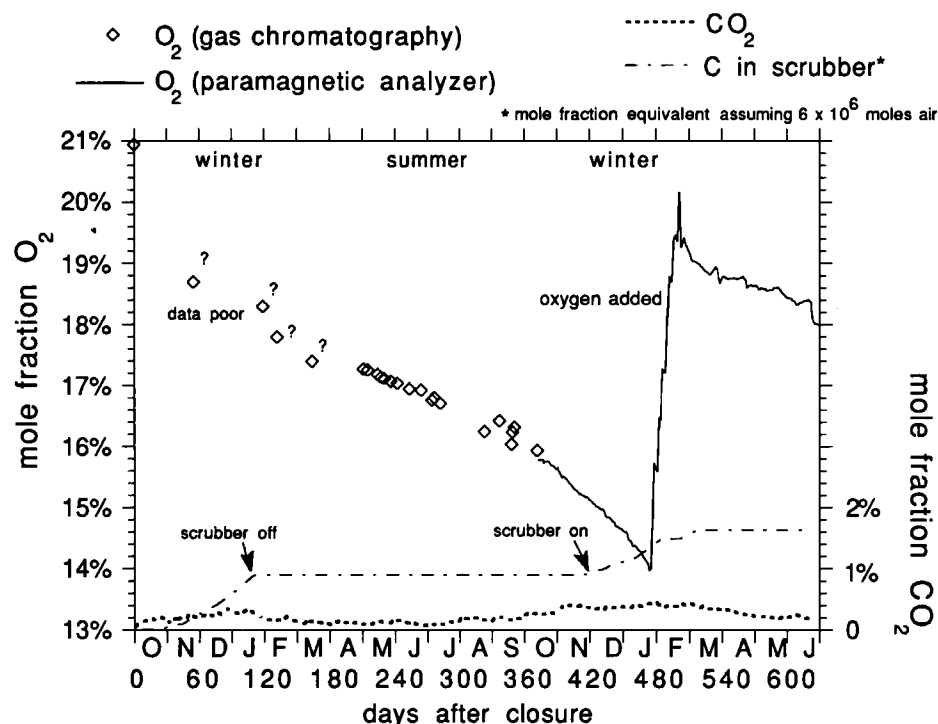
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Fig. 1. Oxygen and CO_2 history in Biosphere 2. The same scale is used for O_2 and CO_2 with a 13% offset. Note that oxygen drop is much greater than CO_2 increase, even taking into account the chemical scrubber. This requires the existence of a sink of O_2 or CO_2 other than respiration or photosynthesis.

sphere 2. For comparison purposes we also took four cores from outside walls of Biosphere 2, in concrete poured at the same time as the concrete on the inside. The four cores were taken from rooms that have humidity similar to the inside of Biosphere 2 but only the ambient ~350 ppm CO_2 instead of the 2000–4000 ppm CO_2 found inside Biosphere 2.

Small ~100-mg chips of concrete at regular depth intervals were removed from the centers of the cores with a hammer and awl. The chips were pulverized and analyzed for $CaCO_3$ content by a standard coulometric technique employing acidification in HCl followed by quantitative titration of the evolved CO_2 in a photoindicator solution. Analytical uncertainty is less than 1%. A total of 136 analyses were made.

The results show that carbonation in Biosphere 2 concrete is deeper and more intense than in outside concrete (Figure 2). Judging from the areas under the curves, carbonation has proceeded about ten times faster in an atmosphere ten times richer in CO_2. This is as expected from Fick's first law of diffusion and confirms other reports that the rate of carbonation is diffusion-limited. The consistently low values found at depths greater than 3 cm reassure us that no contamination occurred during drilling or transport of the cores.

We are interested in the number of moles of C taken up by the concrete since closure in September 1991, not since pouring in 1989. Since carbonation occurs rapidly after pouring, there could be a large difference between these values. To get around this problem we take the difference between the inside and outside profiles (Figure 2). Pre-closure measurements of Biosphere 2 air indicate that pCO_2 was the same as outside, that is, it was well-flushed. Therefore, any difference between inside and outside profiles must have accrued since closure. Table 2 details the calculation.

The result of 750 ± 250 kmol is more than enough to satisfy the 550 ± 38 kmol of respiration CO_2 required to explain the missing O_2 (Table 1), albeit with large error bars. Therefore, the concrete analysis strongly suggests that respiration is the main O_2 sink in Biosphere 2, and concrete is the unidentified CO_2 sink.

Carbon Isotopic Evidence

Samples of soils, plant matter, concrete, and calcium carbonate from inside Biosphere 2 were analyzed for their carbon-13 content. Results are given in the $\delta^{13}C$ notation:

$$\delta^{13}C = \left[\frac{^{13}C/^{12}C(\text{sample})}{^{13}C/^{12}C \ (\text{PDB})} - 1 \right] \times 10^{13} \ \permil$$

PDB = Peedee Belemnite Standard

Soil organic matter is the dominant original source of the C used by the plants in Biosphere 2 to produce any net biomass increase. As shown in Figure 3, soil organic matter in Biosphere 2 has a $\delta^{13}C = -22\pm1$
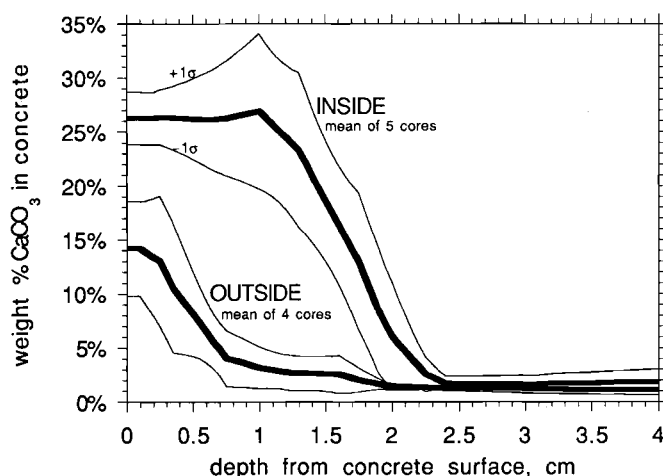

Fig. 2. Carbonation versus depth in Biosphere 2 concrete. Note the carbonation front inside Biosphere 2 at about 2 cm depth and the more intense carbonation on inside than outside. The area between the curves yields an estimate of 550 kmol $CaCO_3$ formed since closure. Artificial rock in Biosphere 2 (not shown) is made of concrete and gives an additional 200 kmol $CaCO_3$.
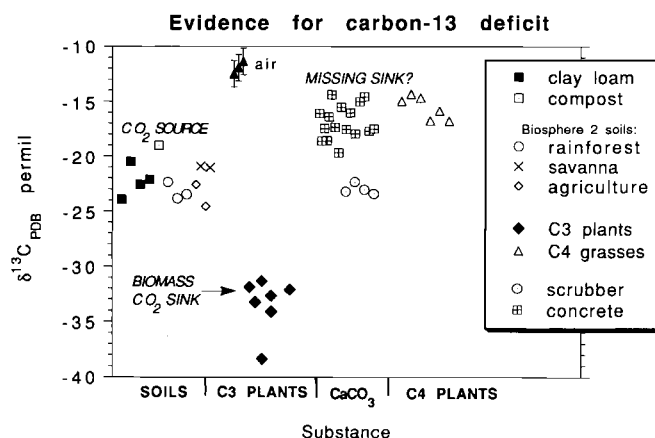

Fig. 3. C isotopic composition versus substance type. Data is spread out arbitrarily on the horizontal axis for visual clarity. Note the deficit between C entering the atmosphere from soil (-22 ‰) and the C leaving the atmosphere in most plants (-33 ‰). Since the mean isotopic composition of C entering and leaving the system must be equal, an unidentified sink rich in ^{13}C must exist. Concrete has the right isotopic composition (-16.8 ‰) to satisfy this constraint.

‰. Since soil respiration does not fractionate C isotopes [Cerling, 1984], and the residence time of CO_2 in the air is only a few days, the mean isotopic composition of new biomass should also be -22 ‰, if the new biomass were the only sink of CO_2. In fact, the new biomass is distinctly depleted in ^{13}C relative to the soil (Figure 3), with an average $\delta^{13}C$ of about -30±2 ‰†.

This depletion requires the presence of an unaccounted-for sink of CO_2 in addition to the new biomass and further requires that this sink be richer in ^{13}C than soil organic matter. Such a sink cannot be the scrubber because its $\delta^{13}C$ is identical to the soil's

† There are two types of plants, C3 and C4. The C4 plants use a different photosynthetic mechanism that results in biomatter richer in ^{13}C than that of C3 plants [Marino and McElroy, 1991], so they tend to raise the mean $\delta^{13}C$ of new biomass. Anecdotal reports from inside Biosphere 2 indicate that C4 plants contribute about 15% of new biomass (L. Leigh, personal communication, 1993), in keeping with estimates for natural ecosystems [Schlesinger, 1991]. The $\delta^{13}C$ of Biosphere 2 C3 plants is about -33 ‰ and that of C4 plants is about -15 ‰ (Figure 3). So the mean $\delta^{13}C$ of new biomass is about (-15 - -33) x .15 + -33 = -30 ‰.

(Figure 3). Concrete, however, could be the unidentified sink, since the average $\delta^{13}C$ of fifteen samples is -16.8±0.4 ‰.

If we assume that the concrete is in fact the missing sink, the quantity of CO_2 taken up by this sink can be roughly estimated from the isotopic data. The concrete is five permil richer and the biomass eight permil poorer in ^{13}C than the soil, so the amount taken up by the concrete should be 8/5 of the amount taken up by the biomass. Independent estimates of the biomass increase are in the range of 300–900 kmol, implying that the concrete has taken up roughly 500–1500 kmol CO_2.

Other Observations

O_2 concentrations in Biosphere 2 appear to fall faster in winter than in summer (Figure 1) but are not matched by the corresponding increase of CO_2 expected of waning photosynthesis. This suggests that the unidentified sink of O_2 or CO_2 must work faster in winter than in summer. Since oxidative processes are temperature-activated, it is difficult to imagine an O_2 sink working faster in winter when temperatures are lower. On the other hand, pCO_2 is much higher in winter than in summer, and concrete is expected to take up CO_2 faster at high pCO_2

Table 1. Atmospheric Budget for Biosphere 2, Sept. 26, 1991—June 7, 1993

| | | kmoles ± 1σ* | |
		O_2	CO_2
Known inputs and outputs			
Air added on day 75		126 ± 4	—
Air dumped on day 474		-31 ± 2	$-1 \pm .1$
Pure O_2 added on days 475–494		441 ± 8	—
Total CO_2 taken up by scrubber		—	-98 ± 10
Estimated net leakage	+	2 ± 24	-2 ± 1
Total known inputs and outputs		538 ± 26	-101 ± 10
Change in atmospheric burden during period		-170 ± 8	11 ± 1
APPARENT O_2 LOSS AND CO_2 GAIN		-708 ± 27	112 ± 10
Possible explanations:			
SCENARIO 1:			
Soil respiration**		-120 ± 12	112 ± 10
O_2 consumed by unidentified O_2 sink	+	-588 ± 30	0
		-708 ± 27	112 ± 10
SCENARIO 2:			
Soil respiration		-708 ± 27	662 ± 40
CO_2 captured by unidentified CO_2 sink	+	0	-550 ± 38
		-708 ± 27	112 ± 10

*Estimated uncertainty
**Assumes O_2:C exchange ratio for soil respiration = 1.07 ± 0.05 [Keeling, 1988]

because of diffusion limitation. Support for this hypothesis is provided by a good linear anticorrelation (R=0.87) between pCO$_2$ and the first derivative of CO_2-corrected O_2 inventory*.

The concentrations of O_2 and CO_2 in soil gas provide another constraint. Soil respiration causes O_2 in soil gas to fall and CO_2 to rise with depth. At steady state, the relative concentrations reflect the relative loss or gain of each gas. Employing the diffusion-reaction equation for O_2 and CO_2 gives

$$\frac{R_{O2}}{R_{CO2}} = \frac{d[O_2]}{d[CO_2]}\frac{D_{O2}}{D_{CO2}} = -O_2\text{:C exchange ratio (3)}$$

where R_i = source/sink of gas i and D_i = diffusivity of gas i

We found $d[O_2]/d[CO_2] = -0.96 \pm 0.08$ in depth profiles of O_2 and CO_2 in Biosphere 2 soil. Since the diffusivity ratio is 1.27 [Handbook of Chemistry and Physics, 1987], the O_2:C exchange ratio appears to be about 1.2 ± 0.1 in the locations sampled. This is close to the value of 1.07 expected for ordinary respiration of typical soils [Keeling, 1988], in contrast to the ~2.0 expected if the missing sink were located in the soils.

We also attempted to measure O_2:C exchange ratios by sealing small samples of Biosphere 2 soils in airtight chambers and measuring the transient O_2 loss and CO_2 gain over time. In all five cases the chamber air lost more O_2 than it gained CO_2 by ratios ranging from 1.2 to 2.4 over a period of 8

days. This is suggestive that a soil reaction other than respiration may also contribute to loss of O_2 in Biosphere 2, but the limited number of samples plus problems with the methodology do not allow a conclusion to be drawn from this data without further work. The quantitative results of the foregoing data on concrete appear to account for the bulk of the O_2/CO_2 loss and would therefore preclude this possible reaction from accounting for a major fraction of the loss.

Discussion

We examined a variety of possible O_2-consuming reactions that could be occurring in Biosphere 2, including oxidation of reduced forms of nitrogen, sulfur, iron, hydrogen, and carbon. A major role for nitrogen and sulfur can be ruled out since Biosphere 2 ambient waters tested orders of magnitude lower in nitrate and sulfate than required, although a depressed Ar/N$_2$ ratio in the air suggests that 5–10% of the O_2 loss may involve nitrogen. A small role for ferrous iron in soil cannot be ruled out, although the soil gas profile does not support it. Oxidation of hydrogen, that is, organic matter rich in hydrogen such as lipids and waxes, seems unlikely because the compost and peat used in Biosphere 2 soils are typically poor in these compounds, and the soil gas profile is indicative of ordinary respiration, not oxidation of lipids.

The preceding evidence strongly supports oxidation of C as the cause of O_2 loss, accompanied by some CO_2 sink (scenario 2). We ruled out permeation leakage of CO_2 through the elastomeric seals and lung membranes based on known permeabilities of CO_2 in these materials [Dempster, 1994]. Under-reporting of scrubbed CO_2 can be ruled out because scrubber C is too depleted in ^{13}C to explain the isotopic deficit in new vegetation. CaCO$_3$ precipitation in soils would satisfy the isotopic evidence but not the wintertime loss rate nor the soil gas profiles. No new CaCO$_3$ precipitate has been found in the soils or soil drain pipes where scale buildup would be expected. Still, a small role for soil CaCO$_3$ cannot be ruled out, as a fraction of the 55 tons required to explain the O_2 loss could be hidden in the 30,000 tons of soil.

Table 2. Moles of CO_2 Taken Up by Concrete in Biosphere 2, Sept. 26, 1991—June 7, 1993

		estimate and estimated 1σ uncertainty
Structural concrete (5 cores):		
exposed unpainted area		$13{,}000 \pm 1000$ m^2
integral between inside and outside average profiles of weight % CaCO$_3$ (Figure 2)		34.7 ± 14 % cm
grams non-gravel fraction per cm^3 concrete	×	1.21 ± 0.16 g cm^{-3}
calculated CaCO$_3$ uptake by structural concrete		550 ± 240 kmole
Unpainted artificial rock (1 core):		
exposed unpainted area		2800 ± 300 m^2
integral between single inside profile and outside average profile of weight % CaCO$_3$ (not shown)		35.3 ± 14 % cm
bulk density	×	2.12 ± 0.07 g cm^{-3}
calculated CaCO$_3$ uptake by unpainted artificial rock		200 ± 90 kmole
Painted artificial rock (6 cores)	+	0
Total calculated CaCO$_3$ taken up by concrete during period of closure		750 ± 250 kmole

* CO_2-corrected O_2 inventory = airborne O_2 + (airborne CO_2 + scrubbed C) x 1.05 (mol)

Conclusions

Carbonation of concrete has proceeded roughly ten times faster inside Biosphere 2 than outside due to elevated CO_2 levels in the sealed structure. This process has absorbed 750 ± 250 kmoles of CO_2, comfortably meeting or exceeding the 550 ± 38 kmoles of CO_2 expected from respiratory consumption of Biosphere 2's O_2. Respiration *is* exceeding photosynthesis by roughly a factor of two, as originally hypothesized in equation (1), but the expected CO_2 increase is being masked by capture of of CO_2 in concrete. The carbon found in the concrete has the needed isotopic composition to explain an isotopic anomaly between vegetation and soil organic matter. Further support for the concrete theory comes from a wintertime increase in the loss rate of O_2 or CO_2 and depth profiles of O_2 and CO_2 in soil gas. We conclude that the cause of oxygen loss in Biosphere 2 is the high organic matter content of the soil combined with reduced light levels.

Acknowledgments

This paper was shortened to meet *Eos* specifications. The complete version with treatment of uncertainties is available in unpublished form from Nancy Mager, Lamont-Doherty Earth Observatory, Palisades, NY 10964.

References

Cerling, T. E., The stable isotopic composition of modern soil carbonate and its relation to climate, *Earth Planet. Sci. Lett., 71*, 229, 1984.

Dempster, W. F., Methods for measurement and control of leakage in Closed Ecological Life Support Systems and their application and performance in the Biosphere 2 facility, Workshop F4.4-M.1.10X, Congress on Space Research, Washington, D.C., Advances in Space Research, March 1994, in press 1994.

Handbook of Chemistry and Physics, CRC Press, Inc., Boca Raton, Fla., 1988.

Keeling, R. F., Development of an interferometric oxygen analyzer for precise measurement of the atmospheric O_2 mole fraction, Ph.D. thesis, Harvard University, 179 pp., 1988.

Nelson, M., T. L. Burgess, A. Alling, N. Alvarez-Romo, W. F. Dempster, R. L. Walford, and J. P. Allen, Using a closed ecological system to study Earth's biosphere: Initial results from Biosphere 2, *BioScience, 43*, 225, 1993.

Schlesinger, W. H., *Biogeochemistry: An Analysis of Global Change*, Academic Press, N.Y., 443 pp., 1991.

Washington, D.C., Schools to Improve Science Education

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The Carnegie Institution of Washington received a 5-year, $3.7-million grant from the National Science Foundation for the Carnegie Academy for Science Education (CASE). CASE is designed to help classroom teachers in the District of Columbia and improve the quality of science teaching in the city's elementary schools.

CASE will offer 6-week teacher training workshops at Carnegie's headquarters in Washington. The first session will take place this summer, and fifty teachers from five elementary schools will be selected to participate. Three of these schools already participate in Carnegie Institution's First Light Program, where third through sixth graders in the area attend "hands-on" science school at Carnegie on Saturdays during the year. Two of the schools also participated in a pilot teacher-training venture with Carnegie in 1992.

The CASE program is aimed at strengthening basic knowledge of science among teachers and providing several innovative methods for introducing science to young children. The program will try to bring children more actively into their own learning—to encourage them to ask questions about nature and to design experiments to answer the questions. By "doing" science, it is believed that the students will develop their critical thinking ability. CASE teachers will experience these same methods, which will better equip them to use the methods in their own teaching.

After the first year, 100 new teachers from other elementary schools will be enrolled in successive summer institutes. Selected CASE graduates will serve as mentor teachers to train new participants and coordinate science activities in their schools. In the 5 years of the NSF grant, CASE expects to form partnerships with about forty-five schools (over one-third of Washington's public elementary schools).

Grass roots planning and leadership for CASE will draw from two professions—science and science education. Ines Cifuentes (202-686-4389), an Earth scientist at Carnegie, will be the program coordinator, and Charles James (202-387-6404), an award-winning science teacher, will coordinate curriculum and instruction.
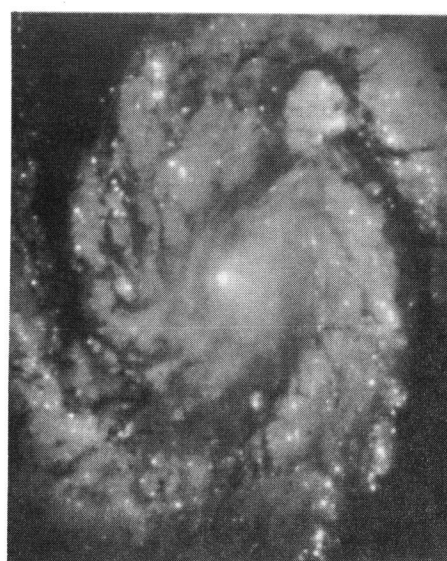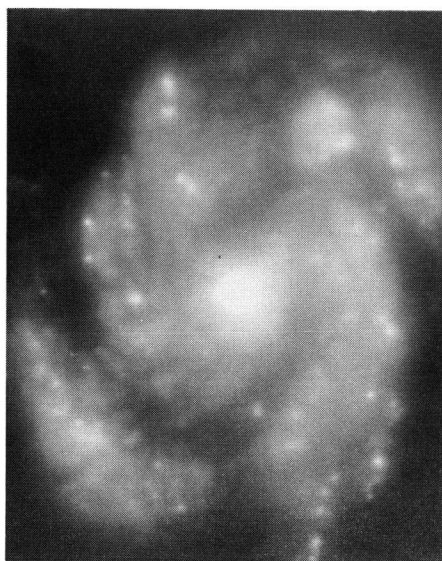
"The trouble with Hubble is over . . . " *said Barbara Mikulski (D-Md.) chairman of the Senate Appropriations Subcommittee on VA, HUD, and Independent Agencies at a press conference held at Goddard Space Flight Center in Greenbelt, Md., on January 13. NASA Administrator Daniel S. Goldin declared the Hubble Space Telescope's December repair mission to correct its optical components a success. Test images were released from the two cameras that received corrective optics during the repair mission. The comparison photographs above of galaxy M100's core show the dramatic improvement in HST's view of the universe.*