Fools' gold found to regulate oxygen

July 23 2012

As sulfur cycles through Earth's atmosphere, oceans and land, it undergoes chemical changes that are often coupled to changes in other such elements as carbon and oxygen. Although this affects the concentration of free oxygen, sulfur has traditionally been portrayed as a secondary factor in regulating atmospheric oxygen, with most of the heavy lifting done by carbon. However, new findings that appeared this week in *Science* suggest that sulfur's role may have been underestimated.

Drs. Itay Halevy of the Weizmann Institute's Environmental Science and Energy Research Department (Faculty of Chemistry), Shanan Peters of the University of Wisconsin and Woodward Fischer of the California Institute of Technology, were interested in better understanding the global sulfur cycle over the last 550 million years – roughly the period in which oxygen has been at its present atmospheric level of around 20%. They used a database developed and maintained by Peters at the University of Wisconsin, called Macrostrat, which contains detailed information on thousands of rock units in North America and beyond.

The researchers used the database to trace one of the ways in which sulfur exits ocean water into the underlying sediments – the formation of so-called sulfate evaporite minerals. These sulfur-bearing minerals, such as gypsum, settle to the bottom of shallow seas as seawater evaporates. The team found that the formation and burial of sulfate evaporites were highly variable over the last 550 million years, due to changes in shallow sea area, the latitude of ancient continents and sea level. More surprising to Halevy and colleagues was the discovery that only a relatively small fraction of the sulfur cycling through the oceans has exited seawater in this way. Their research showed that the formation and burial of a second sulfur-bearing mineral – pyrite – has apparently been much more important.

Pyrite is an iron-sulfur mineral (also known as fools' gold), which forms when microbes in seafloor sediments use the sulfur dissolved in seawater to digest organic matter. The microbes take up sulfur in the form of sulfate (bound to four oxygen atoms) and release it as sulfide (with no oxygen). Oxygen is released during this process, thus making it a source of oxygen in the air. But because this part of the sulfur cycle was thought be minor in comparison to sulfate evaporite burial, (which does not release oxygen) its effect on oxygen levels was also thought to be unimportant.

In testing various theoretical models of the sulfur cycle against the Macrostrat data, the team realized that the production and burial of pyrite has been much more significant than previously thought, accounting for more than 80% of all sulfur removed from the ocean (rather than the 30-40% in prior estimates). As opposed to the variability they saw for sulfate evaporite burial, pyrite burial has been relatively stable throughout the period. The analysis also revealed that most of the sulfur entering the ocean washed in from the weathering of pyrite exposed on land. In other words, there is a balance between pyrite formation and burial, which releases oxygen, and the weathering of pyrite on land, which consumes it. The implication of these findings is that the sulfur cycle regulates the atmospheric concentration of oxygen more strongly than previously appreciated.

Provided by Weizmann Institute of Science