Revision 1: 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 datasets 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 are 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 use of complementary geochemical data such as sulfur isotope trends, in efforts to use pyrite TE to interpret conditions in the global ocean.

Introduction

understanding of when and how TE are incorporated into sedimentary pyrite remains illusive.

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, Huerta-Diaz and Morse 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
was effective, the method was time consuming. Further, 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, were 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
been used to explore long-term trends in ocean chemistry (Large, et al. 2014, Gregory, et al. 2017, Large,
et al. 2019, Stepanov, et al. 2020). This technique has the potential to overcome some common
difficulties encountered with traditional ocean chemistry proxies. First, sedimentary pyrite is ubiquitous
in the geological record so obtaining complete datasets is relatively straightforward for much of Earth
history. Second, sedimentary pyrite TE content can be preserved up to greenschist facies metamorphism
(Large, et al. 2007, Gregory, et al. 2016) whereas this can frustrate whole rock studies due to potential
for metal remobilization (Ardakani et al., 2016). Finally, because sedimentary pyrite is precipitated
directly out of the water column or pore waters it is not as susceptible to dilution from detrital
components as traditional whole rock proxies. That said this technique is not without its difficulties.
Pyrite formed in euxinic conditions tend to be small (Wilkin et al., 1996; Rickard et al., 2019) which
makes them difficult to analyze. However, even though most framboids are small (geometric mean 4.7
µm; Rickard et al., 2019) the range of syngenetic (water column formed) pyrite is 2.9-10.9 µm. It is the
larger end of this range, or clusters of smaller framboids, that were the focus of this study. Rickard et al.,
(2019) also argued that pyrite framboids do not get additional pyrite added to them (at least not such
that there would not be a textural difference) so we are confident that the chemistry of these framboids
is representative of the pyrite framboids in the sample.

Thus far the LA-ICPMS approach to pyrite analyses has been applied almost exclusively to black shales
from ancient sediments. These have shown agreement with several other widely used
caloeocanographic proxies, such as Ni in banded iron formations (Konhauser, et al. 2017) and
molybdenum in euxinic black shales spanning billions of years (Scott, et al. 2008). This agreement has
also been demonstrated at the scale of an individual stratigraphic section (Wuhe, Doushantuo
Formation, China) where pyrite TE analysis has been shown to match traditional whole rock proxies such
the Wuhe section specifically suggest changes in connectivity to the global ocean over the duration of
deposition and by inference that variations in pyrite elemental data capture local rather than global
effects (Ostrander, et al. 2019). This example points to the possibility that both the pyrite proxy and
traditional whole rock data are vulnerable to local controls. One goal of this study is to examine the
degree to which local controls affect pyrite trace element chemistry by comparing a more restricted basin (Black Sea) with a less restricted basin (Cariaco Basin).

To date, only limited analyses have been conducted on pyrite forming in modern ocean waters where the TE content of the water from which the pyrite formed can be known or at least approximated. Some analyses from the Cariaco Basin were undertaken as part of the original proof of concept for the pyrite proxy (Chappaz, et al. 2014, Large, et al. 2014, Gregory, et al. 2015); however, these lacked stratigraphic context. Some stratigraphic analyses were performed to compare between the metal-rich Derwent and metal-poor Huon Estuaries (Gregory, et al. 2013, Gregory, et al. 2014). However, these efforts addressed extremes linked to anthropogenic metal contamination, and while they showed that the pyrite technique was sensitive to changes in metal abundance, a lack of pore water analyses meant that the more subtle relationship between availability of TE and degree of enrichment in pyrite could not be determined.

In this contribution we have obtained samples from the two largest euxinic basins in the modern world, the Black Sea and the Cariaco Basin, which have been euxinic for the past ~8.0 and 14.5 ka BP, respectively (Lyons et al., 2003; Arthur and Dean 1998). Euxinic basins were chosen for this study because the pyrite is likely to have formed largely in the water column (Wilkin, et al. 1996), giving it the best chance of accurately reflecting the TE chemistry of that water. Furthermore, these sites are ideal because the Cariaco Basin is recharged from the Caribbean Sea, while the Black Sea is highly restricted, resulting in pronounced differences in the TE contents of the waters in the two basins (Jacobs, et al. 1987, Haraldsson and Westerlund 1988, Emerson and Huested 1991, Colodner, et al. 1995), with generally significantly lower TE concentrations in the Black Sea (Algeo and Lyons, 2006; Scott and Lyons, 2012), though surface waters have similar Mo concentrations once corrected for salt content (Algeo and Lyons, 2006). These differences allow assessment of the sensitivity of TE content of pyrite to changes in local inventories relative to global availability. Additionally, because the samples have strong stratigraphic control, any temporal differences that may reflect changing local conditions can be identified, including fundamental shifts in depositional redox and associated pyrite overprints.

Pyrite Formation

Pyrite forms when sulfidic conditions are present in the water column or in sediments. Several pathways have been proposed for pyrite formation, and each of those pathways depends on different precursor phases that the resultant pyrite might inherit TE from. Thus, to fully understand the TE concentration of the resultant pyrite, a discussion of how pyrite forms in sediments is needed. A brief summary of how this occurs is presented here, but for a detailed discussion see Rickard (2012) and references therein. Pyrite formation can be summarized via three main reaction pathways:

(1) \( \text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2(\text{pyrite}) + \text{H}_2 \) (Rickard 1975, Rickard 2012)

(2) \( \text{FeS} + \text{S}^{2-}_n \rightarrow \text{FeS}_2(\text{pyrite}) + \text{S}^{2-}_{(n-1)} \) (Rickard 1975, Rickard 2012)

(3) Complex, potentially variable, reactions involving sulfidation of Fe (hydr)oxides (Peiffer, et al. 2015)

Reaction 1 involves the reaction of \( \text{H}_2\text{S} \) with \( \text{FeS} \), a solid precursor such as mackinawite or a dissolved FeS species. However, it has been argued, although often cited as a precursor, that mackinawite is not likely to form in modern sedimentary environments (Rickard and Morse 2005). Further, slight oxidation of FeS is needed for the reaction to proceed (Benning, et al. 2000, Swanner, et al. 2019). Reaction 1 is
more likely to occur at moderate to low pH (Rickard and Morse 2005), because these pH conditions stabilize the \( \text{H}_2\text{S} \) and \( \text{HS}^- \). At higher pH, reaction 2 predominates as the \( \text{H}_2\text{S} \) concentration, relative to \( \text{HS}^- \) and \( \text{S}^{2-} \), approaches 0, although with slower reaction rates (Rickard and Morse 2005). Reaction 3, while important in some settings may be less important for most of the pyrite analyzed here, which is thought to form in the water column, predominantly at the interface between sulfidic waters and the overlying non-sulfidic waters (Lyons 1997). That said, this pathway is likely much more important in the lower most Cariaco Basin samples where sulfidic water has diffused into the underlying sediments that were deposited in a non-sulfidic environment and were likely rich in Fe oxides (Lyons, et al. 2003).

In addition to the requisite reactions, two more processes are needed for pyrite formation. These are nucleation of the pyrite grain and growth by addition of more Fe and S atoms to the initial nucleated mass (Rickard, 2012). The formation of the initial pyrite requires a high degrees of supersaturation; additional later pyrite can form at lower degrees of supersaturation in the presence of seed crystals (Harmandas, et al. 1998, Rickard 2012). Other factors may also affect nucleation rates. Biology has the ability to greatly enhance pyrite formation rates; \( 10^4 \) to \( 10^5 \) times faster reaction rates have been found in S-isotope studies (Canfield, et al. 1998). Even passive presence of biological materials may be important for pyrite formation. Mackinawite has been found to nucleate on live and dead remains of sulfate reducing bacteria, and it is plausible that it may play a similar function for pyrite (Picard, et al. 2017). Trace elements might also affect pyrite formation rates. For example, Morin, et al. (2017) found that the presence of Ni greatly enhanced the rate of pyrite formation in their experiments.

**Pyrite trace element incorporation**

Pyrite has long been recognized as a sink for many TE, especially the chalcophile and siderophile elements. However, the manner in which these elements are incorporated (i.e., inclusions vs. structurally bound) into the pyrite is less well understood. Based on water exchange reaction rates, it has been argued that Ni and Co, with relatively slow water exchange kinetics are more likely to be incorporated into the pyrite structure (Morse and Arakaki 1993), while elements with faster water exchange kinetics (e.g., Zn) are more likely to form nano-inclusions (Morse and Arakaki, 1993). Inspection of time resolved laser ablation output graphs has broadly supported this interpretation (Gregory, et al. 2014, Gregory, et al. 2015). However, it should be noted that neither of these techniques have the resolving power to remove uncertainties, and further analyses are required to distinguish between structurally held TE and those hosted in evenly distributed nano-inclusions.

How these TE are held may affect the ability of the TE to accurately reflect the chemistry of the fluids in which the pyrite formed because the specific mineral phase involved may affect the partition coefficients and thus our interpretation of the past ocean chemistry. This relationship has been particularly well studied for As, and we use it here as an example of how one TE may affect how others are incorporated. Arsenic can be incorporated into pyrite via three main mechanisms: As (-I) substitution for S(-II) (Reich and Becker 2006), As (III) substitution for Fe (II) (Deditius, et al. 2008, Qian, et al. 2013), and as nano-inclusions of amorphous As-Fe-S (Deditius, et al. 2008). Each of these mechanisms may affect how other TE are incorporated into the pyrite and thus the degree of enrichment in pyrite compared to the amount of enrichment of the surrounding fluids. For example, As (III) substitution for Fe (II) results in a charge imbalance, which leads to a vacancy in the pyrite structure, thus creating space necessary for the incorporation of large anions (Cook and Chryssoulis 1990, FLEET 1997). Conversely, if
the As (-I) replaces S (-II), the result is an increase of elements with ionic radii similar to Fe(II) (i.e., Co(II), Ni(II), Cu(II)) (Michel, et al. 1994, Deditius, et al. 2008) in the pyrite.

Molybdenum is of particular importance when discussing both the TE content of pyrite and its use in determining past ocean chemistry because it is redox sensitive and has a long ocean residence time. Further, significant removal is tightly tied to euxinic areas in the oceans (Tribovillard, et al. 2006). Because of this reservoir relationship, in sediments deposited under local euxinic conditions, elevated Mo contents—much as are observe in the Cariaco Basin today—have been used to infer periods of widespread oxygenation (Lyons, et al. 2003, Tribovillard, et al. 2006, Scott, et al. 2008, Asael, et al. 2017). Furthermore, because much of the Mo in the ocean derives from oxidative weathering of sulfide minerals on land, the earliest increases in Mo concentrations in euxinic shales are taken as signs of initial atmospheric oxygenation (Scott, et al. 2008) and transient events leading up to that ‘Great Oxidation Event’ (Anbar, et al. 2007, Gregory, et al. 2015). Further, relatively low Mo concentrations in black shales at times of widespread ocean oxygenation are assumed to reflect local basin restriction (Algeo and Lyons 2006).

How Mo is contained within pyrite is still in question it has been suggested that rather than being incorporated by substitution into pyrite Mo forms Fe-Mo-S colloids which are then accumulated into sediments (Helz and Vorlicek, 2019 and Vorlicek et al., 2018). However, Chappaz et al. (2014) have shown that while a significant amount of Mo is incorporated in matrix material pyrite is still relatively enriched in Mo. While we acknowledge that this is still an active area of research the LA-ICPMS techniques does not give us the resolution to determine how Mo is incorporated into pyrite and we will discuss Mo in pyrite as the amount of Mo that was present in the pyrite ablation volume.

Methods

Samples

The samples from the Cariaco Basin were taken from approximately 900 m depth from site 1002 during Leg 165 of the International Ocean Discovery Program (IODP) cruise in 1996. Following pore water extraction, the samples were frozen continuously until dried, which will have minimized additional reactions between the pyrite in the sample and matrix material. The stratigraphic section from site 1002 has 3 main components. The top unit is approximately 6.5 m thick. It is finely laminated (1 mm to sub-mm thick) and dark olive gray with no evidence of bioturbation (Lyons et al., 2003). This unit has evidence of minor (at most a few % of section) thin (1-2 cm) turbidities. The unit can be subdivided into two subunits based on a transition from nannofossils and foraminifera to diatoms and abundant calcareous microfossils at approximately 4.2 m which corresponds to the end of the Younger Dryas cold period (Lyons et al., 2003). These sub-units were both deposited during the recent 14.5 kyr episode of persistent euxinia in the Cariaco Basin (Lyons, et al., 2003). Below the interval of sediments deposited under euxinic conditions is a massive bioturbated light gray clay interval which is in turn underlain by a massive, bioturbated reddish-brown clay layer. It has been interpreted that both these layers were deposited under oxic conditions but the light gray clay was reduced by diffusion of sulfidic water from the overlying sediments that were deposited under euxinic conditions (Lyons, et al. 2003).

The Black Sea samples were collected during the UNESCO International Oceanography Commission (IOC) training through research cruise in 2001 (Logachev et al., 2002). Samples were taken from two cores. BS-330B (44°18.789’, 35°04.379) sampled the upper layer of the unit I; in this core the sediment seawater...
interface was recovered in tack. BS-315G (43°20.324′, 33°26.752′) over penetrated and the upper most sediments were lost but samples from the lower part of unit I and II were obtained (Kenyon et al., 2001). These samples were frozen after collection. The euxinic interval in the Black Sea is separated into two units, I and II. Unit I consists of finely laminated light (mm scale), calcium carbonate rich layer and dark-gray to black layers (Lyons and Berner, 1992). Unit II is homogeneous, dark-gray, organic rich argued to be due to re-sedimentation of the Black Sea basin margin sediments (Lyons et al., 1992). In core BS-315G the contact between unit 1 and unit 2 occurs at 25 cm. Both units I and II are regionally extensive and were deposited under euxinic conditions (Lyons 1991).

Both the Cariaco Basin and Black Sea samples were subsampled, and the material was mounted in EpoThin epoxy resin under vacuum and subsequently polished using 1 µm diamond paste.

**SEM**

Images were collected of pyrite frambooids from the Cariaco basin mounted in epoxy using scanning electron microscopy (SEM) with back-scattered electron imaging (Fig. 1). Prior to analysis, samples were coated with carbon to avoid charge build up. Analyses were carried out in the Central Facility for Advanced Microscopy and Microanalysis at the University of California, Riverside, using a NovaNanoSEM 450.

**LA-ICPMS**

The pyrite frambooids were analyzed for TE content at the University of Tasmania using a 193 nm ArF excimer ATL Atlex ILR laser coupled with an Agilent 7700 ICP-MS. Twenty 2.5 cm laser mounts (including three standard blocks) were placed in the constant-geometry Laurin Technic ablation chamber where pyrite frambooids or clusters of frambooids were ablated with 13 µm laser spots with a pulse rate of 5 Hz in a pure He atmosphere (flow rate 0.85 l/min). Due to the small size of the pyrite frambooids, a smaller spot size was used compared to many previous studies. Thus, the detection limits were higher, and we did not measure low abundance elements such as Au. The ablated material was mixed with Ar (0.85 l/min) immediately past the ablation point to improve the efficiency of aerosol transport. The masses between 80-240 amu were optimized in the ICP-MS as these were the mass ranges of greatest interest.

Due to the small size of the pyrite frambooids, invariably some matrix (sedimentary material) was ablated with the pyrite. Any analyses with more than 30% matrix (as determined by idealized oxide composition of lithophile elements) were deleted. Remaining analyses were corrected for matrix composition using an algorithm-based linear regression similar to that described in Stepanov et al. (2020) and Gregory et al. (2017). In brief, this method segments the signal relative to time of ablation and uses those segments to calculate an initial composition of the matrix and pyrite followed by recalculation of the compositions to 100% sum of chalcophile elements and oxides for lithophile elements. After this, the new compositions are plotted against S, and a linear regression equation was used to calculate the matrix-free pyrite composition. Iron was used as the internal standard for data reduction and stoichiometric Fe concentration was assumed. Three different standards, with two analyses of each were analyzed every 15 samples and at the beginning and end of each analytical session. Three standards were used to ensure that all elements of interest had a standard with an appropriate concentration and similar ablation behavior. For S, stoichiometric Peruvian pyrite was used (34S; (Gilbert, et al. 2014). GSD-1G (Guillong, et al. 2005) was used for the lithophile elements \( ^{24} \text{Mg}, ^{27} \text{Al}, ^{29} \text{Si}, ^{43} \text{Ca}, ^{49} \text{Ti}, ^{51} \text{V}, ^{55} \text{Mn}, ^{59} \text{Co}, ^{60} \text{Ni}, ^{90} \text{Zr}, ^{157} \text{Gd}, ^{178} \text{Hf}, ^{181} \text{Ta}, ^{182} \text{W}, ^{232} \text{Th}, ^{238} \text{U}, \) and STGL2b2 (Danyushevsky, et al. 2011) was used for the
chalcophile and siderophile elements (65Cu, 66Zn, 75As, 77Se, 95Mo, 107Ag, 111Cd, 118Sn, 121Sb, 125Te, 195Pt, 197Au, 202Hg, 205Tl, 206Pb, 207Pb, 208Pb, 208Bi).

Results

The pyrite analyzed was all framboidal (Fig. 1) except for samples from the sulfide overprint zone in the Cariaco Basin where some pyrite formed later euhedral overgrowths on the earlier framboidal pyrite. In the latter case the euhedral overgrowths and the framboidal centers were analyzed together as the pyrite grain was too small for the laser beam to be used to selectively analyze the different parts of the framboid. Most framboids were ~10 µm in diameter, although exact diameter of the sphere was difficult to estimate due to the 2-D nature of polished blocks. Of the 150 total Cariaco Basin analyses, 73 had to be discounted due to over 30% matrix content. Similarly, of the total 138 Black Sea pyrite analyses, 88 had to be discounted due to over 30% matrix content. Future studies should expect a similar number of analyses to have to be discounted due to elevated matrix inclusions within their analyses and should plan their sampling strategy accordingly.

The TE content of pyrite is plotted against depth of sample in Fig. 2 for the Cariaco Basin and Fig. 3 and 4 for the Black Sea, and these data are summarized as medians and median absolute deviation in tables 1, 2, and 3. Median error estimates (1σ) for the analyses are in table 4. Pyrite trace element content is rarely, if ever, normally data distributed so summarizing the data as a mean and standard deviation is inappropriate (Gregory, et al. 2019, 2020). While in some cases pyrite trace element abundance is lognormal so geometric means and multiplicative standard deviations can be used our data set is too small to be confident that the distribution is lognormal (Gregory, et al. 2015) so instead we summarize the data using the median and median absolute deviation. If analyses were below the detection limits, half of the detection limit was used instead when calculating median values. It should be noted that, while pyrite was present, too few framboids of sufficient size were available to allow for analysis of pyrite framboids from the sediments deposited during the Younger Dryas period (Cariaco Basin; Lyons et al., 2003). In the discussion of the data presented here we use medians and median absolute deviation (MAD) to compare data between different stratigraphic intervals. If a specific interval is less than the median for the entire data set minus the MAD for the entire dataset it is taken to be a significant depletion in that element. Thus, hence forth “significant depletion” will refer to analyses that are below the median minus MAD for the entire dataset. Similarly, if the median of analyses from a specific depth is greater than the median for the entire dataset plus the MAD for the entire dataset it is taken to be a significant enrichment.

Cariaco Basin

In the Cariaco Basin, the pyrite TE concentrations tend to be lower in the top 1 to 3 samples (0-5 cm, 25-30 cm, and 40-45 cm, respectively; Fig. 5). The TE also decrease at the transition from oxic to euxinic deposition marked by a sulfide overprint on the uppermost oxic layers. Cobalt is initially significantly depleted in concentration and slowly rises in the first three samples (to a depth of 42.5 cm; Fig. 2). Further, only one of the other samples deposited under euxinic conditions had significantly depleted Co content, ranging from 15.4 to 110 ppm, with the majority between 15 and 39 ppm. The one significantly depleted sample had a median of 5.49 ppm, but this sample had only two viable analyses, and these low concentrations may be outliers. In the zone of sulfide diffusion, the Co content is similar to the euxinic interval (medians of 22.0 to 76.8 ppm) except for the lowest sample (median of 8.1 ppm Co). Nickel is relatively low in the first three samples (with two significantly depleted; 93.0 and 40.9 ppm), while the
rest of the euxinic interval is not significantly depleted, ranging from 164 to 667 ppm Ni. Again, like Co, Ni in all but the deepest sample in the sulfide diffusion zone is not significantly depleted, ranging from 229 to 303 ppm Ni, while the deepest sample is markedly low with 21.1 ppm Ni. The Pb content follows a similar trend to the Ni content, with two of the three shallowest samples having significantly depleted Pb values (15.3 and 22.7 ppm), and the lowest most sample is also significantly depleted in Pb (11.5 ppm). The rest of the analyses range from medians of 32.7 to 128 ppm Pb.

For Cu, the first two samples have medians (27.6 and 93.9 ppm) that are significantly depleted. The other pyrite deposited under euxinic conditions, except for one that is anomalously high, range from 183 to 894 ppm. Different from Co and Ni, pyrite in the sulfide diffusion zone shows a rapid decrease in TE content with increasing distance from the interval deposited under euxinic conditions (from 193 ppm to 14.1 ppm Cu). A similar trend is observed with Mo, where the top most sample has a median Mo content (168 ppm) that is significantly depleted and a sharp decrease in the sulfide diffusion zone (steady decrease with median of 75.3 ppm near the interface with the sediments deposited under euxinic conditions to 4.02 ppm in the deepest sample). The rest of the euxinic interval had Mo content that were not significantly depleted. Except for a high and low outlier, the median of the analyses in the interval deposited under euxinic conditions ranged from 698 ppm to 1490 ppm Mo. The low outlier was from the -610 cm interval and had only one analysis, so it may not be representative of the sample. There is one sample in the euxinic interval that has markedly high Cu and Mo content (1850 ppm and 2310 ppm, respectively); however, this is the same sample that had the low Co and may be due to a low number of analyses in that sample.

Silver is relatively enriched and depleted in the same intervals as Mo, with a significantly depleted concentration in the top samples (with all but one analysis below detection) and in the sulfide diffusion interval (decreasing from 1.49 ppm near the interface with the euxinic interval to 0.24 ppm in the deepest sample). As for Mo, there is a relative enrichment at -362.5 cm (median of 36.8 ppm Ag) and a depletion at -610 cm (median of 0.71 ppm Ag). Again, these intervals had few viable analyses and may not reflect the true median TE composition of the framboids found there. The median Ag content of the other samples found within the euxinic interval all have values that are not significantly depleted, ranging from 2.50 to 22.3 ppm. Bismuth shows enrichments at depths similar to those for the enrichments of Cu, Mo, and Ag. Bismuth has medians that are significantly depleted in the first two samples (with all but one analysis below detection limits) and the last four samples from the sulfide diffusion zone, decreasing from 0.73 ppm at -670 cm to 0.23 ppm at -725 cm.

Zinc shows behavior in the sulfide diffusion zone similar to the observations for Cu, Mo, Ag, and Bi, with three of the five samples significantly depleted. However, it differs in that all but one of the samples deposited under euxinic conditions are not significantly depleted for the entire Cariaco dataset (ranging from medians of 434 to 1020 ppm Zn). The one data point in the euxinic interval with 205 ppm is from a single analysis and may not be representative of all the pyrite in that sample.

Black Sea

Core 315

The median values in core 315 from the Black Sea all have only the top two samples significantly depleted for Co, Ni, and Cu (37.5 and 51.3 ppm; 212 and 129 ppm; and 566 and 467 ppm for Co, Ni, and Cu respectively; Fig. 3). The rest of the samples ranged from 84.6 to 1340 ppm, 473 to 1450 ppm, and...
647 to 1740 ppm for Co, Ni, and Cu, respectively. Zinc and Bi were similar, however, in that only one of the top two samples was significantly depleted (77.8 and 2.42 ppm for Zn and Bi from this top sample, respectively). Neither Ag nor Pb have medians of analyses from a specific interval significantly depleted. Median values for Ag and Pb range from 2.53 to 6.61 ppm for Ag and 61.3 and 194 ppm for Pb. Molybdenum is similar to Co, Ni, and Cu. It has medians in the top two samples significantly depleted (683 and 428 ppm).

Core 330 shows fewer clear trends than 315 (Fig. 4). The only elements with median values from a specific stratigraphic level significantly depleted are the Co, Ni, Cu and Mo in the uppermost sample (18.3, 18.0, 58.6, and 54.1 ppm for Co, Ni, Cu, and Mo, respectively). The other intervals have medians that range from 42.3 to 964 ppm for Co, 127 to 595 ppm for Ni, 149 to 754 ppm for Cu, 110 to 434 ppm for Zn, 302 to 1332 ppm for Mo, 1.59 to 3.59 ppm for Ag, 44.1 to 208 ppm for Pb, and 2.15 to 3.56 ppm for Bi. Importantly, the median values for all the elements tend to be higher in 315 than in 330, with 427, 986, 1090, and 1220 ppm for Co, Ni, Cu, and Mo, respectively, in core 315, compared to 67.0, 195, 225, and 359 ppm, respectively, in core 330. Similarly, median values of the entire core for Ag and Bi are higher in core 315 compared to 330, but the variation is less extreme (medians for Ag and Bi in core 315 are 3.04 and 3.95 ppm, respectively, compared to 2.14 and 2.82 ppm in core 330). The only elements that show the opposite relationship are Zn and Pb, with slightly higher median values in core 330 (with medians for Zn and Pb in core 315 of 150 and 93.8 ppm, respectively, compared to 177 and 110 ppm in core 330).

Discussion

Cariaco basin

Relatively low abundances for many TE in the top three samples (to a depth of 45 cm; Fig. 5 and Table 1) were observed. Our low TE in pyrite (or TE pyritization) in the most shallow samples is similar to observations based on sequential leach analyses (Huerta-Diaz and Morse 1992) and discrete pyrite analyses in estuarine settings (Gregory, et al. 2014). In these cases, most TE in pyrite generally increase in abundance with increasing depth below the sediment-seawater interface prior to reaching roughly steady levels. Contrary to the idea that pyrite in euxinic settings inherit all of its TE content from the water in which it formed (Gregory et al., 2017), these data suggest that at least a portion of the TE are inherited from the sediments. That being said, as the TE in pyrite equilibrated relatively early, their abundances most likely reflect the contents of weakly bound elements likely adsorbed onto particles from the seawater (that is, the same water column) rather than being bound to detrital grains and transported into the basin. In this way, the pyrite data can capture water chemistry but through a somewhat complicated pathway.

Within the sulfide diffusion zone (Fig. 2), there is a significant difference in the texture of the pyrite, with coarser grained pyrite nucleating on earlier framboids (Fig. 1b) that precipitated at a higher degree of supersaturation—similar to those observed in Green Lake (Suits and Wilkin 1998). These textures are representative of secondary pyrite formation in the Cariaco Basin presumably due to additional Fe being available through Fe (hydr)oxides present in the oxic layers. In fact, sediments below this gray zone of sulfide diffusion are reddish brown from the presence of oxide phases (Lyons et al, 2003). This interpretation is supported by the TE trends observed moving down core. The contents of
most TE of interest decrease markedly below the euxinic interval and into the zone of sulfide diffusion, with a gradual decrease from the top to bottom of the sulfide diffusion zone (Fig. 2). Cobalt, Ni, and Pb are exceptions to this trend, in that they continue to be elevated in the sulfide diffusion zone (except for the deepest sample).

The reason for this exception is likely that at this stratigraphic position, the TE content is less a function of the TE in the ocean water and adsorbed onto euxinically deposited sediments and more a function of the TE contained within Fe (hydr)oxides. Because the TE abundance of Fe (hydr)oxides have not been measured in the Cariaco Basin, literature sources were consulted for the TE content of Fe crusts from the Atlantic Ocean, which show that Co, Ni, and Pb are the most enriched (means of 3608, 2581, and 1238 ppm respectively) (Koschinsky and Hein 2017)—the same elements that were enriched in pyrite in the sulfide diffusion zone in the Cariaco Basin. It should be noted, however, that the enrichments are more complicated than simply reflecting ambient abundance of TE, as the enrichments in the pyrite do not show the same ratios as the enrichments in the (Fe hydr)oxide crusts. Thus, it might be expected the TE patterns will agree much more closely if the pyrite formed via reaction 3. This relationship has an important implication for using pyrite TE chemistry as a proxy for past ocean chemistry—specifically, gray shales interbedded with black shales are potentially depleted in some TE and not others due to replacement of Fe (hydr)oxides by diffusion of sulfide from the organic rich intervals rather than reflecting changes in past ocean chemistry. Such secondary overprints might be expected anytime organic-rich and organic-lean sediments are juxtaposed, such as are observed in Mediterranean sapropels—often reflecting dramatic and abrupt changes in depositional conditions such as primary productivity and redox. That being said, because Fe (hydr)oxides can track broad, first-order ocean chemistry if their mineralogy is correctly identified and put in the correct context, pyrite formed via this mechanism may still allow some inferences to be made about ocean chemistry at the time of formation. Although, except in these ideal circumstances, grey and brown shales should be avoided when using the pyrite proxy method due to the potential for misinterpretation of the data.

Black sea

Core 330 is analogous to the top part of the Cariaco Basin interval, as it contains the uppermost sediments in Unit 1, the most recently deposited sediments in the Black Sea. However, it differs in that we were able to sample at a much higher stratigraphic resolution in the Black Sea. The data show a similar low relative TE abundance in the upper samples compared to the deeper intervals for Co, Ni, Cu, and Mo. It also appears that the core 330 samples have not yet equilibrated as the bottom samples of core 330 have medians for each of these elements that are much less than those of core 315. Core 315 samples a deeper part of unit 1 and unit 2. In core 315 Co, Ni, Cu, and Mo have median values of 427, 986, 1087, and 1220 ppm, respectively, compared to 67.0, 195, 225, and 359 ppm, respectively, in core 330. This trend is consistent with the Cariaco Basin samples where samples had not equilibrated until depths between 45 and 70 cm.

Core 315 over-penetrated and the top sediments were lost but a similar trend can still be observed. The upper most samples contain relatively low amounts of several TE in the top two samples, with Co, Ni, Cu, and Mo all being below the medians for the remainder of the core. These samples, like core 330 and the core from the Cariaco Basin also show that it takes time for the trace elements to accumulate in sedimentary pyrite after deposition, presumably due to desorption from organic matter.
and other detritus during early diagenesis. This is similar to observations of TE enrichment in pyrite from organic rich, oxic depositional setting (Huon Estuary; Gregory et al., 2014).

Comparison of pyrite between the two basins

A comparison between the relatively open Cariaco Basin and the more restricted Black Sea is important to assess how the pyrite proxy may vary with different levels of basin restriction. For all elements of interest, except Co and Zn, the median TE content of pyrite from the equilibrated portion of the core varied by less than a factor of 3.1 between the two basins (Table 5). This is far less than the over an order of magnitude enrichments of TE in sedimentary pyrite that are currently being used to identify broad, first-order trends in ocean chemistry (Large et al., 2014; Gregory et al., 2017).

A common issue when interpreting TE data from bulk sample analyses is variations in concentration due to basin restriction. Here we focus the conversation of Mo, one of the more common elements used to interpret past ocean chemistry using bulk sample analysis (Tribovillard, et al. 2006 Scott et al., 2008) and also one that can be effective using pyrite data (Gregory et al., 2017). Averages of the Black Sea and Cariaco Basin bulk analyses of the euxinically deposited sediments are 45 and 85 ppm, respectively (Algeo and Lyons, 2003; Table 5)—that is, approximately half as much Mo accumulates in the bulk sediments of the more restricted Black Sea versus the less restricted Cariaco Basin. Conversely pyrite is more enriched in the Black Sea versus the Cariaco basin, although the discrepancy is less than that observed for the bulk sample analyses and in the opposite direction. Medians of pyrite from the Black Sea (from analyses with equilibrated pyrite concentrations) is 1.54 times that of the pyrite from the Cariaco Basin. Again, importantly, there is a relatively small difference in pyrite TE content between basins despite the very different degrees of restriction and bulk TE contents. This is likely because the Mo content of the surface waters are similar between the restricted Black Sea and less restricted Cariaco Basin when corrected for salinity (as summarized in Algeo and Lyons, 2006). The near surface environment, at the oxic/sulfidic water interface, is where most pyrite forms and where there is the steepest decrease in dissolved trace elements, suggesting that pyrite is an important TE sink. At the same time dissolved metals that show a systematic decrease across this interface also appear to be scavenged from the water column from detrital components (including organic matter) (Lewis and Landing 1992). Thus, the source of the Mo in the pyrite framboids is direct precipitation from the water column, and incorporation of Mo into pyrite early during sedimentation via desorption from detrital materials with a source of Mo from the upper, enriched, part of the water column that is similar to the open ocean concentrations. Therefore, even though the pathway involves both a direct precipitation pathway and a secondary enrichment pathway following desorption from detrital constituents, pyrite chemistry appears to track the chemistry of the overlying, oxic, water column.

Implications

Here it is shown that pyrite TE content, even in euxinic settings where most pyrite forms in the water column, is at least partially sourced from sediments. These TE adsorbed onto detrital material and still reflect the overlying water column but in a complex way compared to direct incorporation into pyrite in the water column. Importantly, at least for Mo, pyrite deposited under euxinic conditions TE content varies less between the Cariaco Basin and Black Sea than bulk sample analysis. This suggests that the pyrite proxy may be less sensitive to basin restriction than traditional bulk sediment analysis proxies, provided surface waters are similar. Because framboidal pyrite is unlikely to accumulate additional pyrite without the later pyrite having a significantly different texture (Rickard, 2019) this
study suggests that the TE chemistry of framboidal pyrite deposited under euxinic conditions is a valid proxy for past ocean chemistry.

It is also shown that large variation in TE content are present at interfaces between different depositional conditions, such as those marking changing depositional redox. This observation highlights the risk of mistaken interpretations in grey shales or samples from near lithologic boundaries where the pyrite TE content might better reflect the TE content of Fe (hydr)oxide minerals rather than the overlying sea water. We suggest grey and brown shales should not be used in pyrite proxy studies and only consistently black shales should be used for these purposes. That said, the relatively low variation in TE in pyrite between the two basins supports the use of pyrite TE chemistry to understand past ocean chemistry but also highlights the need for continued investigation of pyrite forming in modern settings and experimental work to better understand the relative enrichment factors of different elements into pyrite. With continued proxy validation and careful applications, we are confident that pyrite TE content can be an important tool to understand the chemistry of past oceans.

Acknowledgements

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Figure Captions

Figure 1: SEM images of framoidal pyrite from the Cariaco basin. A) image of representative framoids
cluster from the interval deposited under euxinic conditions (70 cm), both Black Sea and Cariaco Basin
pyrite framoids formed under euxinic conditions and look similar to these framoids. B) SEM image of
pyrite from the sulfide over print zone of the Cariaco Basin (670 cm). Note the distinct coarsening of the
pyrite on the rim edge with an early framoidal pyrite. This is indicative of later, slower pyrite formation
after initial nucleation that formed the framoids. This interval also had several euhedral crystals.

Figure 2: LA-ICPMS analyses of pyrite with depth of sediment core from the Cariaco Basin.

Figure 3: LA-ICPMS analyses of pyrite with depth of sediment core from core 315 from the Black Sea.

Figure 4: LA-ICPMS analyses of pyrite with depth of sediment core from core 330 from the Black Sea.

Figure 5: Detailed view of the top 200 cm of the Cariaco Basin analyses for Cu and Ag. These elements
show most clearly the increase in TE down core over the first 70 cm.

Tables

Table 1: Median and MAD for LA-ICPMS pyrite TE analyses from different sample depths in the Cariaco
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Table 3: Median and MAD for LA-ICPMS pyrite TE analyses from different sample depths in the Black Sea core 330.

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<th>Cu (ppm)</th>
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<th>Bi (ppm)</th>
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Table 4: Median % error

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Table 5: Comparison of pyrite chemistry between the Cariaco Basin and Black Sea
Microlaminated, dark olive gray, organic-rich silty clay with nannofossils and foraminifera deposited under euxinic conditions

Microlaminated, dark olive gray, organic rich, diatom-rich clayey mud with abundant calcareous microfossils deposited under euxinic conditions.

Massive bioturbated light gray clay. Sulfide diffusion zone of sediments deposited under oxic conditions.

Massive bioturbated reddish-brown clay deposited under oxic conditions.

LA-ICPMS pyrite analysis (Large et al., 2014)

LA-ICPMS pyrite analysis (this study)

Median - MAD
Figure 3

The figure shows a series of scatter plots displaying the distribution of various elements (Co, Ni, Pb, Cu, Mo, Ag, Bi, and Zn) across different depths of a core sample. Each plot represents the concentration of an element in parts per million (ppm) across a range of depths.

Key features of the figure include:
- **LA-ICPMS pyrite analysis (this study)**: These are indicated on the plots with small blue circles.
- **Median - MAD**: These are represented by dashed lines on the plots.

Depth of the core is marked along the y-axis, ranging from -45 cm to -1 cm. The x-axes represent the concentration of specific elements ranging from 1 ppm to 10,000 ppm.

**Legend**:
- **Unit I**: Finely laminated light (mm scale), calcium carbonate rich layer and dark-gray to black layers.
- **Unit II**: Homogeneous, dark-gray, organic rich mud.
Figure 4

- LA-ICPMS pyrite analysis (this study)
- Median - MAD
- Unit 1 - finely laminated light (mm scale), calcium carbonate
- Rich layer and dark-gray to black layers
Figure 5

- LA-ICPMS pyrite analysis (Large et al., 2014)
- LA-ICPMS pyrite analysis (this study)
- Median values of pyrite analyses