

analytical  
chemistry  
feature

## Charles David Keeling and the Story of Atmospheric CO<sub>2</sub> Measurements<sup>†</sup>

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When he was a postdoc in geochemistry at Caltech, Charles David Keeling found himself ideally prepared for the moment when funding for the International Geophysical Year enabled him to design and build a CO<sub>2</sub> monitoring station on Mauna Loa in Hawaii in 1957. He applied rigorous analytical procedures to a geophysical study with enormous implications for humanity.

The influence of Charles David Keeling (1928–2005) was described in 2005 with little exaggeration by his colleague C. F. Kennel at the Scripps Institution of Oceanography: “Keeling’s measurements of the global accumulation of carbon dioxide in the atmosphere set the stage for today’s profound concerns about climate change. They are the single most important environmental data set taken in the 20th century.”

### KEELING’S EDUCATION

Dave Keeling (Figure 1) was raised in the suburbs of Chicago during the Great Depression.<sup>1</sup> His Yale-educated investment banker father stimulated young Keeling’s interest in science by explaining how Earth’s tilt and orbit caused seasons. His mother, who studied English literature at the graduate level at Yale, endowed her son with a life-long love of music. Keeling “was not predominantly interested in science,” but took all the science offered in his high school, including a wartime aeronautics course that exposed him to aerodynamics, meteorology, navigation, combustion engines, and radio. At the age of 17, he entered the University of Illinois Urbana–Champaign where he “drifted into chemistry” and earned a general liberal arts degree because he refused to take the economics course required of chemistry majors. He had had enough economics from his father.

At the age of 20, Keeling accepted a graduate fellowship in polymer chemistry at Northwestern University offered by Malcolm Dole, a family friend who had known Keeling as a precocious youngster. Required to take a “noncontiguous minor”, Keeling

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MAUNA LOA OBSERVATORY IN 2006. COPYRIGHT FORREST M. MIMS III.  
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considered astrophysics but found no course of study. One day, he noticed the book *Glacial Geology and the Pleistocene Epoch* on a friend’s bookshelf. Keeling became so interested in the book that he bought a copy, read it between experiments in the lab, and imagined himself “climbing mountains while measuring the physical properties of glaciers.” In graduate school, he completed most of the undergraduate geology curriculum. Twice he went hiking and climbing in the Cascade Mountains of Washington



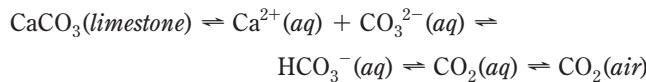
**Figure 1.** Dave Keeling (center) with project engineer Dave Moss (right) and data analyst Tim Whorf (left) on Mauna Loa. Photo courtesy of Ralph Keeling, Scripps Institution of Oceanography, University of California San Diego.

State and once joined a canoe trip in Canada during which he met his future wife, Louise.

Upon graduation in 1953, Keeling had job offers from chemical companies in the blossoming plastics industry in the eastern U.S., but he “had trouble seeing the future this way.” Though his graduate adviser considered it “foolhardy” to turn down good jobs, Keeling wrote letters offering his “services as a Ph.D. chemist exclusively to geology departments west of the...continental divide.” He soon became the first postdoctoral fellow with Harrison Brown in the new Department of Geochemistry at Caltech.

### FINDING A RESEARCH PROJECT

One day, Brown suggested to his group that the concentration of carbonate in ground water might be estimated by assuming that the water is in equilibrium with both limestone ( $\text{CaCO}_3$ ) and atmospheric  $\text{CO}_2$ :



Keeling proposed a test of Brown’s hypothesis. He saw an opportunity to build a practical apparatus that would function in a real environment and was excited by the prospect of working outdoors. He chose to study ground water in the pristine Big Sur wilderness.

Keeling built a spray chamber that allowed him to equilibrate  $\text{CO}_2$  between air and water and then to separate the two phases. Carbonate in the water could be released by acidification. He constructed a vacuum extraction system that would condense  $\text{CO}_2$  from the gas phase with liquid nitrogen, which had recently become commercially available. To measure  $\text{CO}_2$ , he commissioned the construction of a mercury manometer modified from plans published in 1916. The precision of the manometer was 0.1%, which was as good or better than that of other methods to measure  $\text{CO}_2$ .

A key problem confronting Keeling was that the concentration of  $\text{CO}_2$  in the air was not well known. The literature stated that  $\text{CO}_2$  was ~300 parts per million (ppm) by volume, but published values ranged from 250 to 550 ppm.<sup>2</sup> It had even been proposed that different  $\text{CO}_2$  concentrations could be used as “tags” for different air masses.

Keeling decided that he needed to measure  $\text{CO}_2$  in air himself. He had several 5-L flasks constructed with vacuum stopcocks and measured the volumes of the flasks from the mass they contained when filled with water. He collected air at Caltech, extracted the  $\text{CO}_2$ , and measured its concentration with his manometer. The  $\text{CO}_2$  varied significantly from sample to sample, undoubtedly affected by a variety of man-made sources.

As a result of this experience, Keeling decided that in his experiment at Big Sur, he would sample the air every few hours throughout the day and night. “At the age of 27, the prospect of spending more time at Big Sur State Park to take suites of air and water samples instead of just a few didn’t seem objectionable,” Keeling wrote. “I was having fun. I did not anticipate that the procedures established in this first experiment would be the basis for much of the research that I would pursue over the next forty-odd years.” At the urging of Sam Epstein of Caltech, Keeling also brought back air samples so Epstein could measure the ratios of

carbon and oxygen isotopes with his newly constructed mass spectrometer.

Keeling found that ground water at Big Sur and several other sites was supersaturated with  $\text{CO}_2$ , which was apparently coming from decaying organic matter. However, his attention was drawn to diurnal patterns he observed in atmospheric  $\text{CO}_2$ .

Keeling observed that air contained more  $\text{CO}_2$  at night than in the day and that  $^{13}\text{C}/^{12}\text{C}$  was lower at night than in the day. Air on sunny afternoons always contained close to 310 ppm  $\text{CO}_2$ , but at night the concentration was highly variable. The  $^{13}\text{C}/^{12}\text{C}$  ratio was nearly constant in the daytime but varied at night in a systematic manner with  $\text{CO}_2$  concentration. Similar patterns were observed in the rain forest of the Olympic Peninsula, in elevated forests of Arizona, on barren mountain tops, and over tropical ocean waters.

Eventually, Keeling discovered a book called *The Climate Near the Ground*, which enabled him to explain his observations. On clear days, turbulence from solar heating causes air near the ground to be mixed upward in the troposphere, giving nearly constant readings of 310 ppm  $\text{CO}_2$  in all locations in the daytime—reflecting the mean concentration of  $\text{CO}_2$  in the atmosphere. At night, a cool layer of relatively stagnant air near the ground accumulates an elevated concentration of  $\text{CO}_2$  from plant respiration. The low  $^{13}\text{C}/^{12}\text{C}$  ratio in plants compared with that of  $\text{CO}_2$  in the upper atmosphere reduces the nighttime  $^{13}\text{C}/^{12}\text{C}$  ratio in the air near the ground. By 1956, Keeling had concluded that the highly variable values reported for atmospheric  $\text{CO}_2$  concentration in the literature were not correct. He felt confident enough to begin disseminating his conclusions.

### SEIZING AN OPPORTUNITY

Harry Wexler, head of the Division of Meteorological Research in the Weather Bureau in Washington, D.C. heard of Keeling’s findings from a Weather Bureau scientist stationed at Caltech. The Bureau had received funding to participate in the International Geophysical Year—a worldwide effort to make geophysical measurements over an 18-month period beginning in July 1957. Wexler was already planning to measure atmospheric  $\text{CO}_2$  at several locations, including an observatory opened in 1956 at an elevation of 3.4 km on the Mauna Loa volcano in Hawaii.

Wexler invited Keeling to Washington, D.C. to discuss  $\text{CO}_2$  measurements. Keeling explained why he thought that prior measurements were incorrect. In a courageous leap of faith, he proposed to use an infrared (IR) gas analyzer to measure atmospheric  $\text{CO}_2$ . The gas analyzer could make frequent measurements, with accuracy to be ensured by use of calibration gases certified by manometry (see box, “Manometric Measurement of  $\text{CO}_2$ ”). To corroborate field measurements, some air samples would be collected in 5-L flasks and brought back to the lab for manometric measurement.

Within an hour, Wexler agreed to Keeling’s proposal, and the next day, Wexler offered Keeling a job. Keeling was taken to what could be his new workplace a “dim basement of the Naval Observatory where the only activity seemed to be a cloud-seeding study being carried out by a solitary scientist.” This setting did not appeal to the young man who had imagined himself “climbing mountains while measuring the physical properties of glaciers.”

Good fortune shone on Dave Keeling. A colleague who had collected air samples for him over the Pacific Ocean brought

## Manometric Measurement of CO<sub>2</sub>

Manometry is key to the accuracy of atmospheric CO<sub>2</sub> measurements. The procedure measures the temperature ( $T$ ), pressure ( $P$ ), and volume ( $V$ ) of a large volume of dry air and of the small volume of CO<sub>2</sub> condensed from the air with liquid nitrogen.

To measure the CO<sub>2</sub> content of a calibration gas or an unknown air sample, the gas is first dried by passage through a series of dry ice traps. Dry gas is collected in a 5-L vessel whose volume is known within 0.01%. Ambient temperature is measured with a thermometer that can be read to  $\pm 0.01$  K. Pressure is measured by a manometer, which is a U-tube filled with mercury.



Cathetometer reads the height of mercury in the manometer to within  $\pm 0.02$  mm.



Peter Guenther has been measuring CO<sub>2</sub> at Scripps since 1969. One measurement takes half a day (2007 photo).

The pressure is the difference in height of the mercury in the two sides of the tube. A cathetometer, which consists of a telescopic sight mounted on a precision-threaded vertical shaft, reads the mercury level to  $\pm 0.02$  mm. The telescope is raised or lowered by rotating the shaft until the mercury meniscus is centered in the crosshairs of the sight. Vertical position is given by the number of turns of the threaded shaft required to position

the telescope.  $T$ ,  $P$ , and  $V$  of the dry gas are now known.

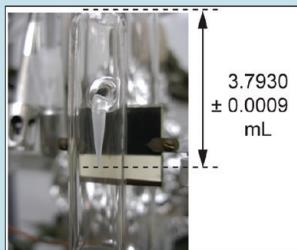
Next, CO<sub>2</sub> from the dry gas is quantitatively condensed with liquid nitrogen into an accurately known 4-mL volume. From  $T$ ,  $P$ , and  $V$  of gas in the small volume, the moles of CO<sub>2</sub> are calculated. The ideal gas law would be in error by 0.3% for CO<sub>2</sub> near atmospheric pressure. Instead, a virial equation of the following form is used:

$$PV_m = RT \left( 1 + \frac{B}{V_m} \right)$$

where  $V_m$  is the molar volume,  $R$  is the gas constant, and  $B$  is the second virial coefficient for CO<sub>2</sub>. The molar volume is

$V_m = V/n$ , where  $n$  is the number of moles of gas. Air contains 0.3 ppm of N<sub>2</sub>O, which condenses with CO<sub>2</sub> and interferes with the measurement. The ratio N<sub>2</sub>O/CO<sub>2</sub> in air is separately measured by gas chromatography. Then, the mixing ratio of N<sub>2</sub>O is subtracted from that of CO<sub>2</sub> + N<sub>2</sub>O measured with the manometer.

The 0.025% uncertainty in measuring the 4-mL volume of isolated CO<sub>2</sub> limits the precision to 0.1 ppm for CO<sub>2</sub> levels of 400 ppm in air. To estimate systematic error, CO<sub>2</sub> in a calibration standard was measured by two different methods at Scripps and independently at the National Oceanographic and Atmospheric Administration. The three measurements agreed within 0.2 ppm CO<sub>2</sub>, which is considered to be the uncertainty for the Mauna Loa measurements.



Small chamber used to condense CO<sub>2</sub> from a 5-L volume of dry air. When the meniscus of a mercury column just touches the bottom of the glass pointer inside this glass tube, the enclosed volume is 3.7930  $\pm 0.0009$  mL.

Keeling's findings to the attention of Roger Revelle, Director of the Scripps Institution of Oceanography near San Diego, California. Revelle invited Keeling to Scripps, where he was treated to lunch in a back yard under "brilliant sunshine wafted by a gentle sea breeze."

"Brilliant sunshine and gentle sea breeze," thought Keeling, or a "dim basement laboratory?" Keeling moved to Scripps in August 1956. Wexler magnanimously agreed to support Keeling to make atmospheric CO<sub>2</sub> measurements for the International Geophysical Year.

### MAUNA LOA

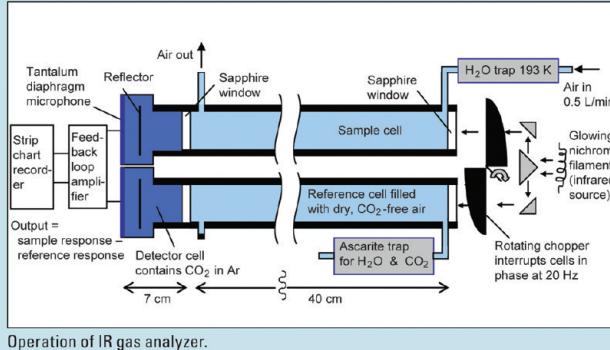
Revelle believed that the value of Keeling's work would be to obtain a "snapshot" of CO<sub>2</sub> concentration, to be followed  $\sim 20$  years later by a second "snapshot" to learn if atmospheric CO<sub>2</sub> was increasing. Others were skeptical of Keeling's intention to make precise measurements. They argued that the concentration of atmospheric CO<sub>2</sub> was too variable to warrant high precision measurements. They also noted that CO<sub>2</sub> belched by the Mauna Loa volcano would confound the measurements. Keeling persisted in making the highest quality measurements that he could and discovering what he could from the data.

Keeling had only cursory knowledge of IR gas analyzers when he suggested their use to Wexler (see box, "The IR Gas Analyzer"). No current analyzer had been designed to measure

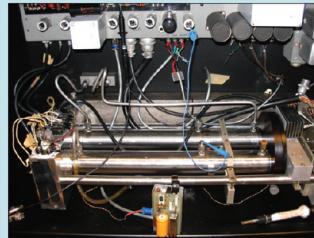
the low concentration of CO<sub>2</sub> in the atmosphere. Keeling tested an instrument made by Applied Physics Corp., which was the only company in which he "was able to get past a salesman and talk directly with an engineer." He constructed a gas-handling system and a power supply for use in remote areas. One analyzer was shipped to Antarctica. A second instrument was mounted on a ship. The third instrument went to Mauna Loa, and the fourth was installed at Scripps. The instrument at Mauna Loa operated for 48 years before its retirement in 2006. Keeling's methods replaced the less accurate titrimetry that was used elsewhere until 1960 (see box, "Measuring Atmospheric CO<sub>2</sub> by Titrimetry").

Weather Bureau personnel installed the gas analyzer on Mauna Loa in 1958 with the intent to measure pristine air over the Pacific Ocean. Four air intakes located 90° apart were each 7 m above the ground and 175 m from the observatory. Two upwind intakes were selected for monitoring. Every half hour, the analyzer monitored air from one intake for 10 minutes, then monitored the other for 10 minutes, and then measured a reference gas for 10 minutes.

Figure 2 shows hourly average readings. Some readings are steady and others vary when CO<sub>2</sub> emerges from volcanic vents or when other disturbances occur. To obtain representative data for pristine air, Keeling rejected readings for any hour when the variation was  $>0.5$  ppm. An average reading for a given day was



Operation of IR gas analyzer.



Applied Physics Corp. IR gas analyzer with vacuum tube electronics. The two prominent steel tubes are the reference and sample cells. The IR source is attached to the right of the tubes and detectors are attached at the left.

### The IR Gas Analyzer

Duplicate Applied Physics Corp. Model 70 Infrared Analyzers operated on Mauna Loa and at Scripps from 1958 to 2006.<sup>3,4</sup> This instrument does not disperse IR radiation into its component wavelengths.

Unknown dry air is pumped through the 40-cm-long sample cell. The reference cell contains dry,  $\text{CO}_2$ -free air. Broadband IR radiation from a glowing nichrome filament is split into two beams and chopped at 20 Hz before passing

through the gas cells. In the sample cell,  $\text{CO}_2$  absorbs some radiation, which is not absorbed in the reference cell. Therefore, more radiation reaches the reference detector than reaches the sample detector.

The detectors contain  $\text{CO}_2$  in Ar. IR radiation absorbed by  $\text{CO}_2$  in the detectors causes the gas in the detectors to expand and contract at a frequency of 20 Hz. The back side of each detector is

a tantalum diaphragm (a microphone), which vibrates at 20 Hz in response to expansion and contraction of the detector gas. The detection circuit measures the difference in response between the two microphones. Results are displayed on a strip chart recorder. The  $\text{CO}_2$  content of an unknown air sample is measured by comparing the response of the unknown with that of a calibration gas with known  $\text{CO}_2$  content.

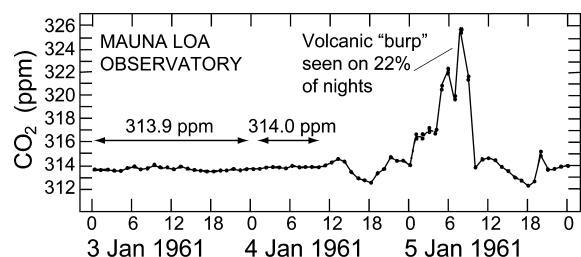
only reported if there were at least six consecutive hours of steady data. If readings varied too much, no value was reported that day.

Figure 3 shows daily average readings obtained during the first two years at Mauna Loa. From March to May 1958,  $\text{CO}_2$  drifted upward by 3 ppm, leading Keeling to wonder if his hard won precision of 0.1 ppm was worth the cost and effort. A power failure prevented data from being taken in June. When operation resumed in July,  $\text{CO}_2$  had fallen by 3 ppm and continued to drift downward. Data were lost to another power

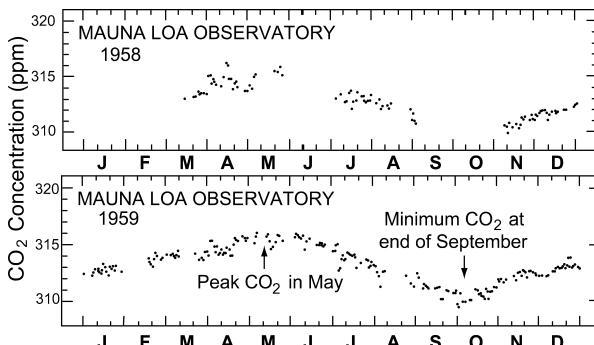
failure in September and October. Keeling was finally allowed to make his first trip to Mauna Loa in November to repair the equipment. Readings at the end of the year were low and drifting upward. Conclusions were difficult to draw.

However, nearly uninterrupted results in the second year, shown at the bottom of Figure 3, reproduced the trends of the first year and demonstrated that the oscillating pattern was real.  $\text{CO}_2$  peaked in May just before plants in the temperate northern hemisphere put on leaves.  $\text{CO}_2$  reached a minimum at the end of the growing season in September. Keeling concluded that "we were witnessing for the first time nature's withdrawing  $\text{CO}_2$  from the air for plant growth during the summer and returning it each succeeding winter."<sup>1</sup> The peak-to-valley effect was only 5 ppm and would have been difficult to see if care had not been taken to achieve a precision of 0.1 ppm.

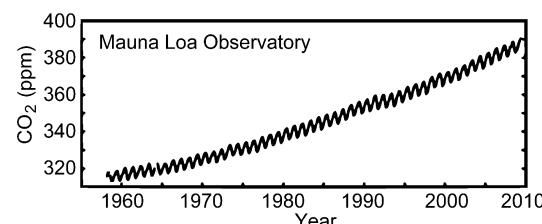
In the 50 succeeding years, annual oscillations shown in Figure 4 are superimposed on a rising background.<sup>7</sup> Approximately half of the  $\text{CO}_2$  released by combustion of fossil fuels is found in the atmosphere. The other half dissolves in the oceans, where it relentlessly lowers the pH. The increase in atmospheric  $\text{CO}_2$  was  $\sim 0.7 \text{ ppm/year}$  in 1960 and is now  $\sim 2.0 \text{ ppm/year}$ . Figure 4 is known today as the "Keeling curve".



**Figure 2.** Hourly  $\text{CO}_2$  readings. A daily average was reported only from periods of  $\geq 6 \text{ h}$  of constancy. Data from ref 3.



**Figure 3.** Daily  $\text{CO}_2$  readings from the first two years of monitoring on Mauna Loa. Data from ref 3.

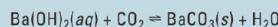


**Figure 4.** Keeling Curve: a half century of  $\text{CO}_2$  data from Mauna Loa Observatory. Data from ref 7.

## Measuring Atmospheric CO<sub>2</sub> by Titrimetry

While Keeling was a postdoc at Caltech in 1955, a Scandinavian group led by the Institute of Meteorology of Stockholm University (Sweden) mounted a serious effort to measure atmospheric CO<sub>2</sub> at 15 ground stations. Samples were taken in 250-mL flasks on the 1st, 10th, and 20th day of each month around 1:00 p.m.

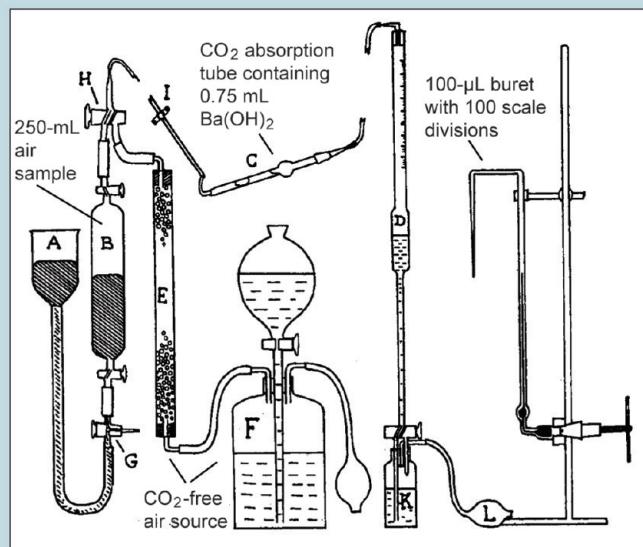
To measure CO<sub>2</sub>, 100.0 mL of the air sample were passed as small bubbles for one hour through 0.750 mL of standard Ba(OH)<sub>2</sub> solution containing cresolphthalein indicator. One mole of CO<sub>2</sub> consumes one mole of Ba(OH)<sub>2</sub>:



Unreacted Ba(OH)<sub>2</sub> was then titrated with standard HCl from a 100-μL microburette to determine how much Ba(OH)<sub>2</sub> had been consumed by CO<sub>2</sub>. Solutions were protected under a blanket of CO<sub>2</sub>-free air.

As a measure of precision, three sets of replicate air samples were analyzed in two different laboratories. The difference in replicate measurements was 0.9–2.0%. The stated uncertainty in the method was ±3 ppm, or about 1% of the ~300 ppm of CO<sub>2</sub> in the air.

After Keeling introduced IR measurements of CO<sub>2</sub>, the Stockholm group adopted their own IR gas analyzer in 1959. The new method reduced their stated un-



Titrimetry apparatus, adapted from ref. 5. A) Leveling bulb containing Hg. B) Pipette with air sample. C) Absorption tube containing standard Ba(OH)<sub>2</sub> (~15 mM) + 0.5% BaCl<sub>2</sub>. D) 60- or 100-mL measuring burette filled with water by compressed air from bottle K. E) Tube containing Ascarite to remove CO<sub>2</sub>. F) Compressed air source. G) and H) 3-way stopcocks. I) Pinch clamp. L) Air bulb. The 100-μL burette containing standard HCl is controlled by a mercury and screw piston at the lower end.

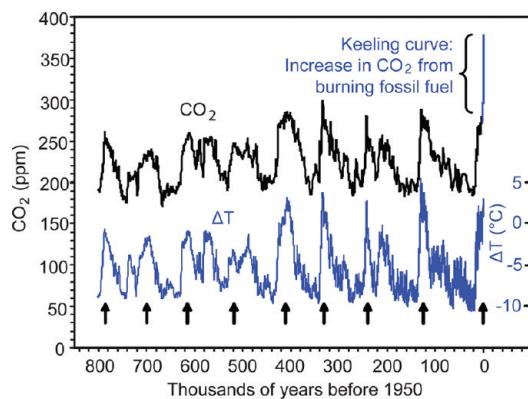
certainty from ±3 ppm to ±1 ppm CO<sub>2</sub>.<sup>6</sup>

Keeling's IR gas analyzer with manometric calibration standards provided a precision of ±0.1 ppm CO<sub>2</sub> with a stated uncertainty of ±0.2 ppm. Keeling observed that atmospheric CO<sub>2</sub> oscillated only by ~5 ppm over the course of a year. The range reported for different samples in the Scandinavian study was 150–450 ppm. In 1960, duplicates of two samples

from the Scandinavian program were sent to Scripps for independent measurement. At Scripps, the CO<sub>2</sub> concentrations were found to be nearly the same as those measured on Mauna Loa, "proving that the errors in the Scandinavian program were mainly analytical rather than due to variable CO<sub>2</sub> in the air being sampled." The Scandinavian program was "quietly abandoned."<sup>1</sup>

## CO<sub>2</sub> IN CONTEXT

Figure 5 places the Keeling curve in context by superimposing it on a record of atmospheric CO<sub>2</sub> and temperature derived from measuring ice cores drilled from the Antarctic ice pack.<sup>8</sup> Cores of up to 3 km in length can be analyzed and can contain water that was deposited up to 800,000 years ago. Microscopic air bubbles trapped in the ice retain CO<sub>2</sub> from the time they were formed. If a section of frozen ice core is crushed under vacuum,



**Figure 5.** Atmospheric CO<sub>2</sub> and temperature data derived from Antarctic ice core measurements. Arrows mark 100,000-year cycles. Data from ref 8. The Keeling curve is the vertical segment appended to the ice core data at the upper right.

CO<sub>2</sub> is released and can be measured. Temperature is inferred from the <sup>2</sup>H/<sup>1</sup>H ratio in the ice: as the temperature of the atmosphere rises, so does the content of <sup>2</sup>H and the <sup>2</sup>H/<sup>1</sup>H ratio in the ice.

In the last 800,000 years, we see a series of peaks and valleys in temperature and CO<sub>2</sub>, which are remarkably similar to one another (Figure 5). The 100,000-year cycles, marked by arrows, are clearest in the most recent five peaks. Cyclic changes in temperature are thought to arise from known, periodic changes in Earth's orbit and the tilt of Earth's axis. The solubility of CO<sub>2</sub> in the ocean decreases with increasing temperature. When Earth warms, CO<sub>2</sub> is liberated from the oceans and further warms the Earth by the greenhouse effect. When orbital changes cool the Earth, CO<sub>2</sub> redissolves in the oceans, causing further cooling by the decreased greenhouse effect. In the historical cycles in Figure 5, temperature changes are thought to drive CO<sub>2</sub> changes, which reinforce temperature changes. This cycle has persisted for at least 800,000 years.

The Keeling curve is superimposed on the ice core data at the upper right of Figure 5. Now, for the first time, an abrupt change in CO<sub>2</sub> comes ahead of a temperature change. On the timescale of Figure 5, the CO<sub>2</sub> curve will probably continue to rise vertically until fossil fuel on Earth is consumed. Whether it takes us 200

years or 2000 years to consume that fuel, the line will appear vertical. Man's activities have jolted CO<sub>2</sub> from its historical pattern, with effects that will become known to future generations.

Charles David Keeling spent his life defending the need for continuous, high precision measurements of atmospheric CO<sub>2</sub>. Every few years, funding agencies sought to end his support because the work was judged to be "routine" rather than novel research. Keeling's lab provided calibration gases for measurements by other laboratories in other nations until 1995. U.S. government agencies sought to take over the work from Keeling, but alternate, less expensive methods proposed by those agencies did not produce the precision and accuracy that Keeling had attained. For today's understanding of atmospheric CO<sub>2</sub>, we are indebted to Keeling's insistence on analytical quality and his dogged defense of his work.

#### ACKNOWLEDGMENT

This account was drawn from the autobiography *Rewards and Penalties of Monitoring the Earth* by Charles David Keeling (ref 1). I am grateful to Ralph Keeling, Peter Guenther, David Moss,

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