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

INTRODUCTION

Pyrite trace element (TE) contents are used in a variety of ways in the Earth sciences, ranging from understanding different mechanisms of ore deposit formation (Large et al. 2007; Revan et al. 2014; Genna and Gaboury 2015; Cook et al. 2016; Gadd et al. 2016, 2019; Mukherjee and Large 2017) to tracing deleterious construction materials to their source (Dornan et al. 2020) to tracing past ocean chemistry (Large et al. 2014; Gregory et al. 2017; Mukherjee et al. 2019). However, a rigorous understanding of when and how TE are incorporated into sedimentary pyrite remains elusive.

Several studies have addressed TE incorporation into sedimentary pyrite. In the earliest of those studies, chemical analyses of sequential leaches of bulk sediments were used to isolate the pyrite fraction for subsequent elemental analysis (Huerta-Diaz and Morse 1990, 1992) and how the TE concentration changed with distance below the sediment-seawater interface. While useful in understanding which phase held different TE, a lack of specificity of the reagents used, a problem commonly encountered with sequential extractions (Martin et al. 1987), frustrated these efforts. Next, pyrite was isolated for analysis by rock crushing, treatment with different chemicals, and hand picking of pyrite grains (Tribovillard et al. 2008; Berner et al. 2013; Piszarzowska et al. 2014). While this approach was effective, the method was time consuming. Furthermore, different textures of pyrite, which are often very small, were difficult to extract. For example, the small framboidal pyrite, like those analyzed in this study, was the most difficult if not impossible to isolate (Berner et al. 2013). More recently, the adoption of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICPMS) analyses has allowed in situ analysis of fine pyrite grains and thus focus on specific pyrite types. This methodology has...