

Ground-truthing the pyrite trace element proxy in modern euxinic settings

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ABSTRACT

Pyrite trace element (TE) chemistry is now widely employed in studies of past ocean chemistry. Thus far the main proof of concept has been correlation between large data sets of pyrite and bulk analyses emphasizing redox sensitive TE data from ancient samples spanning geologic time. In contrast, pyrite TE data from modern settings are very limited. The sparse available data are averages from samples from the Cariaco Basin without stratigraphic resolution and from estuarine sediments. To fill this gap, we present TE data (Co, Ni, Cu, Zn, Mo, Ag, Pb, Bi) from the two largest euxinic basins on Earth today, locations where the majority of the pyrite formed within the water column, the Black Sea and Cariaco Basin. These locations have different water column TE contents due to their relative degrees of restriction from the open ocean, thus providing an ideal test of the relationship between pyrite precipitated under euxinic conditions from basins with different degrees of basin restriction and dissolved TE concentration.

At each site we observed that down-core trends for pyrite increase before reaching relatively steady values for most TE. This observation suggests that instead of all the TE being sourced directly from the water column, some are incorporated from the sediments, presumably desorbing from detrital materials. However, since much of the adsorbed TE is adsorbed from the overlying water, the pyrite chemistry still seems to reflect the water chemistry at or near the surface. Indeed, for Mo, there is less variation in pyrite than in bulk sediment. Additionally, we found that pyrite formed during diagenesis due to sulfide diffusion into iron-rich muds revealed low-TE contents, except for siderophile elements likely to have been adsorbed onto Fe (hydr)oxides, highlighting the risk of potential false negatives from pyrite formed under these conditions. This relationship highlights the need for detailed understanding of the full context, including the use of complementary geochemical data such as sulfur isotope trends, in efforts to use pyrite TE to interpret conditions in the global ocean.

Keywords: LA-ICPMS, Cariaco, Black Sea, trace elements, pyrite, framboid; Understanding Paleo-Ocean Proxies: Insights from in situ Analyses