DRAFT Fingerprinting Carbon: How we know that CO_2 from human activities is causing climate change

OVERVIEW

More than 97% of climate scientists agree that the current increase in average global temperatures is caused by humans. The scientific consensus is clear, burning of fossil fuels, agricultural activities, and other human activities have increased the concentration of greenhouse gases in the atmosphere. However, how can we demonstrate this quantitatively? Put another way, if someone were to say to you, the rise in CO_2 is real, but it is natural and has nothing to do with human activities, how could you show them, using empirical evidence, that we can directly link the rise in CO_2 to the burning of fossil fuel?

One of the most striking pieces of evidence for anthropogenic climate change is found in the chemistry of carbon atoms in carbon dioxide itself.

Atoms of carbon on Earth are found in three different flavors that differ based on their weights, which are termed ‘isotopes’. Isotopes and elements differ in the following way. The identity element is dictated by its number of protons, which for carbon is 6. The isotope of an element differ in the number of neutrons they have in their nuclei and these differing amounts of neutrons change the weight of the different isotopes.

Carbon has three isotopes that are found in the environment: carbon-12, carbon-13, and carbon-14 (^{12}C, ^{13}C, and ^{14}C). Carbon-14 is a radioactive isotope and decays with time — this is the isotope used for ‘radiocarbon’ dating of old materials. In contrast, carbon-12 and carbon are ‘stable’ isotopes and do not decay. The abundance of these isotopes are given in the table below.

Isotope	Protons	Neutrons	Typical Abundance	Stable or Unstable?
Carbon-12	6	6	98.9%	stable
Carbon-13	6	7	1.1%	stable
Carbon-14	6	8	0.00000001%	unstable

Overview of the isotopes of carbon

It turns out that the abundances of the different isotopes of carbon vary in different materials. For example, the concentration of ^{13}C in the atmosphere is elevated by about 1.5-4% relative compared to typical organic carbon in plants and the hydrocarbon products of plants (e.g., coal, oil, and natural gas).

Globally, the ratios of these carbon isotopes in atmospheric carbon dioxide are changing due to the burning of fossil fuels, which contain lower levels of ^{13}C and are too old to contain ^{14}C, the unstable (radioactive) form of carbon. Fossil fuels are made of ancient plants, which like plants today, contain less of the heavier isotopes of carbon because plants take in more of the light isotope of carbon (^{12}C) during the process of photosynthesis. In this way, we can “fingerprint” the sources of carbon in the atmosphere. The reduction in heavy carbon isotopes in our atmosphere has occurred since the burning of fossil fuels began during the Industrial Revolution and is called the ‘Suess effect’, after the scientist who first described this phenomenon in the 1950s-1970s (Hans Suess).

In this activity, students will connect what they know about climate change and the carbon cycle and interpret carbon isotope data to explain how shifts in isotope ratios are evidence of anthropogenic climate change.

KEY CONCEPTS

- Atmospheric carbon dioxide is increasing.
- Carbon comes in three isotopes.
- Different Earth materials (e.g., rocks, plants) have different ratios of carbon isotopes.
- If carbon isotope ratios change over time, this indicates that carbon is being added or subtracted from particular sources.
- Photosynthesis changes the relative amount of different carbon isotopes incorporated into plant material compared to the relative amounts found in the atmosphere.
- The increase in ^{12}C and decrease in ^{13}C in the atmosphere and ocean indicates that most of the carbon that has been added to the atmosphere over the last 200 years is from fossil fuels, which formed from biological (plant) material.

STUDENT LEARNING TARGETS

- Analyze and interpret CO_2 and $\delta^{13}C$ data.
- Explain how depletion of $\delta^{13}C$ values in atmospheric CO_2 is evidence of changes in the carbon cycle and indicative of anthropogenic climate change.

PRIOR KNOWLEDGE

- Atoms are made of protons, neutrons, and electrons.
- Chemical elements, such as carbon, are defined by the number of protons in their nuclei.
- Isotopes of the same element have the same number of protons, but differ by the number of neutrons in their nuclei and therefore have different masses.
- Students should be familiar with the carbon cycle and understand that various processes move carbon through different parts of the Earth system
- The greenhouse effect describes the role of certain gases (carbon dioxide, water vapor, methane, nitrous oxide) in Earth's atmosphere in trapping energy, and thus warms the planet.

MATERIALS

- Datasets in the activity, linked and provided below
- Blank paper
- Understanding Global Change Earth Scene: https://ugc.berkeley.edu/teaching-download/earth-scene/

TEACHING TIPS

- This activity was designed for students to work in groups of two to four, since it incorporates collaborative dialogue throughout.
- Depending on the amount of time allotted for this activity, sharing can be done either through class discussion or group sharing.
- The data provided in this activity are from various resources, and may be complex for some students. Leave time to "unpack" the figures using a technique such as Identify and Interpret (I^2,https://media.bscs.org/icans/Icans_I2_SE.pdf).
- This activity focuses on important evidence indicative of the anthropogenic causes of climate change, but should be taught within a larger sequence of study about climate change consequences and solutions.

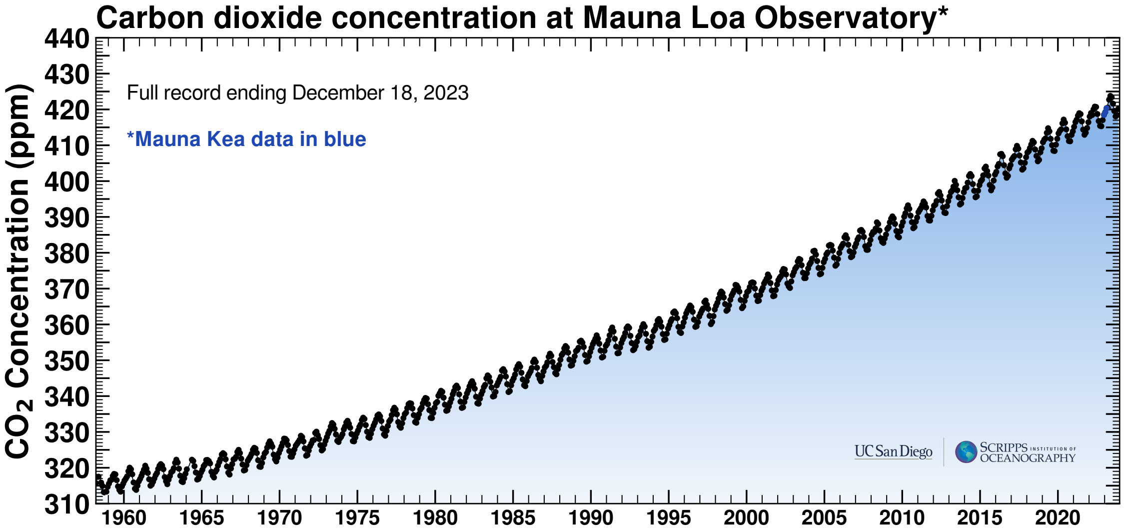
PROCEDURE

Part 1: Introduction to the 'Keeling Curve' (30-40 mins total)

1. Have students work with a partner or in small groups of 3-4. To start group discussions, ask students what they know about how carbon dioxide levels are currently changing in the atmosphere. Tell them to use drawings or to sketch a graph to represent their thinking. There are no wrong answers, this is just to get their initial ideas on paper. (5 min)

2. Ask students to share their group ideas with the whole class. Alternatively, you could engage students in a brief gallery walk. (5 min)

3. Now provide each group with a copy of the Keeling Curve of atmospheric CO_2 levels and ask students to compare and contrast their initial ideas and sketches with the measured data. Students might have drawn lines with various slopes, but not included the seasonal fluctuations in CO_2 that coincide with seasonal changes in photosynthesis in the northern hemisphere. (5 min)



You can download the most current graph at: https://keelingcurve.ucsd.edu/

4. Discuss as a class the similarities and differences that students notice when comparing their ideas about how CO_2 levels have changed to the Keeling curve. Students will likely notice the seasonal fluctuations. Have students share ideas about what might cause these seasonal changes. (5 min)

5. Provide students with one or more of these background resources to help them understand seasonal changes in CO_2 and the significance of the Keeling Curve. Students could read independently and discuss or groups of students could receive different resources and then students could share what they have learned with students from other groups (jigsaw activity) (10-20 min):

   Why does atmospheric CO_2 peak in May? https://keelingcurve.ucsd.edu/2013/06/04/why-does-atmospheric-co2-peak-in-may/

Why are Seasonal CO2 Fluctuations Strongest at Northern Latitudes?
https://keelingcurve.ucsd.edu/2013/05/07/why-are-seasonal-co2-fluctuations-strongest-in-northern-latitudes/

KQED, The Keeling Curve Explained: https://www.kqed.org/quest/73187/the-keeling-curve-explained

Please also see the Understanding Global Change website pages related to understanding the Keeling Curve:

Greenhouse gases: https://ugc.berkeley.edu/background-content/greenhouse-gases/

Respiration: https://ugc.berkeley.edu/background-content/respiration/

Photosynthesis: https://ugc.berkeley.edu/background-content/photosynthesis/

Part 2: Fingerprinting Carbon: Sources and Isotopes (80-90 min total)

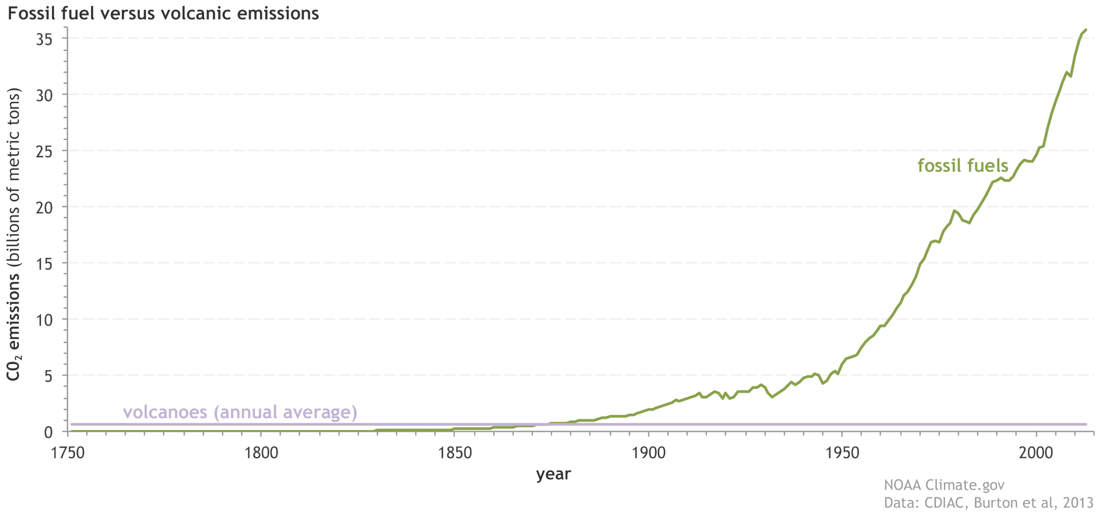
6. So why are atmospheric CO_2 levels rising? Ask students to share what they know about what human and non-human processes are contributing CO_2 to the atmosphere today. Have students draw their ideas on the Understanding Global Change Earth Scene using the words and arrows to explain the rise in CO_2.

   Ask students to draw a star next to the arrows that represent the 1-2 sources that currently contribute the MOST CO_2 to the atmosphere. This will help you know if students have any misconceptions about what is causing the global rise in atmospheric CO_2. (10 min)

Optional: You could provide the following word bank to help focus student thinking: atmosphere, ocean, rocks, fossil fuels, volcanoes, fire, photosynthesis, respiration, productivity & biomass

7. Now, compare student ideas about the major sources of atmospheric carbon with graphs

from IPCC and NOAA showing the relative contribution of volcanic activity vs. burning of fossil fuels to help address any misconceptions. Share the data below and ask students to discuss in groups before sharing their ideas with the class. (10 min)



https://www.climate.gov/news-features/climate-qa/which-emits-more-carbon-dioxide-volcanoes-or-human-activities

Yearly CO_2 emitters	**Billion metric tons per year (Gt/y)**
Global volcanic emissions (highest preferred estimate)	0.26
Anthropogenic CO_2 from fuel combustion 2015	32.3
Worldwide Road Transportation 2015	5.8
Approximately 24 1000-megawatt coal-fired power stations	0.22
Argentina 2015	0.19
Poland 2015	0.28
United States 2015	4.99
CO_2 emission events	
Mount St. Helens, 18 May 1980	0.01 Gt
Mount Pinatubo, 15 June 1991	0.05 Gt
Number of Pinatubo-equivalent eruptions equal to 2010 global anthropogenic CO_2	700
Number of Mount St. Helens-equivalent eruptions equal to 2010 global anthropogenic CO_2	3500

https://www.usgs.gov/programs/VHP/volcanoes-can-affect-climate

Supplemental information about measuring carbon dioxide and understanding gigatons: https://gml.noaa.gov/outreach/behind_the_scenes/gases.html

8. How could we know where CO_2 is coming from? One way is from the carbon atoms themselves! Provide the information below to students and discuss the data provided (10 min).

Remind students of where carbon is located in the periodic table, and that this element has six protons. The number of protons defines each element and most of the mass of atoms comes from the protons and neutrons in their nuclei. Carbon comes in three forms, called isotopes. All three isotopes have the same number of protons; thus, they are all the same element (carbon), but differ by the number of neutrons in their nuclei.

Carbon Isotope	Number of neutrons	Mass number	Percentage on Earth*	Stable or unstable (radioactive)
carbon-12 (^{12}C)	6	12	98.98%	stable
carbon-13 (^{13}C)	7	13	1.11%	stable
carbon-14 (^{14}C)	8	14	$<10^{-10}$%	Unstable (radioactive)

*(1998) Carbon isotopes. In: Geochemistry. Encyclopedia of Earth Science. Springer, Dordrecht. https://doi.org/10.1007/1-4020-4496-8_45

Most carbon on Earth is carbon-12 (^{12}C), which contains six neutrons (and six protons); 6 protons + 6 neutrons = a mass number of 12. (Note: the mass number is approximately the same as the atomic mass but does not include the weight of electrons.) Carbon-12 is the "light" form of carbon. Carbon-12 and carbon-13 are known as stable isotopes because they do not change (decay) into other isotopes or elements over time. The rarest carbon isotope, carbon-14 (^{14}C), is unstable (radioactive), and decays into nitrogen-14 (^{14}N).

Scientists can measure the relative amounts of each carbon isotope present various materials (e.g., air, water, rocks, soil, and organic materials, etc.) to determine the ratio of heavy (^{13}C or ^{14}C) to light (^{12}C) carbon atoms in a sample. These measurements are commonly made using a mass spectrometer, which uses a magnetic field to separate and measure molecules of different masses. (Note: To learn more about how mass spectrometers work, see: https://www.khanacademy.org/science/ap-chemistry-beta/x2eef969c74e0d802:atomic-structure-and-properties/x2eef969c74e0d802:mass-spectrometry-of-elements/v/mass-spectrometry)

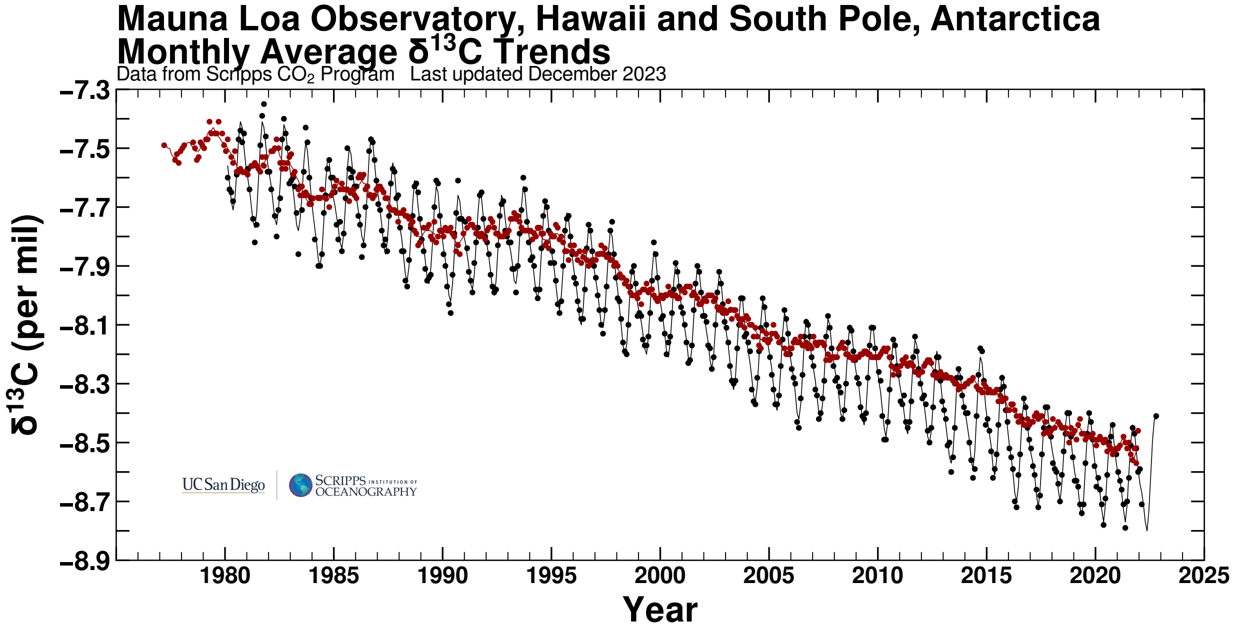
The relative amounts of isotopes in a sample are measured as a ratio. Scientists compare ratios of isotopes in their samples, such as $^{13}C/^{12}C$, and represent their results as a difference, or delta, from a known "standard." These standards have isotopic ratios that are used as a point of comparison in labs around the world. When a sample has a negative $\delta^{13}C$ value, it contains relatively less ^{13}C than the standard with which it is being compared. This $\delta^{13}C$ (said delta, carbon-13) value is measured in parts per thousand (per mil or ‰).

9. In addition to measuring the amount of CO_2 in the atmosphere, Keeling and other scientists have been interested in understanding how the ratios of light to heavy carbon isotopes in CO_2 have changed over time, and what these changes could tell us about how the carbon cycle works. Here are isotopic data from the 1970s-present, also collected from Mauna Loa Observatory in Hawaii.

   Ask students to take a look at the graph and think about the following questions (10 min):
   - What do you notice about the overall trend in $\delta^{13}C$ over the last 40+ years?
   - What do you notice about the fluctuations in $\delta^{13}C$?
   - Look back at the Keeling Curve. Remember that overall atmospheric CO_2 levels are increasing, so what might it mean if the ratio of ^{13}C to ^{12}C in that CO_2 is

decreasing?

- What are the sources of CO_2 that could contribute to this change in the ratio of heavy to light carbon in the atmosphere?
- What similarities or differences do you notice between the Hawaii and Antarctica data? What might cause these similarities or differences?



https://scrippsco2.ucsd.edu/graphics_gallery/isotopic_data/mauna_loa_and_south_pole_isotopic_c13_ratio.html

Black Dots: Monthly average reduced isotopic ratio of atmospheric carbon dioxide, $\delta^{13}C$, versus time at Mauna Loa Observatory, Hawaii (20°N, 156°W) where $\delta^{13}C$ is in per mil.
Black Curve: The sum of 4 seasonal harmonics and a spline function to the Mauna Loa $\delta^{13}C$ data. The seasonal harmonics include a linear gain factor, to represent increasing amplitude with time.
Red Dots: Monthly average atmospheric carbon dioxide reduced isotopic ratio, $\delta^{13}C$, versus time at South Pole, Antarctica where $\delta^{13}C$ is in per mil.
Red Curve: The sum of 4 seasonal harmonics and a spline function to the South Pole $\delta^{13}C$ data. The seasonal harmonics include a linear gain factor, to represent increasing amplitude with time.

10. Next, have students take a look at the first graph on this NOAA website which shows the how CO_2 and $\delta^{13}C$ vary over time. Students should notice that the peaks in the Keeling Curve and the troughs in the $\delta^{13}C$ data. Ask students why this might occur (10 min) https://gml.noaa.gov/ccgg/isotopes/c13tellsus.html

11. To get a better idea of what is happening in our atmosphere over longer periods of time, now have students look at $\delta^{13}C$ data from the last 1000 years from Figure 5A in Rubino et al. (2013). https://agupubs.onlinelibrary.wiley.com/doi/full/10.1002/jgrd.50668

    These measurements were taken from bubbles of ancient air trapped in in ice in Antarctica and can give us a better idea of $\delta^{13}C$ of CO_2 and its concentration has changed recently in comparison with more long-term trends.

Ask students to look at the graph and write down responses to the following questions (10 min):

- What do you notice about the overall trend in $\delta^{13}C$ over the last 1000 years?
- When do $\delta^{13}C$ values change the most? What else is changing at this time?
- What are the sources of CO_2 that could contribute to this change in the ratio of heavy to light carbon in the atmosphere?
- In contrast, what are the processes that could result in smaller changes in $\delta^{13}C$ values over time?

12. Ask students to revisit their Earth Scene diagram to discuss the processes that they think contribute CO_2 to the atmosphere. Tell students that over decades of research, scientists determined that different sources of carbon have different $\delta^{13}C$ ratios. These values are summarized in the table below. In groups, compare students' ideas about the sources of CO_2 that would decrease $\delta^{13}C$ ratios with the information in the diagram below. Then ask students to share their ideas with the rest of the class. Students should recognize that the parts of the carbon cycle with the most negative $\delta^{13}C$ values are vegetation, marine biomass, soils, and oil, gas, and coal. (10 min)

Source of Carbon	**Isotopic composition ($\delta^{13}C$ ratio)**
Terrestrial vegetation and soils	-22‰ to -25‰
Oil and gas	-27‰ to -44 ‰
Coal	-24‰
Volcanic emissions	-5‰
Atmosphere (pre industrial value)	-6.5‰

13. Share the following explanation with students to help them understand why $\delta^{13}C$ values of vegetation, marine biomass, soils, and oil, gas, and coal are so depleted relative to volcanic emissions and rocks. (10 min)

Why plants and soils have lower $\delta^{13}C$ values than the atmosphere:

The most important process that results in plants and algae having lower ^{13}C values than the atmosphere actually occurs during photosynthesis. The enzyme ribulose-1,5-bisphosphate carboxylase/oxygenase, also known as RuBisCO, used in the Calvin cycle, preferentially reacts with ^{12}C over ^{13}C. Therefore, more ^{12}C becomes fixed in the plant.

In addition to the effect of the enzyme, ^{13}C is heavier than ^{12}C, and heavier atoms and molecules move slower than light ones like ^{12}C. When plants photosynthesize they capture air in small openings in the leaves called stomata by a process called diffusion. Diffusion is the random movement of particles from areas of higher concentration to areas of lower concentrations (think of food coloring in a glass of water). As air randomly moves into a leaf, less of the heavy ^{13}C passes through the stomata than the lighter, faster ^{12}C meaning that the air in the leaf (which is used for photosynthesis) is naturally depleted in ^{13}C vs. ^{12}C

Fossil fuels (oil, coal, and gas) have lower ^{13}C values than the atmosphere and volcanic emissions because they are made of ancient organic material. Fossil fuels form over millions of years from the burial of photosynthetic organisms, including plants on land (which primarily forms coal and natural gas) and plankton in the oceans (which primarily form oil and natural gas). To grow, these ancient organisms removed carbon dioxide from the atmosphere and the ocean, and their burial inhibited the movement of that carbon through the carbon cycle. The burning of this fossil material returns this carbon back into atmosphere as carbon dioxide, at a rate that is hundreds to thousands of times faster than it took to bury, and much faster than can be removed by the natural carbon cycle. Thus, the carbon dioxide released from the burning of fossil fuels accumulates in the atmosphere, some of which then dissolves in the ocean causing ocean acidification, and also lowering the $\delta^{13}C$ values in the ocean.

14. **Optional Extension:** Based on what students now know about $\delta^{13}C$, ask them to predict how $\delta^{13}C$ might have changed from 1800-present in the three carbon sources listed below. Would $\delta^{13}C$ values have likely increased, decreased, or stayed the same? Students should provide a brief explanation for each prediction. (10 min)

Carbon source	**Predicted change in $\delta^{13}C$ from 1800-present (increase, decrease, stay the same)**	**Explain why…**
Corals in the ocean		
New volcanic rocks from eruptions in Hawaii		
Algae in the ocean		