Not all the carbon dioxide being added to the atmosphere originates from the activities of humans; the Earth makes its own contribution through geological processes. **Sam Holloway, Jonathan Pearce** and **Vicky Hards** describe some important examples.

Natural carbon dioxide flow

Much of the naturally occurring carbon dioxide (CO_2) emitted from the geosphere originates from the degassing of magma (molten rock). When magma rises towards the Earth's surface, its pressure is lowered. This enables dissolved CO_2 and other gases to come out of solution as free gas. Most of the CO_2 originating from magma degassing is emitted through volcanoes and associated fissures, or hydrothermal sites such as the one in Yellowstone National Park in the USA. However, a proportion may travel up deep-seated faults rooted in the lower crust and make its way into sedimentary basins.

A distinction can be made between natural CO_2 emissions that occur in volcanic areas and those in sedimentary basins. Volcanic and hydrothermal regions are often tectonically unstable. Moreover, because heat and steam are usually present they can contain gas under great pressure, commonly in voids. The occasional large sudden emissions of CO_2 that have occurred in volcanic and hydrothermal areas have resulted from the accumulation of CO_2 in underground voids or stratified crater lakes.

By contrast, sedimentary basins are large areas of the Earth's crust which are actively subsiding, or have subsided in the past, allowing thick successions of sediments to accumulate. Some high purity carbon dioxide fields found in sedimentary basins are thought to have formed by heating and metamorphism of carbonate rocks, such as limestones, most commonly by magmatic intrusions. In addition CO_2 can form by the thermal alteration of coal and other organic material. Most of this CO_2 is thought to dissolve in water and eventually precipitates as carbonate cements in the pore spaces of nearby reservoir rocks. Furthermore CO_2 can originate from the biodegradation of oil and gas. Under favourable circumstances, microbes living in the pore spaces of sedimentary rocks can feed on oil and gas, and their respiration produces CO_2. Some fields of CO_2-rich hydrocarbons are thought to have formed in this way. CO_2 may also originate from the dissolution of limestone and other carbonate rocks.

Sedimentary basins are widely spread around the world and many occur in tectonically stable regions. They normally

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The Soufrière Hills Volcano, Montserrat, part of the Lesser Antilles Volcanic Arc resulting from the subduction of the Atlantic plate under the Caribbean plate, 27 January 2007.

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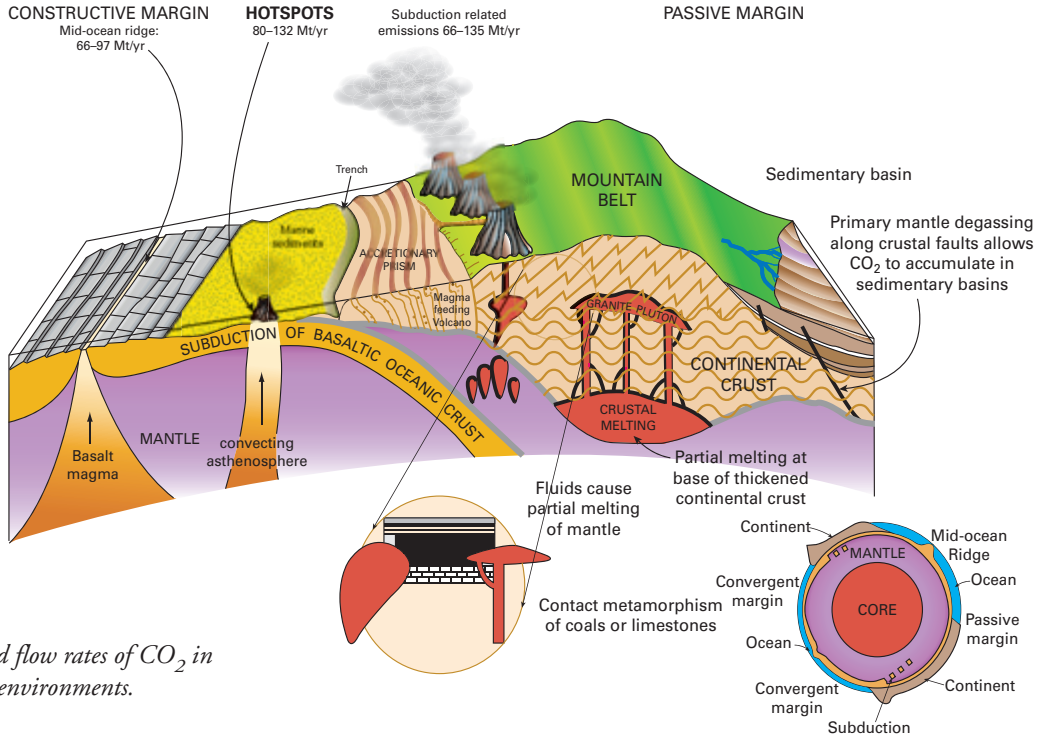
A pyroclastic flow — an avalanche of volcanic debris and superheated volcanic gases on the north-west flank of the Soufrière Hills Volcano during a partial dome collapse event, 8 January 2007.

Both the images above are a product of the programme of work carried out in Montserrat by the BGS under contract to the GoM.



Typical estimated flow rates of CO_2 in selected tectonic environments.

contain both porous and permeable reservoir rocks and very low permeability cap rocks. These cap rocks act as natural seals that prevent gases migrating upwards and are an important element of oil and natural gas fields. In a similar manner, naturally occurring CO_2 may be confined in the pore spaces of sedimentary rocks where these have been folded into domes or other structures that do not contain any pathways to the ground surface or sea bed. One example is the natural CO_2 field in the Pisgah Anticline in Mississippi, USA, which is thought to be around 65 million years old. The Pisgah Anticline holds over 200 million tonnes of CO_2 and is of comparable size to the large engineered CO_2 storage sites that are being considered for CO_2 sequestration.

Compared to both rock and groundwater, CO_2 is buoyant and consequently tends to migrate upwards towards the Earth's surface. Much of the CO_2 generated in natural systems does not encounter suitable subsurface structures that could trap it and so it is able to migrate both laterally and vertically along permeable pathways. These pathways may be beds of porous and permeable sedimentary rock, such as sandstone, and/or fractures and fissures that cut through both permeable and otherwise less permeable rocks. Its migration is in many ways analogous to that of natural gas (mainly methane).

Most rocks buried to shallow depths of a few tens of metres or less contain fractures that are open and highly permeable. Consequently in most natural CO_2 emission sites the CO_2 tends to flow along these fractures, though it does not necessarily escape along the entire length of a fracture or fault; it will tend to emerge at one or more discrete points along it. This is because the permeability of the fault will vary along its length and once 'breakthrough' occurs at one point, a channelling effect will occur.

In offshore areas the migration of gases through the sea bed commonly produces pits called pockmarks or, where gases emerge along with mud or muddy water, a mound on the sea floor called a 'mud volcano', which may also occur onshore.

Sometimes CO_2 emerges at the sea bed dissolved in water or as a free gas. If in a free gas phase it may form a train of bubbles that will rise through the water column. However, CO_2 bubbles are much more soluble than the commonly detected natural gas bubbles and would probably dissolve in the first 50 metres or so of seawater unless the emission rate was very high. Examples of natural emissions of CO_2 from the sea bed are found in the Tyrrhenian Sea offshore from the Aeolian Islands in Italy.

In onshore sedimentary basins, migrating CO_2 will pass through two hydrogeological zones on its way to the surface. Most of its passage will be through the lower saturated (or phreatic) zone, beneath the water table, where the pore spaces, and any fractures found within the rocks, are fully saturated with water. The upper (or vadose) zone is above the water table and is largely filled with soil gas (air modified by soil processes). Once CO_2 emerges through the saturated zone it will tend to disperse within the vadose zone. It may pool on top of the water table and disperse laterally before emerging at the ground surface.

The other way in which naturally occurring CO_2 typically emerges from the geosphere in onshore sedimentary basins (and also volcanic and hydrothermal areas) is in carbonated springs. These occur when CO_2 has dissolved in the groundwater in the saturated zone. There are many examples of naturally carbonated water springs in France (Perrier, Badoit, Vichy) and elsewhere. These have been used as sources of drinking water for centuries.

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