Origins of sulfur in rocks tells early oxygen story

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(PhysOrg.com) -- Sedimentary rocks created more than 2.4 billion years ago sometimes have an unusual sulfur isotope composition thought to be caused by the action of ultra violet light on volcanically produced sulfur dioxide in an oxygen poor atmosphere. Now a team of geochemists can show an alternative origin for this isotopic composition that may point to an early, oxygen-rich atmosphere.

"The significance of this finding is that an abnormal isotope fractionation (of sulfur) may not be linked to the atmosphere at all," says Yumiko Watanabe, research associate, Penn State. "The strongest evidence for an oxygen poor atmosphere 2.4 billion years ago is now brought into question."

The researchers, who also include James Farquhar, associate professor of geology, University of Maryland and Hiroshi Ohmoto, professor of geoscience, Penn State, present the possibility that the rocks with an anomalous sulfur isotope fractionation came from locations on the ocean floor where hydrothermal fluids seeped up from submarine vents through organic carbon rich sediments and mixed with the ocean water. Watanabe used laboratory experimentation to test their theory and report on the results in today's (Apr. 17) issue of *Science*.

Chemical elements often have more than one form. While the number of protons and electrons are all the same, the element may have forms with a greater or lesser number of neutrons and consequently a different atomic weight. Sulfur has four naturally occurring isotopes none of which are radioactive. Although 95 percent of sulfur has an atomic weight of 32, the other 5 percent is composed of sulfur with atomic weights of 33, 34 or 36. The relationship between the amounts of 33, 34 and 36 are predictable based on the differences in their weights, but in the early rocks examined, the relationship was often anomalous. Other scientists have previously determined that the sulfur dioxide, ultraviolet light reaction in the absence of oxygen can produce the anomalous isotope fractionation.

Watanabe looked at samples of amino acids and sodium sulfur compounds to try to recreate the anomalous sulfur isotope composition in another way. She chose amino acids as a proxy for organic material because the anomalous sulfur isotopes often come from sedimentary rock, black shale, that also contains abundant mature kerogen -- a mixture of organic compounds. She chose sodium compounds because of the large amounts of sodium and sulfate in the ocean.

Initial experiments used two amino acids -- alanine and glycine -- and sodium sulfite, which is less oxidized compared to sulfate. When heated, these did not produce abnormal fractionation. Watanabe then tested five amino acids, adding histidine, arginine and tryptophan, and mixed them with sodium sulfate. In this case, alanine and glycine produced the anomalous isotope composition found in the rocks. In all, she ran 32 series of experiments with more than 100 individual samples.

"At high temperatures it sometimes took 24 hours for the sulfate to reduce to sulfide," said Watanabe. "At lower temperatures it took about two months, 1,000 hours. I ran the experiments until I had enough product to test the isotopic distribution."

Although Watanabe captured the sulfur from the experiments as hydrogen sulfide gas, she converted it to silver sulfide for analysis because it is easier to work with a solid than a gas.

"People never thought that anomalous sulfur isotope fractionation could be caused by a process other than atmospheric reactions," said Ohmoto. "Our study significantly shifts possibilities to something different, to a biological and thermal regime. There are now at least two ways that the anomalous sulfur isotope fractionation seen in some rocks could be achieved."

While sulfate-reducing bacteria do not produce anomalous isotope relationships, the remains of simple organisms coupled with thermal sulfate reduction does produce the anomalous isotope signature.

The researchers plan to look at dead cyanobacteria -- blue green algae -- next to see if their organic material will fuel the thermal reaction to produce anomalous sulfur isotope relationships.

Source: Pennsylvania State University (news : web)