Sulfur signature changes thoughts on atmospheric oxygen

August 23 2006

Ancient sediments that once resided on a lake bed and the ocean floor show sulfur isotope ratios unlike those found in other samples from the same time, calling into question accepted ideas about when the Earth's atmosphere began to contain oxygen, according to researchers from the U.S., Canada and Japan.

"The popular model is that there was little oxygen in the Earth's atmosphere before about 2.4 billion years ago," says Dr. Hiroshi Ohmoto, professor of geochemistry and director, Penn State Astrobiology Research Center. "Scientists use the ratio of the various sulfur isotopes as their strongest evidence for atmospheric oxygen."

All isotopes of sulfur behave the same chemically but have slightly different masses. Sulfur has four isotopes. About six years ago, researchers began measuring the abundance of these isotopes and determined their ratios in the natural world. These ratios are called mass dependent isotope fractionation and are the way sulfur fractionates today.

But rocks dating before 2.4 billion years ago have abnormal ratios, or exhibit mass independent fractionation. Generally, scientists attributed this abnormal fractionation to atmospheric chemical reactions. The reaction thought to occur before 2.4 billion years ago is that sulfur dioxide produced by volcanos is separated into native sulfur and sulfuric acids by ultra violet light. Because ozone forms an ultra violet impenetrable shield around the Earth, this reaction could not occur if ozone existed.

Ozone is a common component of our atmosphere and is composed of three atoms of oxygen. If the atmosphere has no ozone, it is assumed the atmosphere has no oxygen.

Ohmoto, working with Dr. Yumiko Watanabe, research associate, Penn State; Dr. Hiroaki Ikemi, former Penn State post doctoral fellow; and Dr. Simon R. Poulson, former Penn State doctoral student now a professor at University of Nevada, and Dr. Bruce E. Taylor, Geological Survey of Canada, report in today's (Aug. 24) issue of *Nature* the isotopic, mineralogical and geochemical results of drilling cores recovered by the Archaean Biosphere Drilling Project in the Pilbara Craton, Pilbara, Australia.

The two core segments represent one of the oldest lake sediments -- 2.76 billion years old -- and one of the oldest marine shale sediments -- 2.92 billion years old. Surprisingly, both samples' sulfur isotope ratios fall in the mass-dependent fractionation range and do not show the signal of an oxygenless atmosphere.

"We analyzed the sulfur composition and could not find the abnormal sulfur isotope ratio," said Ohmoto. "This is the first time that sediment that old was found to contain no abnormal sulfur isotope ratio."

One possible explanation is that perhaps oxygen levels during that time period fluctuated greatly creating a "yo yo" atmosphere: Going from oxygenless before 3 billion years ago to oxygenated between 3 billion and 2.75 billion years ago and then back to oxygenless from 2.75 billion to 2.4 billion years ago. The researchers suggest that future investigation of different geologic formation could indicate that oxygen fluctuation was even more frequent.

Another explanation could be that the atmosphere contained oxygen as early as 3.8 billion years ago and that mass independent isotope ratios of sulfur occurred because of violent volcanic eruptions and enormous amounts of sulfur dioxide released into the atmosphere. Investigation of ash sediments from recent Mt. Pinatubo eruptions and other major volcanic events show a signature of mass independent isotope ratios of sulfur, while sediment from minor eruption does not.

The photochemical reaction of volcanic sulfur dioxide may not be the only method of creating a mass independent fractionation of sulfur. Reactions between sulfate-rich seawater and organic material in the sediment during the formation of sedimentary rock layers might produce sulfur with mass independent fractionation. If so, the commonly believed linkage between the abnormal sulfur isotope ratios in sediments and an oxygen-free atmosphere must be reevaluated.

Source: Penn State