MILESTONE 3

Isotopes and ancient environments

Glacial landforms can be dated by mass spectrometry, using radioactive isotopes such as ^{14}C and ^{10}Be.

In the early twentieth century, the relatively new technique of mass spectrometry provided an opportunity to assess whether there were systematic variations in the ratio of the isotopes of matter. In 1939, Alfred Nier and Earl Gulbransen showed that this was the case for carbon. They found that the isotopic composition of carbon varied depending on how and when the various types of rock and organic matter formed. For example, they found subtle but consistent differences between carbon minerals formed by volcanic processes and those derived from seawater. The isotope composition even varied between the flesh and the shell of clams.

It later became clear that carbon isotope ratios are even more variable than initially found in this early work: they also reflect changes in carbon cycling in the terrestrial biosphere and throughout the oceans . These discoveries opened up the possibility of tracing the evolution of life and the carbon cycle through time.

Stable oxygen isotopes, particularly ^{18}O and ^{16}O, also proved to be important tracers. The work of Willi Dansgaard demonstrated that the oxygen isotope composition of precipitation could be used to trace both the temperature at which the water droplets formed and the history of the air mass the water originated from as it moved away from the initial vapor source. Oxygen isotopes became the primary means to interpret ice cores collected from the Greenland and Antarctic ice sheets, and are also key to interpreting biogenic carbonates in marine sediment cores.

Mass spectrometry–based analyses of ice and sediment cores soon showed that dramatic and repeated periods of climate upheaval had occurred for the past few million years. But there were impediments to fully realizing the potential of these environmental archives, including the large sample size required for isotopic analyses, particularly with radioisotopes. The decay counting techniques of the early 1970s required large amounts of often irreplaceable samples to be destroyed.

Richard Muller's report of the use of a cyclotron to measure tritium in water samples in 1977 was therefore a welcome development. In conventional mass spectrometry, stable isotopes overwhelm any radioisotope signal, but at the high energy reached in the cyclotron, it was possible to distinguish the radioisotopes from other isotopes with similar mass-to-charge ratios. Muller estimated that similar techniques should allow ^{14}C and ^{10}Be to be measured in far smaller samples than had been possible at the time. Indeed, the cyclotron proved useful in measuring ^{10}Be, a powerful method for determining the age of glacial landforms such as moraines. In a slight variation on the cyclotron technique, Charles Bennett and colleagues showed that a linear accelerator coupled with a negative ion source could detect very small amounts of radiocarbon.

The issue of sample size for stable isotope analysis was solved with a modification to the gas inlet system of the mass spectrometer developed by Nicholas Shackleton. In his setup, the molecular leak system by which carbon dioxide produced from carbonate samples entered the mass spectrometer was applicable to small sample sizes, but this system also caused the sample to undergo further fractionation. Automation of the inlet valves enabled the amount of time the sample and a reference standard flowed through the leak to be equalized, thus allowing for correction of the fractionation. With this system, samples as small as 100 μl could be analyzed.

Collectively, these developments meant that for fossil material such as tooth or bone, only small parts of the fossil needed to be sacrificed. This also allowed measurements of fossil carbonate within marine sediments to be made at a much higher resolution, resolving the patterns of glacial-interglacial temperature change as well as the timing of more recent fluctuations. Such high-resolution measurements ultimately revealed that swings from glacial to interglacial states over the past half million years were paced by changes in the Earth's orbit around the sun.

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