

# Pyrite formation in the water column and sediments of a meromictic lake

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## ABSTRACT

**We compared concentrations of organic carbon, partitioning of iron and sulfur, stable isotopic ratios of major sulfur species, and pyrite morphologies in the water column and sediments of oxic and euxinic portions of a sulfate-rich, meromictic lake (Green Lake near Fayetteville, New York) in order to examine the effects of euxinic conditions on pyrite formation and sedimentary Fe-S-C relations. About 15% of the pyrite in sediments of the euxinic basin of Green Lake forms in the water column. The bulk of pyrite in both euxinic and oxic sediments forms in the upper ~10 cm of the sediment and is limited by availability of reactive iron. Oxic and euxinic sediments in Green Lake cannot be clearly distinguished on the basis of concentrations of organic carbon or pyrite, degree of pyritization, or sulfur isotopic ratios of pyrite, but can be distinguished by using size distributions of pyrite framboids. Therefore, Fe-S-C relations in ancient shales must be used with caution when attempting to reconstruct paleoenvironmental redox conditions.**

## INTRODUCTION

In normal-marine sediments, i.e., those deposited under an oxic water column, pyrite is formed exclusively within the sediment (diagenetic pyrite). In contrast, in euxinic environments, pyrite can form in the water column (syngenetic pyrite), as well as below the sediment-water interface (Raiswell and Berner, 1985; Muramoto et al., 1991; Wilkin and Barnes, 1997). For example, in the modern Black Sea, nearly all of the pyrite in laminated sediments of the central basin forms in the water column (Lyons, 1997). On the other hand, in euxinic sediments of the Pettaquamscutt estuary (Rhode Island, United States), at least 30% of pyrite forms below the sediment-water interface (Wilkin and Barnes, 1997). Consequently, the chemical and physical properties of pyrite in Black Sea sediments reflect conditions in the chemocline, whereas pyrite properties in the Pettaquamscutt estuary sediments reflect conditions in the water column and sediments. Therefore, the ratio of pyrite formed in the water column to that formed in the sediments (syngenetic pyrite/diagenetic pyrite) can be an important consideration when interpreting the Fe-S-C relationships and stable isotopic ratios of pyrite in ancient shales.

On the basis of concentrations of total dissolved solids (TDS), Green Lake is a fresh-water environment. In spite of this, there are several reasons why it is an appropriate analogue for ancient euxinic marine shales. First and most important, the primary concern when comparing Fe-S-C relationships in marine and fresh-water environments is availability of sulfate (Berner and Raiswell, 1984). Concentrations of sulfate in Green Lake are approximately half that of seawater. Thus, pyrite formation in Green Lake is probably not limited by availability of sulfate. Second, most modern euxinic environments are

not marine, but rather marine influenced. The salinity of modern, euxinic water columns ranges from the nearly fresh-water conditions observed in Green Lake to the submerged, hypersaline basins of the Mediterranean Sea (e.g., Henneke et al., 1997). In this context, Green Lake offers a unique opportunity not only to compare pyrite formation in oxic and euxinic environments with similar terrigenous inputs, but also to examine the influence of low salinity on pyrite formation in the water column.

## GREEN LAKE

Green Lake is a small (0.26 km<sup>2</sup>) meromictic lake located 1.7 km northeast of Fayetteville, New York, United States. It formed as a plunge pool at the base of a waterfall, during the late Wisconsinan stage of glaciation, and penetrates the Silurian Syracuse Formation and Vernon Shale (Thompson et al., 1990). Because ground-water seepage is the dominant source of water for Green Lake, the surrounding bedrock has a strong influence on chemistry of the water column (Takahashi et al., 1968; Brunskill and Ludlam, 1969). In particular, calcium and sulfate, leached from the gypsum-rich Vernon Shale, is concentrated in ground water entering the lake below ~18 m. The differences in total dissolved solids (TDS) of ground-water sources cause Green Lake to be permanently stratified below a water depth of ~18 m. This produces two different portions of the basin with nearly identical detrital inputs, but distinctive water-column chemistries.

Although the TDS content of the deep water in Green Lake is <3000 ppm, the concentration of dissolved sulfate is 13.5 mM ( $\pm 1.4$ ), or about half that of seawater. Dissolved sulfide is present below ~19 m. Concentrations generally increase with water depth, reaching a maximum of about 1.2 mM near the bottom of the deep basin at

~55 m (Brunskill and Ludlam, 1969). The top of the chemocline (~18–20 m) is inhabited by zooplankton, cyanobacteria, and a thriving population of green and purple photosynthetic sulfur bacteria (Culver and Brunskill, 1969; Fry, 1986; Thompson et al., 1990), similar in many respects to that observed in the modern Black Sea (Jørgensen et al., 1991).

Green Lake sediments are rich in carbonate, which precipitates inorganically above the chemocline during seasonal whiting events (Brunskill, 1969). Sediments of the euxinic basin are varved and contain some slump deposits. Sedimentation rates in the euxinic basin are approximately 0.14 cm/yr (Ludlam, 1969). Rates of sedimentation in the oxic sediments are unknown, but are probably lower because the sides of the oxic portion of the basin are less steep.

## ANALYSES

Concentrations of total carbon and organic carbon were analyzed using a UIC Coulometer System 140. Concentrations of acid-volatile sulfide (AVS) and chromium-reducible sulfur (CRS) in sediments and filters from the water column were determined by reacting vacuum-dried samples sequentially with boiling 6N HCl and a solution of 1M CrCl<sub>2</sub>·6H<sub>2</sub>O in 1N HCl. Hydrogen sulfide that evolved during the reactions was titrated on a sulfur coulometer. AVS generally comprises iron monosulfide minerals. CRS is composed of pyrite and elemental sulfur. Concentrations of pyrite and elemental sulfur in the water column were determined by the difference between CRS analyses on filters before and after extraction of elemental sulfur with methylene chloride. Morphology and size distribution of pyrite were studied by using the reflected-light and scanning electron microscope techniques described in Wilkin et al. (1996).

Iron fractions (amorphous and crystalline iron oxides) were separated by using ascorbate and dithionite extractions as outlined in Kostka and Luther (1994). Total iron, aluminum, and iron released during extractions were determined via inductively coupled plasma-atomic emission spectroscopy. The fraction of total iron in iron silicates was calculated from the difference between total iron and the sum of all other iron fractions. Sulfur isotopic ratios of hydrogen sulfide and CRS are reported using standard delta notation relative to Canyon Diablo Troilite.

## RESULTS AND DISCUSSION

### Fe-S-C Partitioning

Organic carbon (TOC) content of both cores ranges from 3 to 6 wt%. TOC increases with depth in the oxic core and is quite variable in the euxinic core (Fig. 1). Although these two cores

cannot be distinguished on the basis of bulk TOC, there are small differences in hydrogen indices. Hydrogen index values are a measure of organic matter type and oxidation state. In Green Lake, hydrogen indices (HI) are greater in the euxinic sediments (mean HI = 240) than in the oxic sediments (mean HI = 170). This distinction could be due to differences in mechanisms of organic matter degradation under oxic and euxinic conditions, but it can also result from different organic matter inputs. In particular, while both sediments receive leaf litter and algal remains, sediments of the euxinic basin also receive the remains of hydrogen-rich bacteria from the chemocline.

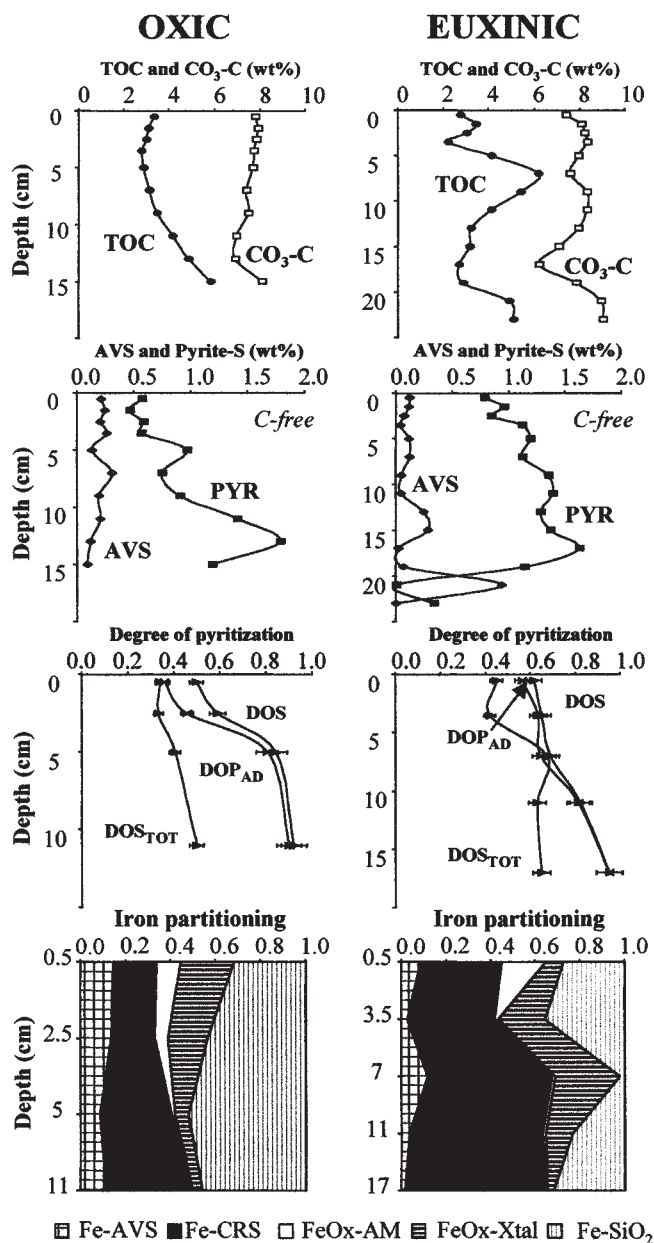
Concentrations of AVS in the oxic core decrease from 0.25 wt% near the surface to 0.10 wt% at the base (Fig. 1). In the euxinic core, AVS is generally less abundant (~0.1 wt%), but

there are several subsurface peaks as high as 0.94 wt%. Pyrite concentrations are slightly higher in surface sediments of the euxinic core compared to the oxic core; however, concentrations of pyrite in both cores increase with depth, reaching ~1.5 wt% by 15 cm. Although S/C ratios in sediments near the bases of the cores (0.1 to 0.3) are slightly lower than the "normal-marine" ratio (0.4), the S/C ratios in sediments of both cores are significantly higher than those generally observed in lacustrine sediments (Bernier and Raiswell, 1984).

We infer from relatively constant Fe/Al ratios (0.21 to 0.23), and the restricted nature of the drainage basin, that inputs of iron do not qualitatively change over time (Fig. 1). In both the oxic and anoxic regions of Green Lake, iron used in the formation of pyrite is initially derived from amorphous and crystalline iron oxides. Amorphous iron oxides are the most reactive and first to be consumed. This statement is particularly true in sediments underlying the euxinic water column, where amorphous iron oxides are rapidly converted to pyrite in the water column and upper 1 cm of the sediment. Below 13 cm, however, iron partitioning and concentrations of pyrite in sediments of the oxic and euxinic basins are nearly indistinguishable.

Degree of pyritization (DOP) and degree of sulfidation (DOS) measure the extent to which iron available for pyrite formation is actually converted to pyrite or other inorganic sulfides (Bernier, 1970; Boesen and Postma, 1988). There are several ways to express DOP and DOS. Usually DOP is equal to  $[\text{pyrite}_{\text{Fe}} / (\text{pyrite}_{\text{Fe}} + \text{extractable}_{\text{Fe}})]$ . The assumption is that extractable iron represents a labile fraction of sedimentary iron that is available for pyrite formation. Generally HCl is used to extract the iron from sediments ( $\text{DOP}_{\text{HCl}}$ ). An alternative method uses ascorbate and dithionite ( $\text{DOP}_{\text{AD}}$ ) in order to target amorphous and crystalline iron oxides, respectively (Kostka and Luther, 1994). Values of  $\text{DOP}_{\text{AD}}$  cannot be directly compared to  $\text{DOP}_{\text{HCl}}$ , because HCl releases some iron from iron silicates as well as iron oxides.  $\text{DOP}_{\text{AD}}$  values should be lower than  $\text{DOP}_{\text{HCl}}$  values, but because iron silicates are generally slow to react with dissolved sulfide,  $\text{DOP}_{\text{AD}}$  may be a better indication of the pyrite-forming capabilities of a sediment than is  $\text{DOP}_{\text{HCl}}$ . We have also calculated values for degree of sulfidation,  $\text{DOS} = (\text{AVS}_{\text{Fe}} + \text{pyrite}_{\text{Fe}}) / (\text{AVS}_{\text{Fe}} + \text{pyrite}_{\text{Fe}} + \text{extractable}_{\text{Fe}})$ , and total degree of sulfidation,  $\text{DOS}_{\text{TOT}} = (\text{AVS}_{\text{Fe}} + \text{pyrite}_{\text{Fe}}) / \text{total}_{\text{Fe}}$ .  $\text{DOP}_{\text{AD}}$ ,  $\text{DOS}$ , and  $\text{DOS}_{\text{TOT}}$  increase with depth in both cores (Fig. 1).  $\text{DOS}_{\text{TOT}}$  is slightly higher in the euxinic core, indicating that iron in the euxinic sediments is more reactive than iron in sediments of the oxic core. This is consistent with observations in marine sediments (Raiswell and Canfield, 1998) and suggests that there is an additional source of reactive iron to sediments of euxinic basins. In spite of these

Figure 1. Concentrations of organic carbon (TOC), carbonate carbon ( $\text{CO}_3\text{-C}$ ), acid volatile sulfide (AVS), and pyrite sulfur (pyrite-S) on a dry-weight basis. Concentrations of pyrite-S and AVS are calculated on a carbon-free basis. Degree of pyritization using ascorbate and dithionite extractions is  $\text{DOP}_{\text{AD}}$ . Degree of sulfidation and total degree of sulfidation are  $\text{DOS}$  and  $\text{DOS}_{\text{TOT}}$ , respectively. Iron partitioning is designated as follows: iron in AVS ( $\text{Fe-AVS}$ ), in chromium-reducible sulfur ( $\text{Fe-CRS}$ ), in amorphous iron oxides ( $\text{FeOx-AM}$ ), in crystalline iron oxides ( $\text{FeOx-Xtal}$ ), and in iron silicates ( $\text{Fe-SiO}_2$ ).  $\text{Fe-CRS}$  includes both pyrite and elemental sulfur. Data markers indicate the precision of the measurements, except for  $\text{DOP}_{\text{AD}}$ ,  $\text{DOS}$  and  $\text{DOS}_{\text{TOT}}$ , where error bars are included based on analytical and experimental uncertainties.



slight differences, it would be difficult to discriminate between oxic and euxinic sediments in Green Lake using  $DOP_{AD}$ ,  $DOS$ , or  $DOS_{TOT}$ .

### Pyrite Textures

At the top of the chemocline (~19 m) there is a peak in the concentration of suspended CRS (3.75  $\mu M$ ). Of this CRS, ~90% is elemental sulfur; the balance is pyrite. Pyrite framboids were collected from the water column at this same depth. Framboidal pyrite is present in both oxic and euxinic cores and shows significant pyrite overgrowth, which was not observed on framboids collected from the water column (Fig. 2). Pyrite framboids and euhedral grains in sediments of the euxinic basin of Green Lake are generally smaller and less variable in size (diameter  $x = 4.7 \mu m$ , standard deviation  $\sigma = 2.1 \mu m$ , number of grains  $n = 464$ ) than those found in the oxic sediments ( $x = 7.4 \mu m$ ,  $\sigma = 4.9 \mu m$ ,  $n = 323$ ). This pattern reflects the contrasting environmental conditions in which the pyrite crystallized and can be used to distinguish the oxic and euxinic sediments (Fig. 3). Pyrite nuclei formed in the water column are affected by chemical and hydrodynamic conditions in the chemocline and generally have less time to grow

than those formed in sediments (Wilkin et al., 1996). After nucleation and an initial period of growth, framboidal aggregates settle to the sediment-water interface, where they serve as sites for heterogeneous nucleation and continued pyrite growth. Diagenetic pyrite can be texturally distinctive, occurring as fillings and overgrowths (Fig. 2). Pyrite framboids and single crystals were also recovered from sediments of the oxic basin. Framboids formed in the oxic sediments are generally more variable in size and larger than those in the sediments of the euxinic basin. This trend in size distribution may reflect either a longer period of time available for growth near the redox transition or an overall lower proportion of pyrite nucleation sites.

### Sulfur Isotopes

$\delta^{34}S$  values of dissolved sulfide in the top 4 m of the chemocline (19–21 m) are uniform at  $-29.9\text{‰} \pm 0.2\text{‰}$  (Fig. 4). Below 21 m,  $\delta^{34}S$  of dissolved sulfide increases to  $-21.3\text{‰}$  at the sediment surface (50 m).  $\delta^{34}S$  of pyrite in the upper 15 cm of the euxinic sediments is relatively constant (Fig. 4). In contrast,  $\delta^{34}S$  of pyrite in the oxic sediments decreases by almost 15‰ over the same depth interval. Consequently, even though pyrite in surface sediments of the oxic core is enriched in  $^{34}S$  by ~10‰ relative to pyrite in surface sediments of the euxinic core, the relative differences in  $\delta^{34}S$  values of pyrite in the two cores have reversed by a sediment depth of 15 cm, and pyrite within oxic sediments is depleted in  $^{34}S$  relative to pyrite within euxinic sediments.

The cause of the depletion of  $^{34}S$  in pyrite with depth in the oxic sediments is uncertain, but three mechanisms are possible. First, there may be sub-

stantial differences in the magnitude of bacterial isotope effect in the upper 15 cm of the sediment. These differences could result from variations in rates of bacterial sulfate reduction (Kaplan and Rittenberg, 1964). Second, oxidation and recycling of dissolved sulfide near the sediment-water interface may enhance the net isotopic fractionation between dissolved sulfate and sulfide (Canfield and Thamdrup, 1994; Canfield and Teske, 1996). Finally,  $\delta^{34}S$  of pyrite in the oxic core could reflect a long-term increase in rates of sulfate reduction due to increases in rates of sedimentation and/or organic matter fluxes.

In Green Lake, only a small fraction of pyrite in euxinic sediments precipitates in the water column. If  $\delta^{34}S$  values of pyrite formed in the water column and sediments are the same as those of the coexisting dissolved sulfide, then mass and isotopic balance calculations indicate that approximately 15% of pyrite in euxinic sediments forms in the water column. The substantial pyrite overgrowth on framboids collected from euxinic sediments is also consistent with this interpretation. The low percentage of syngenetic pyrite in sediments of Green Lake's euxinic basin is in sharp contrast to the Black Sea, where nearly all of the pyrite is syngenetic (e.g., Lyons, 1997). These differences arise primarily from variations in properties of iron-bearing detrital phases, the mode of sediment transport, and, to a lesser extent, the physical, chemical, and biological conditions in the chemocline. Higher rates of sedimentation may be associated with greater fluxes of iron detritus and lower rates of iron reduction in the water column. In general, euxinic basins with very low sedimentation rates ( $\leq 0.1$  cm/yr), such as the Black Sea and Framvaren Fjord, tend to

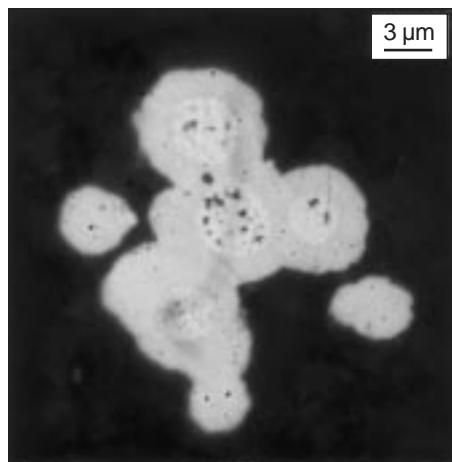


Figure 2. Pyrite framboids with overgrowths from the euxinic sediments of Green Lake.

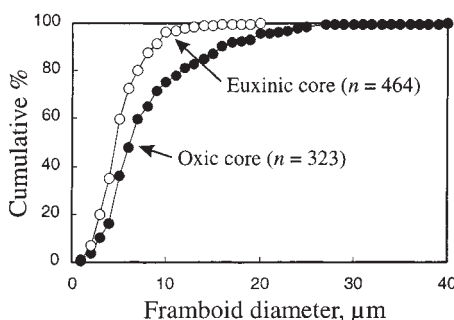


Figure 3. Framboid size distribution in oxic and euxinic sediments of Green Lake.

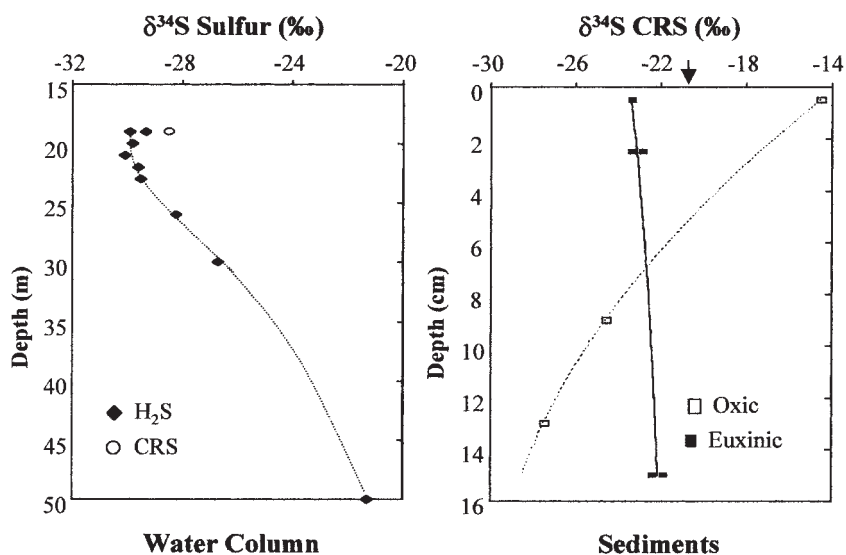


Figure 4. Stable sulfur isotopic ratios of dissolved sulfide and CRS (elemental sulfur and pyrite) in water column and pyrite in oxic and euxinic sediments of Green Lake. Arrow at top of right graph indicates  $\delta^{34}S$  value of dissolved sulfide at sediment-water interface of euxinic sediments.

have high ratios of syngenetic to diagenetic pyrite (Lyons, 1997; Raiswell and Canfield, 1998, and references therein). In contrast, euxinic basins with higher and/or more variable sedimentation rates ( $\geq 0.1$  cm/yr), such as Green Lake and the Pettaquamscutt estuary, tend to have a lower ratio of syngenetic to diagenetic pyrite (Wilkin and Barnes, 1997).

In the modern Black Sea,  $\delta^{34}\text{S}$  of pyrite in oxic sediments is enriched by  $\sim 10\%$  relative to  $\delta^{34}\text{S}$  of pyrite in laminated sediments from the central basin (Calvert et al., 1996; Lyons, 1997). Consequently, sedimentary pyrite depleted in  $^{34}\text{S}$  is sometimes thought to be characteristic of ancient euxinic depositional environments (Anderson et al., 1987; Beier and Hayes, 1989).  $\delta^{34}\text{S}$  of pyrite in Green Lake sediments suggests that it may be difficult to use sulfur isotope ratios of pyrite to interpret paleoenvironmental redox conditions. Below a depth of 13 cm,  $\delta^{34}\text{S}$  of pyrite in the oxic sediments is depleted by  $\sim 6\%$  relative to  $\delta^{34}\text{S}$  of pyrite in the euxinic sediments. Furthermore, even if all of the pyrite in the euxinic sediments of Green Lake was formed in the water column,  $\delta^{34}\text{S}$  values of pyrite could not be reliably used to differentiate between the oxic and euxinic sediments.

## CONCLUSIONS AND IMPLICATIONS

Both oxic and euxinic sediments of Green Lake show similar distributions of TOC, iron and sulfur partitioning, and conventional DOP values. On the other hand, pyrite morphologies and size distributions of framboids are distinctly different in oxic and euxinic sediments, and therefore may also be useful in determining redox conditions during deposition of ancient shales.

Although diagenesis continues below  $\sim 15$  cm in the sediment, reactions at greater depths do not influence the eventual Fe-S-C relations as seen in the ancient record as much as reactions near the sediment-water interface. All DOP parameters are high at 15 cm, suggesting that little additional pyrite will be formed below this depth. If this interpretation is the case, then  $\delta^{34}\text{S}$  values of pyrite observed in these sediments should not alter significantly during lithification.

In modern euxinic environments, the proportion of pyrite formed in the water column (i.e., syngenetic pyrite) to that formed in the sediments (i.e., diagenetic pyrite) varies. In the Black Sea, the bulk of pyrite in euxinic sediments originates in the water column. In Green Lake, the pyrite burial flux is dominated by growth below the sediment-water interface. This variability is related to the extent that iron is scavenged in the sulfidic water column (Wilkin and Barnes, 1997) and is a function of the reactivity of iron-bearing detritus, the mode of sediment transport, as well as the physical, chemical, and biological conditions in the chemocline. Similar

variability in the ratio of syngenetic to diagenetic pyrite should be expected in ancient shales deposited under euxinic water columns, and should be taken into account when using interrelationships in the Fe-S-C system for interpreting paleodepositional environments.

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