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Revision 2

Pyrite: fool's gold records starvation of bacteria

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Pyrite (FeS_2) is the most common sulfur-bearing mineral in the Earth's crust and can be found in all major types of rock: igneous, metamorphic, and sedimentary. It is the shiny, brass-colored mineral that you may know as fool's gold because it looks like gold and has fooled people throughout recorded history (Figure 1). In some areas, it can be observed at the sides of roads or trails, especially where the ground has been recently disturbed. If you have ever caught the scent of rotten eggs while digging at the beach, in mud flats, or swamps, you were probably in an area where pyrite was forming. That smell is caused by hydrogen sulfide (H_2S), and the black or blue muds that you were digging in would have contained microscopic pyrite that formed when the hydrogen sulfide that you smelled bonded with iron in the pore waters (Rickard, 2015).

Despite pyrite's bad rap as fool's gold, it has some interesting geochemical properties that may help us uncover how the ancient oceans, atmosphere, and life evolved on Earth; including how oxygen changed during these processes. Here we specifically discuss how pyrite can record bacterial processes and how we can use pyrite's isotopes (see Nitty Gritty Details) to understand how the pyrite formed.

To gain energy for survival, bacteria must combine organic matter with an oxygen-bearing molecule. Oxygen (O_2) itself is the best molecule for this and the one that we and most multicellular life forms use; however, at low oxygen levels other molecules are used. In descending order of energy gained after oxygen these are: nitrate (NO_3), manganese oxides (e.g., MnO_2), iron oxides (e.g., FeO_2), and sulfate (SO_4) (Loyd et al., 2012). When bacteria combine organic matter with the oxygen in sulfate (SO_4), smelly H_2S forms and reacts with iron (Fe) to make pyrite (FeS_2).

$$SO_4^{2-} + CH_4 \leftrightarrow HS^- + HCO_3^- + H_2O$$

$$Fe^{2+} + 2HS^- \leftrightarrow FeS_{2(pyrite)} + H_2$$

In the ocean, many bacteria use sulfate to help produce energy because it is can be relatively abundant – it's a feast! However, bacteria can run out of sulfate in deep sediments or even in the oceans, such as at times in Earth's history when oxygen was low – it's a famine.

The sulfur isotopes contained within the pyrite we find in the rock record can provide us with information about how much sulfate was consumed by this process. The isotopes of sulfur provide us with additional information about how much sulfate is used up. Sulfur has an atomic mass of 32.07. The reason for the decimal is that sulfur has 4 different stable isotopes (^{32}S, ^{33}S, ^{34}S, and ^{36}S), that is atoms with the same number of protons but different numbers of neutrons and 32.07 is the average of the atomic masses of these isotopes. The relative abundances of these isotopes can be used to understand the source of the sulfur and what reactions it underwent. Here we focus on the most abundant isotopes of sulfur, ^{32}S and ^{34}S. Sulfur isotope ratios are reported as a comparison to a standard with known ratio of isotopes and how our sample differs from that standard is reported as a $\delta^{34}S$ value, with units of ‰ or ('per mil') (see Nitty Gritty Details).

Bacteria use sulfate to get energy by oxidizing organic matter in a manner analogous to burning. During this process sulfate is transformed to hydrogen sulfide (H_2S) which can then form pyrite. When bacteria do this they preferentially use the lighter S^{32} isotope, meaning that the H_2S that forms does not incorporate heavier isotopes and therefore the ratio of heavy (S^{34}) sulfur to lighter (S^{32}) sulphur is much lower than normal. This means that the pyrite that forms from this process would have a negative $\delta^{34}S$ value (typically -40‰; see Nitty Gritty Details). In the open oceans, because there is always a lot of sulfate around, the $\delta^{34}S$ value remains nearly constant. When pyrite forms deep in the sediments at the ocean's floor, the $\delta^{34}S$ of that pyrite will start out low (approximately -40‰ compared to starting sulfate $\delta^{34}S$) as long as there is ample sulfate to consume, the bacteria will choose to use the S^{32} first, and the $\delta^{34}S$ will remain low. But as the initial sulfate is used up the bacteria will become less selective about which isotopes to use, and they start to consume the heavier ^{34}S. More and more consumption leads to less and less sulfur overall, producing higher and higher $\delta^{34}S$ values. Therefore, high $\delta^{34}S$ in the rock record tells us that the sulfate reducing bacteria at that location and time, were running out of sulfate and, in a manner of speaking, starving.

Approximately 2.33 billion years ago there was a sudden increase in atmospheric oxygen. This event it known as the Great Oxygenation Event (GOE; Luo et al., 2016). Prior to the GOE, oxygen levels in the atmosphere were extremely low, possibly 100,000 times lower than present day. Today, with our oxygenated atmosphere, much of the sulfate in the oceans comes from the oxidation of sulfide minerals on land. Because very few sulfide minerals were oxidized on land, very little sulfate was formed, and sulfate levels in the ocean were quite low before the GOE. This meant that bacteria were in famine mode, as reflected in high $\delta^{34}S$ values. However, after the GOE, atmospheric oxygen may have approached modern day levels (c. 21%; Lyons et al., 2014). This rise in oxygen increased sulfate levels, and $\delta^{34}S$ values decreased dramatically as sulfate conditions transitioned from limited ("famine") to unlimited ("feast").

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Due to its abundance and the information held within in its building blocks pyrite holds important information on the history of oxygenation of the oceans and atmosphere throughout Earth History. Because these processes are inextricably linked to the process of evolution of life, it is an important part of the puzzle that allowed us to become who we are today. Pyrite may be called fool's gold, but for geoscientists it's a goldmine for understanding Earth's processes and history.

Nitty-Gritty Details

Isotopes: Each atom is made up of protons, neutrons and electrons. The number of protons for a given element is always the same, but the number of neutrons can vary. Atoms with the same number of protons, but a different number of neutrons are isotopes. In the case of sulfur, there are 16 protons and 16, 17, 18 or 20 neutrons, corresponding to atomic masses of 32, 33, 34, and 36.

^{34}S: We designate each particular isotope by using a superscript before the elemental symbol. For example, ^{34}S refers to the sulfur isotope that has an atomic mass of 34 (16 protons plus 18 neutrons).

$\delta^{34}S$: Isotopic ratios are normalized to a standard compound, which is a material that contains the same element with known isotopic abundances. For sulfur, the standard is a specific mineral in the Canyon Diablo meteorite, whose ^{32}S, ^{33}S, ^{34}S and ^{36}S contents are known. To determine $\delta^{34}S$, the $^{34}S/^{32}S$ ratio in a sample is measured and compared to the ratio in the meteorite. If the ratio is higher in the sample, $\delta^{34}S$ is positive (higher values for higher ratios). If the ratio is lower in the sample, $\delta^{34}S$ is negative (lower values for lower ratios).

See Also

[1] Pyrite: A Natural History of Fool's Gold, David Rickard, Oxford University Press.

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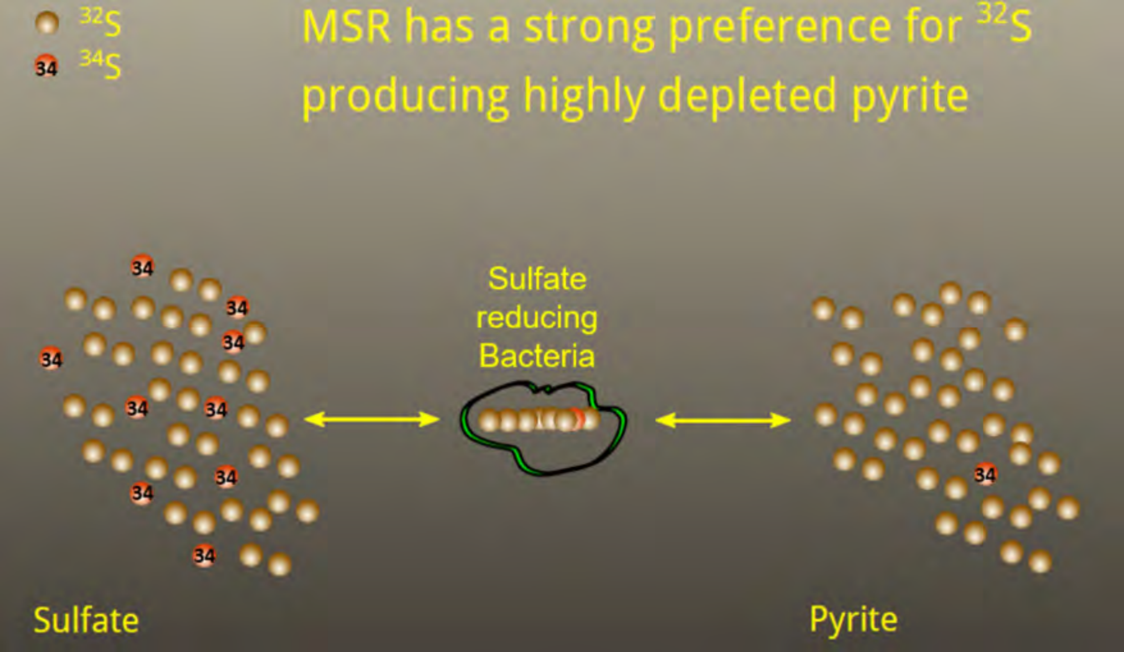
Figure 1: A) Coarse grained pyrite showing the distinctive cubic form. B) Pyrite nodule in shale. Both photos provided by the Royal Ontario Museum.

Figure 2: Cartoon showing the process of enrichment of S^{32} in pyrite. Figure provided by Ulrich Wortmann.


Figure 1A


Figure 1B



32S
34S
34
MSR has a strong preference for 32S
producing highly depleted pyrite
Sulfate
reducing
Bacteria
Sulfate
Pyrite