

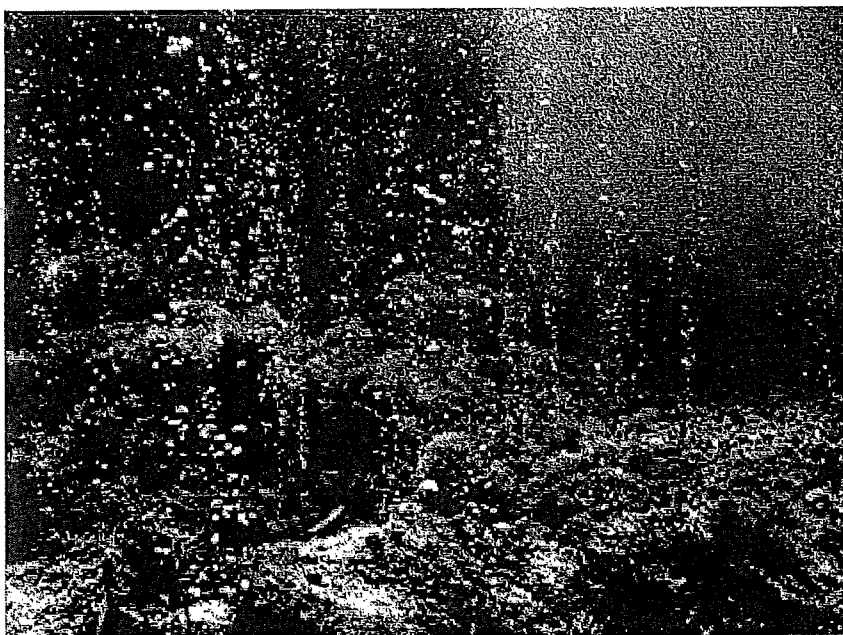
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Geology and Climate

ACS Climate Science Toolkit | Oceans, Ice, and Rocks

The CO₂ bubbles in this photograph contain carbon that is completing (or just beginning) its several-million-year journey from the atmosphere to the ocean to marine organisms' carbonate structures to ocean sediment to limestone subducted beneath a tectonic plate to release by magma heating and return to the surface by volcanism to begin the cycle once more. The diagram further down the page is a schematic representation of this pathway. Along the way, the carbon's journey might have been interrupted by more rapid reactions, such as incorporation into organic molecules via photosynthesis, but as the organics decay most of the carbon on the oxygen-rich Earth ends up in its most stable oxidized form, as CO₂ and carbonate.

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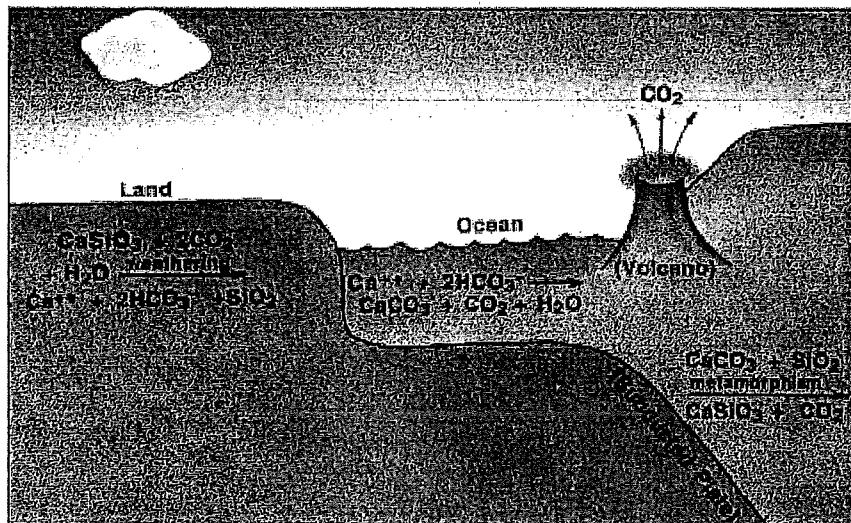
Source: Chemical & Engineering News, 2012, 90, 12-17 (April 9, 2012) by Luca Tiberti

This photo shows an ocean acidification experiment the Earth has been carrying out in a few localized areas for a very long time. The bubbles are essentially pure CO₂ being emitted from the shallow floor of the Mediterranean Sea off the volcanic island of Ischia in Italy's Bay of Naples. Unlike the mixture of hot gases and liquids emitted by the thermal vents at the juncture of tectonic plates in the deep ocean, the vents here emit the CO₂ at ambient temperature. The pH of the sea in the vent area can be as low as 7.3, increasing to the usual 8.2 about 150 m from the vents. Studies of the biodiversity in this setting can help us understand the consequences of ocean acidification by increasing fossil fuel CO₂ emissions.

"Venting of volcanic CO₂ at a Mediterranean site off the island of Ischia provides the opportunity to observe changes in the community structure of a rocky shore ecosystem along gradients of decreasing pH close to the vents. Groups such as sea urchins, coralline algae and stony corals decline in abundance or vanish completely

with decreasing pH. Sea grasses and brown algae benefit from elevated CO_2 availability close to the vent by increasing their biomass. Similar high CO_2 /low pH conditions are on the verge of progressively developing ocean-wide through the uptake of fossil-fuel CO_2 by the surface ocean." (U. Riebesell, *Nature* **2008**, 454, 46-47)

CO_2 is stabilized by delocalization of its π electrons that make the compound about $108 \text{ kJ}\cdot\text{mol}^{-1}$ more stable than calculated from the bond enthalpy of two isolated carbon-oxygen double bonds.



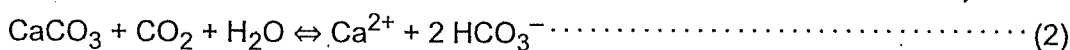
Source: J. F. Kasting, *Science Spectra*, 1995, Issue 2, 32-36 posted on J.F. Kasting's research interests webpage: <http://www3.geosc.psu.edu/~jfk4/PersonalPage/ResInt2.htm>.

Geologists estimate that about 90% of the Earth's crust is made up of silicates—quartz, clays, and zeolites are among the very large number of complex mineral structures ... Exposure of the silicates to CO_2 in Earth's humid atmosphere leads to the weathering reaction shown in the diagram.



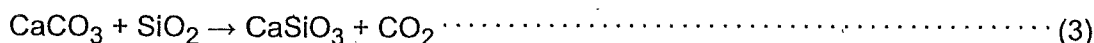
This diagram represents the carbonate-silicate cycle (Urey reaction), the long-term control on the Earth's carbon cycle.

Carbonate rocks—limestone and marble, for example—also react with CO_2 and H_2O .



The products of these reactions are ultimately washed into the ocean where marine organisms use them to build shells and other structures by the reverse of reaction (2) or analogous reactions by other organisms that build silicate structures. When these organisms die, their remains either dissolve or sink to the bottom of the ocean. Some of this sediment forms sedimentary rocks that may be uplifted to the surface (to begin the weathering process all over) or, as the diagram shows, subducted beneath tectonic plates as the plates move over one another.

Beneath the plate, under high pressure and heated by the magma (the molten rock on which the plates float), the subducted carbonates and silicates can undergo metamorphism (change in form). For our purposes, this complex process can be characterized by this reaction.



The CO_2 from this reaction can escape through cracks and fissures in the crust, especially where it is thin and the magma is close to the surface, as in areas of volcanic activity. Thus, the CO_2 finishes its journey through the rock cycle by reentering the atmosphere via volcanoes and surrounding vents, as in the photograph that began this discussion.

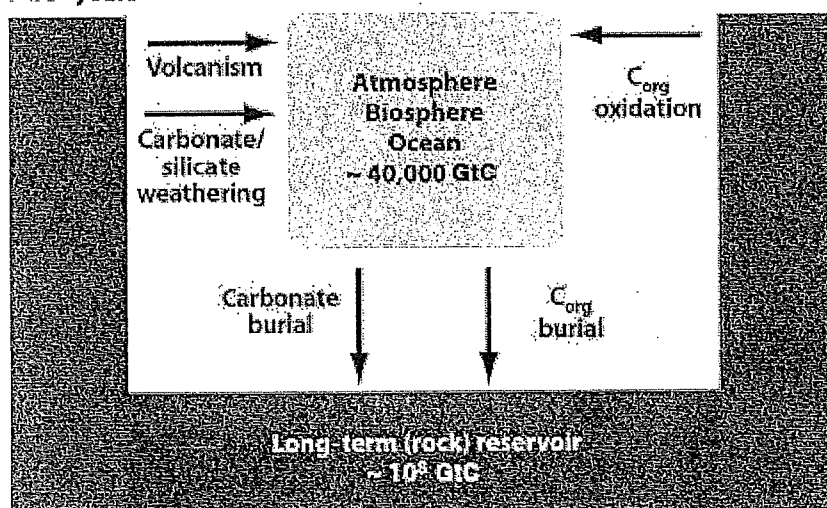
Note that reaction (3) can be obtained as the combination of forward reaction (1) and reverse reaction (2) and it is sometimes shown with arrows in both directions. This is unfortunate because it obscures the role of water in the weathering processes ["reverse" of reaction (3)] that occur at atmospheric pressure and ambient surface temperature. This contrasts with the high pressure and temperature conditions required for metamorphism. It also obscures the essential role of the marine biological chemistry that produces the sediments from which the reactants are formed.

This reaction of limestone is responsible for the dissolution that forms most of the caves on Earth. The reverse reaction builds the stalactites and stalagmites that decorate these caves. Reversible reaction (2) is not a net sink for CO_2 . Reaction (1) is irreversible, driven by the formation of SiO_2 , and is a net sink for atmospheric CO_2 .

As indicated above, over a couple of billion years, essentially all the carbon on Earth has been oxidized to carbonate. The graphic below shows that about 99.6% of the carbon is now sequestered in the rock reservoir. The rock cycle briefly outlined above has been the long-term control on the carbon in the atmosphere, the oceans, and the land surface of the Earth, including the biosphere—represented by the blue area in the graphic.

To put this percentage and the large numbers in the graphic in perspective, there are about 2000 GtC in the biosphere (including 7,000,000,000 human beings and counting), which is only about 0.002% of all the carbon on Earth.

Timescale:
> 10^5 years



Source: Modification of Figure 2b from R.E. Zeebe, "History of Seawater Carbonate Chemistry, Atmospheric CO_2 , and Ocean Acidification," *Annu. Rev. Earth Planet. Sci.*, 2012, 40, 141-165.

Human activity has increased the atmospheric level of CO_2 in this system to levels unprecedented in at least a million years and done so essentially instantaneously on a geological time scale. Given another million years or so and assuming that the marine biological chemistry continues to work in a more acidic ocean, the rock cycle could probably bring the carbon cycle back into balance. Although a mere blink of an eye in the time scale of life

on Earth, a million years is five times longer than humans have been part of that life. On this time scale, it is unlikely that increased rock weathering will play much of a role in mitigating any other effects of increased atmospheric CO₂ levels.

This figure represents how carbon is stored and interchanged between Earth's long-term and the shorter-term reservoirs introduced in the [Ocean Chemistry](#) page of this ACS Climate Science Toolkit. The numbers in the labeled boxes are gigatonnes (10¹⁵ g) of carbon, GtC, in that reservoir. The timescale is an indication of about how long it takes a change within the reservoirs to come to equilibrium.

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