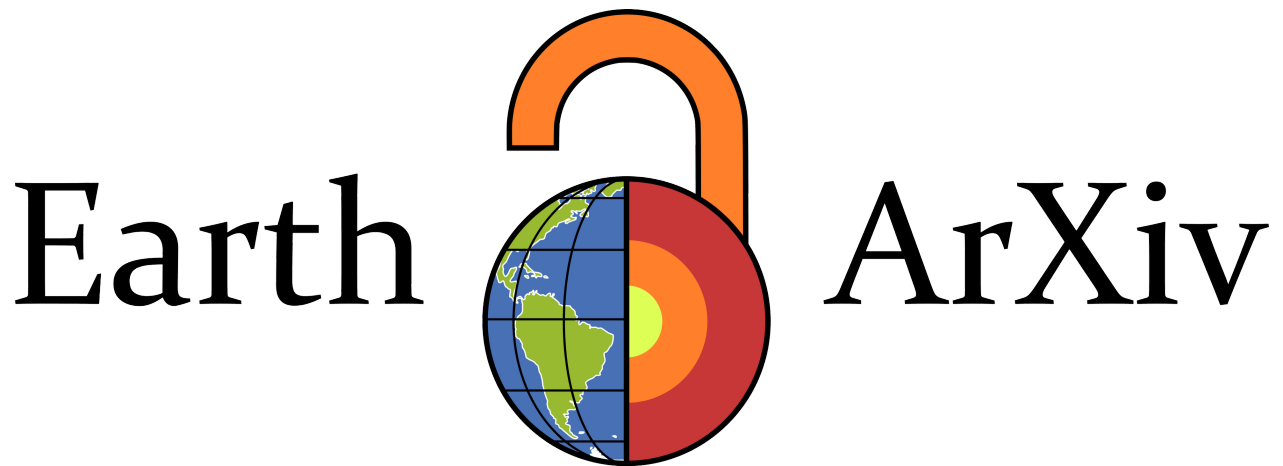




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BULK IRON-SULFUR RATIO (Fe/S) CONDITIONAL PROXY FOR SULFURIZED, TOC-RICH SEDIMENTS: INSIGHTS AND COMPARISON OF COMPOSITIONAL MODEL WITH REAL DATA UTILIZING THE PYRITE-TOC-Fe-S COMPOSITIONAL SPACE

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ABSTRACT

Bulk iron-sulfur (Fe/S) ratio can be a proxy for sulfurized organic matter in organic-rich shales, particularly those prone to be siliceous or carbonate. First part uses a theoretical model of a compositional system consisting solely of iron, sulfur, TOC, and pyrite to demonstrate how the Fe/S ratio can indicate the presence of sulfurized organic matter using the model's assumption of sulfur being only in either in pyrite as sulfide or in TOC as organic sulfur. The second part identifies 25 studies where iron, sulfur, TOC, and pyrite content measurements (or have elemental data for organic matter) are made for organic-rich shales in 11 countries and 16 formations spanning Devonian to Plio-Pleistocene geologic time scales. These datasets clearly shows that Fe/S ratios less than 0.87 correspond to sulfurized TOC in organic-rich sedimentary rocks. Also a checklist is provided to assist researchers assess the validity of the Py-TOC-Fe-S model to their datasets and if so how to interpret the Fe/S proxy. In a way, the Fe/S ratio could be thought of complementary to degree of pyritization (DOP) since DOP is valid fore Fe/S > 0.871 while Fe/S proxy is valid for Fe/S < 0.871

1 INTRODUCTION

I observed from my ED-XRF dataset acquired during my dissertation work, that certain intervals of Eagle Ford Group sediments (mainly the Lower Eagle Ford which is regarded as the primary unconventional reservoir in south Texas, USA) had very low bulk rock Fe/S ratio and I realized that even taking into account the ratio of sulfur and iron in pyrite, there was an excess of sulfur relative to iron that is not explained by pyrite. At the time, I hypothesized that most of that "excess" sulfur in organic-rich mudstones is present as organic sulfur both in the kerogen and any retained hydrocarbons. If so, this could lead to the use of the Fe/S ratio as a conditional proxy for sulfur-rich organic matter in preserved sediments. The proxy is described as conditional to allow for a range of situations where it would not be valid or would require additional data to validate. This study includes a "checklist" for practitioners to evaluate for common situations that would negate the use of Fe/S as a proxy. Qualitatively, this proxy will work best when both iron and sulfur are measured at levels well above detection values of chemical instrumentation (i.e. ED-XRF or ICP-MS). Also, it is expected to be valid for source rocks that have relatively low clay content (clay/quartz < 2 for any amount of carbonates) or low content of non-sulfide iron-rich minerals. Being able to detect under certain circumstances the presence of sulfurized organic matter has implications for interpreting pyrolysis and maturity data in situations such as basin analysis or source rock analysis.

2 ASSUMPTIONS AND SETUP

To test the hypothesis that in organic-rich mudstones "excess" sulfur is usually present as organic sulfur, I will do two tasks to explore the validity of this idea. I decided to consider an idealized scenario (a conceptual geochemical model) where iron is present only in stoichiometric pyrite and sulfur could be present in pyrite and/or as organic sulfur. This model makes the following assumptions:

1. Iron is present only in pyrite (so excess or deficit is relative to this assumption)
2. That pyrite is stoichiometrically ideal (FeS₂, implying an Fe/S ratio of 0.871). Also, for literature that use S/Fe, the criteria would be S/Fe > 1.15
3. Sulfur can be present either in pyrite or as organic sulfur
4. That TOC that is measured in a pyrolysis measurement contains the sum of kerogen and its hydrocarbon byproducts

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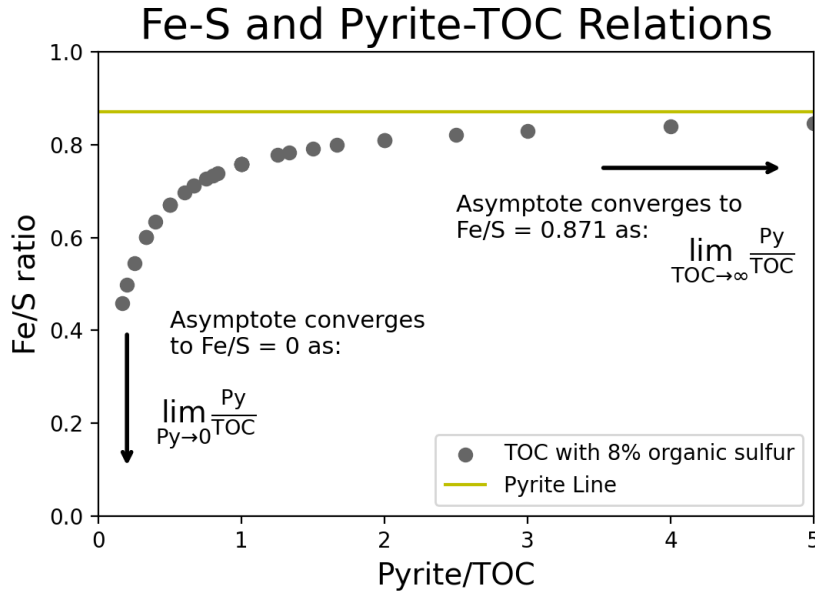


Figure 1: A sample curve that plots Fe/S ratio for a range of pyrite and TOC (including organic sulfur) proportions for fixed sulfurization rate (can be approximated by c_{su} and in this example was set to 0.08). The asymptotes are clearly marked for the limits of pyrite/TOC and Fe/S ratios. The Fe/S and pyrite/TOC values are hypothesized to be more coherent for Fe/S < 0.871 (Fe/S for pure stoichiometric pyrite is 0.871) because mathematically $\text{Fe/S} = f(\text{pyrite}, \text{TOC})$ for the scenario of mixture of pyrite and TOC with constant sulfurization content.

5. All instrumentation is calibrated

So, I will refer to this as the Py-TOC-Fe-S (which stands for pyrite-total organic carbon-iron-sulfur) model. Py is the recommended abbreviation for pyrite per [Whitney and Evans \(2010\)](#) and TOC is a well-established abbreviation for total organic carbon in petroleum geology. Given the above assumptions, I will simulate the variation of Fe/S ratio as a function of pyrite/Total Organic Carbon (TOC) ratio for a given sulfurization content (the percent sulfur in kerogen and its hydrocarbon byproducts). Fig. 1 shows a generic form of this conceptual model, while Fig. 2 shows actual results for the Eagle Ford Group sediments. The results of this model are shown as a cross-plot of Fe/S as a function of the pyrite/TOC ratio. The results of this Py-TOC-Fe-S model is that it is entirely possible (and probably quite common) for organic-rich mudstones to contain enough organic sulfur to noticeably lower Fe/S ratio even if there is abundant pyrite.

The second part of this study was to perform a literature survey (I did not intend for it to be an exhaustive survey, just found enough examples for validation) but it has rather stringent requirements: it must have elemental abundances of iron and sulfur, pyrite content, and TOC content. My own study ([Wehner, 2017](#)) had Fe and S data from calibrated handheld ED-XRF (according to method and original calibration set from [Rowe et al. \(2012\)](#)), and Rock-Eval TOC but did not have a budget for XRD so have no independent measure of pyrite content (it was not intended for this study despite the author making his initial observations based on this dataset). In general, a dataset that has handheld ED-XRF (for Fe and S), XRD (for pyrite), and a pyrolysis-based TOC was adequate for this study. Often if the original study was relying on Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for major elements, an additional analysis to get sulfur would be needed but is commonly absent since sulfur is not often included as a major element of analysis for many studies.

Some useful conversions I used for converting the data from the literature (which exhibit a diversity of formats, units, and definitions) into a consistent format for ease of comparison. It should be noted that often sulfurized TOC can be classified as kerogen type II-S. [Orr \(1986\)](#) defined kerogen type II-S in terms of atomic ratio (which is abbreviated as AR) as $S_{\text{org}}/\text{TOC (AR)} > 0.04$ but when converted to be in terms of wt. %, this inequality becomes $S_{\text{org}}/\text{TOC (wt. \%)} > 0.1068$ so the following is used for conversions:

$$S_{\text{org}}/\text{TOC (AR)} \text{ multiply by } 2.67 \rightarrow S_{\text{org}}/\text{TOC (wt. \%)}$$

$$S_{\text{org}}/\text{TOC (wt. \%)} \text{ multiply by } 0.375 \rightarrow S_{\text{org}}/\text{TOC (AR)}$$

Pyrite line or ratio is either 0.871 for Fe/S or 1.15 for S/Fe (both in wt. % and calculated from stoichiometry of pure pyrite). $S_{\text{org}}/\text{TOC}$ is equivalent to S/C (AR) once the atomic to wt. % conversion is converted. One word of warning though, S/C in the

Modeling Proportions for Pyrite and Sulfurized TOC

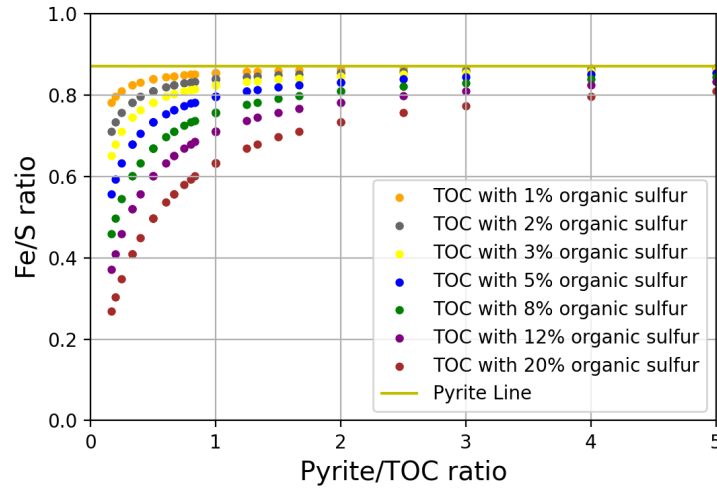


Figure 2: The hypothesis of Fe/S ratio being influenced by proportion of pyritic sulfur, pyritic iron, and organic sulfur can be easily modeled, and in this case, I show results for sulfurization rate from 0.01 to 0.20 in the 4-component compositional space of pyrite-TOC-Fe-S. The most asymptotic curves are those with low sulfurization and for higher sulfurization rate, the curve diverge from pyrite line (stoichiometric ratio of Fe and S for pyrite) for higher pyrite/TOC ratios.

organic geochemistry literature often refers to S/C ratio of kerogen (or bitumen or similar organic material) while in this study we are sometimes comparing bulk ratios versus those of organic matter. In this study if it is not specified the ratios refer to bulk quantities while if it that of kerogen or organic matter it would be specified. In the remainder of the study, S_{org}/TOC without reference to a unit is assumed to be a ratio of wt. % and will be otherwise be specified (for instance, the abbreviation “AR” for atomic ratio as commonly reported in organic geochemistry research). In the Model Section, the variable c_{su} represents the apparent sulfurization value. c_{su} may appear to be the same as the S_{org}/TOC but they should not be confused or conflated as the same. S_{org}/TOC represents the actual measurement of organic sulfur over total organic carbon usually after separating the organic matter from the matrix, while c_{su} is simply the non-pyritic sulfur divided by total organic carbon based on a formula derived later in Model section; a bulk sediment measure unlike S_{org}/TOC which is a measurement of the organic matter fraction of sediments. As derived later, c_{su} , as computed, assumes there is no sulfur in pyrite or TOC (i. e. Fe-rich clays, dolomite, siderite) and thus could be considered an “apparent” sulfurization rate. For some organic-rich source rocks, c_{su} should approximate S_{org}/TOC as I show later.

3 MODEL

The numerical model for assessing the conditional proxy Fe/S as it relates to pyrite and sulfurized TOC is simple. Fe/S vs. pyrite/TOC data are plotted assuming the conditions for proxy validity for the data included in the model are met. First assumption is that Fe is only in pyrite and sulfur is partitioned between pyrite and TOC. This leads to the simple conceptual formula:

$$\frac{Fe}{S} = \frac{Fe_{py}}{S_{py} + S_{TOC}}$$

To build the model I will allow the following definitions for convenience:

$$a * \text{Pyrite} = Fe_{py}$$

$$b * \text{Pyrite} = S_{py}$$

$$c * \text{TOC} = S_{TOC}$$

This leads to the model being defined in terms of Fe, S, pyrite, and TOC, along with 3 constants, momentarily and quite arbitrarily, rendered as a , b , and c using the above definitions.

Table 1: A list of assumptions and guidelines for evaluating the validity of the Fe/S conditional proxy on a given dataset. One should review these and test their own data for possible violations of these guidelines before using the Fe/S conditional proxy.

No.	Assumption	Description
1	no chlorine-sulfur covariance	If Cl and S covary, it might suggest that the sulfur is associated with the brine trapped in the sample
2	No sulfate minerals present	If sulfate minerals are present, Fe/S would be low
3	No barium-sulfur covariance	A subset of #2, but focused on barium because of its ubiquity in drilling mud and ease of detection
4	No weathering	Outcrop samples might undesirable effects like pyrite -> gypsum or oxidation of organic carbon
5	no non-pyritic sulfide minerals	Basically the presence of sulfide minerals beside pyrite greatly interpretation of Fe/S proxy
6	At least "modest" TOC levels	Violation of this just means it will be hard to estimate sulfurization level but still valid for interpreting presence of sulfurized TOC
7	No H ₂ S	It's unknown how often this occurs
8	Fe/S > 0.871 & high TOC ≠ no sulfurized TOC	If Fe/S > 0.871 and TOC is high, that is not proof that the TOC is not sulfurized; the ratio may be masked by other Fe-bearing materials
9	That sediment is NOT overly mature	Immature sediments (experienced low pressure-temperature conditions) best preserve the original Fe-S-TOC proportions. One can use maturation indicators like vitrinite reflectance to assess the degree of maturity

$$\frac{\text{Fe}}{\text{S}} = \frac{a * \text{Pyrite}}{b * \text{Pyrite} + c * \text{TOC}}$$

The numerator contains the Fe while the denominator is the sum of the pyritic sulfur and organically-bound sulfur. This would imply that “a” and “b” are constants based on the stoichiometry of Fe and S in pyrite. This means that $a = 0.4655$ and $b = 0.5345$ while c is a variable based on the sulfur content of TOC. I will rewrite c as c_{su} to indicate that it is the sulfurization “constant” of TOC. Basic algebra and rearranging reveals that:

$$c_{\text{su}} = \frac{\text{Pyrite}}{\text{TOC}} \left(0.4655 * \frac{\text{S}}{\text{Fe}} - 0.5345 \right)$$

This equation is valid for $\text{S}/\text{Fe} > 1.15$ and $c_{\text{su}} = f(\text{py}, \text{TOC}, \text{Fe}, \text{S})$. On the other hand, $\text{Fe}/\text{S} = f(\text{py}, \text{TOC}, c_{\text{su}})$ for geologic samples fulfilling the requirements listed in Table 1 and described in detail under the Caveats section of this study. A cross-plot of Fe/S and pyrite/TOC where iron is only in pyrite and sulfur is partitioned between pyrite and TOC will have the form of a curve with two asymptotes (Fig. 1). The horizontal asymptote is referred to as the “pyrite line” defined by pyrite stoichiometry (e.g., 0.871 for Fe/S), with a vertical asymptote of 0. The vertical asymptote represents either the limit of pyrite/TOC as it approaches zero or as TOC goes to infinity or when pyrite is zero (mathematically can be rendered as $\lim_{\text{TOC} \rightarrow \infty} \left(\frac{\text{pyrite}}{\text{TOC}} \right)$ or $\text{pyrite} \rightarrow 0$, respectively).

Data that plot below the pyrite line indicate the presence of “excess sulfur” (relative to pyritic sulfur) that occurs within kerogen; this “excess sulfur” is organic sulfur. In Table 2, statistics for c_{su} are reported for $\text{Fe}/\text{S} < 0.871$ because the degree of excess sulfur and characterization of sulfurization is of interest.

4 RESULTS

4.1 Eagle Ford Group Sediments

For Eagle Ford Group, the data (3 datasets) found so far tend to plot above the pyrite line, on the Fe/S vs. pyrite/TOC crossplot, indicating “excess” Fe relative to total Fe included in pyrite (Fig. 3). The three datasets are from: Harbor (2011), Gibson (2015), and French et al. (2019). The reader should keep in mind that the data of Harbor (2011) and French et al. (2019) are from central and north-central Texas, which means the bulk lithology is mixed argillaceous and carbonate mudstones. To avoid issues with assumption about data distributions (i.e. normality), data range is reported as quartiles (meaning median instead of mean and instead of min-max; range is for between first and third quartiles, which is also known as interquartile range or IQR). Also, outliers often represent data that does not meet the criteria laid out later under the Caveats Section. The results are shown in Table 2. Data from Harbor (2011) is split between those above the pyrite line and about 30 out of 40 values are below the pyrite line. Of the ones that meet the criteria of being less than 0.871, the median Fe/S is 0.72 with the interquartile range between 0.57 to 0.97, while the median c_{su} is 8% and its interquartile range is 4-23%. These kinds of numbers are consistent with a designation of the

Pyrite-TOC-Fe-S for Eagle Ford Group

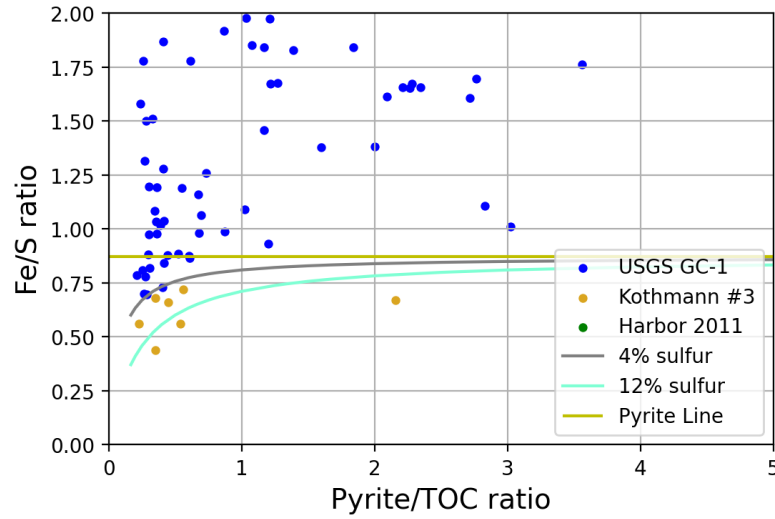


Figure 3: A cross-plot of bulk Fe/S ratio vs. pyrite/TOC for actual Eagle Ford Shale samples. The blue dots are from USGS Gulf Coast #1 drill core in East Texas Basin and does not meet the requirements of the Fe/S conditional proxy. However, the data from Kothmann #3 well and Harbor (2011) do. The median c_{su} for Kothmann #3 is 0.119 and 0.083 for Harbor (2011); this implies apparent sulfurization rates up to 12 wt. %

Table 2: A list of 10 datasets that the author found to include data that meet the criteria, includes their source and geologic context. There are 10 studies from over 6 formations and 4 countries. The c_{su} is a calculation of “apparent sulfurization” assuming sulfur is in either pyrite or organics; see formula in text. The statistics are restricted only for samples with Fe/S < 0.871 to assess how deviated these values are from the pyrite ratio.

Dataset	Source	Formation	No. Total	No. Fe/S < 0.871	Fe/S median	c_{su}
Kothmann #3	Gibson (2015)	Eagle Ford	8	8	0.61	0.119
USGS GC-1	French et al. (2019)	Eagle Ford	119	9	0.79	0.012
Harbor 2011	Harbor (2011)	Eagle Ford	40	30	0.64	0.083
Aristocrat well	Nakamura (2015)	Niobrara	37	9	0.75	0.052
Nordeg Shale	Riediger and Bloch (1995)	Gordondale Member	24	18	0.57	0.082
Belqa Group	Sanchez (2022)	Belqa Group	11	11	0.19	0.282
Dinur et al 1980	Dinur et al. (1980)	Ghareb Formation	5	5	0.24	0.080
Abubakar et al 2022	Abubakar et al. (2022)	3 formations	4	2	0.36	0.120
Gordondale	Ross and Bustin (2007)	Gordondale Member	11	6	0.67	0.016
Minster 1992	Minster et al. (1992)	Ghareb & Mishah Fm	55	52	0.46	0.024

kerogen as Type II-S based on the definition given by [Orr \(1986\)](#). The data reported by [Gibson \(2015\)](#) plotted closely with the 12% apparent sulfurization curve, c_{su} , (interquartile range is 6.5-30%). These values are not all that different from those for [Harbor \(2011\)](#) while the majority of the data from [French et al. \(2019\)](#) do not meet criteria leading to a skewing of the results. If all “excess” sulfur is organic sulfur, then estimating S_{org}/C is possible in practice as a lower bound to sulfurization wt. % of kerogen. In contrast, Eagle Ford Group samples from north Texas ([French et al., 2019](#)) generally plot above the pyrite line, suggesting that iron occurs in phases not in or in addition to pyrite (not surprising for argillaceous mudstones as various clay phases can contain Fe). Common candidate hosts and minerals in sedimentary rocks for iron include: siderite, magnetite, hematite, ankerite, ferroan dolomite, glauconite, chlorite, and goethite.

4.2 Other Formations

From Fig 4, the Fe/S and pyrite/TOC ratios from three datasets, each from a different, organic-rich formation (Niobrara Fm, Fernie Fm, and the Belga Group), are plotted similarly to Fig 3. The data from the Niobrara Fm (Denver Basin, Colorado) vary in terms of the “apparent” sulfurization, ranging from pyrite line to c_{su} values slightly greater than 0.12 sulfurization (up to 12 wt. % sulfur of TOC). The data from the Gordondale Member (formerly Nordeg Member as indicated by [Knapp et al. 2023](#)) of the Fernie Formation (Canada) ranges from 0.04-0.12 apparent sulfurization, suggesting that these samples have similar kerogen sulfurization

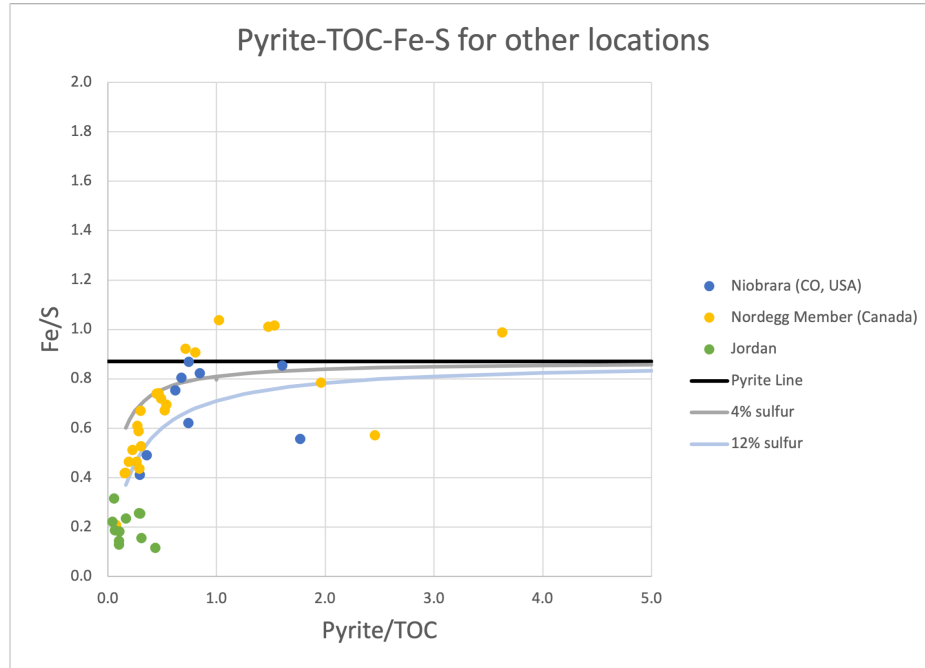


Figure 4: A cross-plot of bulk Fe/S ratio vs. pyrite/TOC for data of select formations other than Eagle Ford Group. The gold line is the pyrite line and is defined as $\text{Fe/S} = 0.871$ based on the stoichiometry of ideal pyrite. The various curves (green, blue, and orange) under the pyrite line represent the mixing line for a fixed apparent sulfurization constant, c_{su} , for a range of pyrite/TOC proportions. It convincingly shows that for the Niobrara and Nordegg Member samples that the apparent sulfurization (c_{su}) is between 0.04 and 0.12 although the samples from Jordan include higher values (1st to 3rd quartile range is 0.135-0.389) which are unexpectedly high. Data are from Nakamura (2015), Riediger and Bloch (1995), and Sanchez (2022); representing three geologic formations in USA, Canada, and Jordan.

(the wider the scatter the greater range of sulfurization values present). The data from the oil shale (Cretaceous-aged Belqa Group) of Jordan seems to represent an extreme case where the Fe/S and Pyrite/TOC are converging to the value of the $S_{\text{org}}/\text{TOC}$ of the kerogen. This normally would be hard to infer only from Fe/S and pyrite/TOC data, but the c_{su} value of 0.20 for the kerogen approximates the Jordanian data well with the highest kerogen sulfurization value being 0.26 (the latter does not take gypsum's sulfur content into account which would mean the value could be higher but gives an idea of the range of values possible for sulfurization of kerogen).

What was revealing in Fig. 5 was that in terms of bulk composition, Fe/S ratio (sorted by those <0.871 and those >0.871), and TOC content. In Fig. 5, there are two subplots based on 238 measurements from 9 studies. What is striking is that for the vast majority of data where $\text{Fe/S} < 0.871$ (Fig. 5a) had low quartz (more generally SiO_2) typically less than 20 wt. % and rest on a coherent trend line that has quartz/(clay+feldspar) ratio ≈ 0.2 yet can have any proportion of carbonate (0-100 wt. %). This is in contrast to the data for $\text{Fe/S} > 0.871$ (Fig. 5b) which has much more scatter but quite biased towards higher carbonate content (excess of 70 wt. %) that by most definitions are organic-rich carbonates or organic-rich siliceous carbonates. The implication is that high Fe/S ratios correlate with argillaceous mudstones (approaching the Quartz/(Clay+Feldspar) trend line ratio ≈ 0.2) while sediments with low Fe/S ratio typically are either siliceous organic-rich mudstones or very calcareous organic-rich mudstones.

As part of the literature survey to find data that met my criteria of having pyrite, TOC, Fe, and S content, I found many datasets that did not have low Fe/S (< 0.871). These included Utica Shale of Ohio (Kemeh, 2021), Hue Shale of North Slope of Alaska (Williams, 2020), and a private dataset (some of the results from this dataset published by Richards et al. 2023) from Wolfcamp Formation of south Midland Basin, Texas. Interestingly, the tar sands of Alberta, Canada (McMurray Formation) did not meet the pyrite line cutoff either (Zheng, 2013) since the bitumen appears to have low sulfur content. These data did not reveal characteristic low Fe/S ratio (< 0.871) and tended to have high clay content (which either masks the low Fe/S ratio of organics or contain low sulfur organics or very low organic content or maybe a combinations of these) for interpreting Fe/S ratio for sulfurized organics. Also, from the Nakamura (2015) dataset the following formations Denver Basin, Colorado had high Fe/S ratios: Pierre Shale, Carlile Formation, Greenhorn Formation, and Graneros Formation.

5 CONDITIONAL INTERPRETATION

Assuming reasonable compliance to stated assumptions above, the interpretation of the Fe/S ratio is simple:

Effects of TOC sulfurization by lithology and TOC content

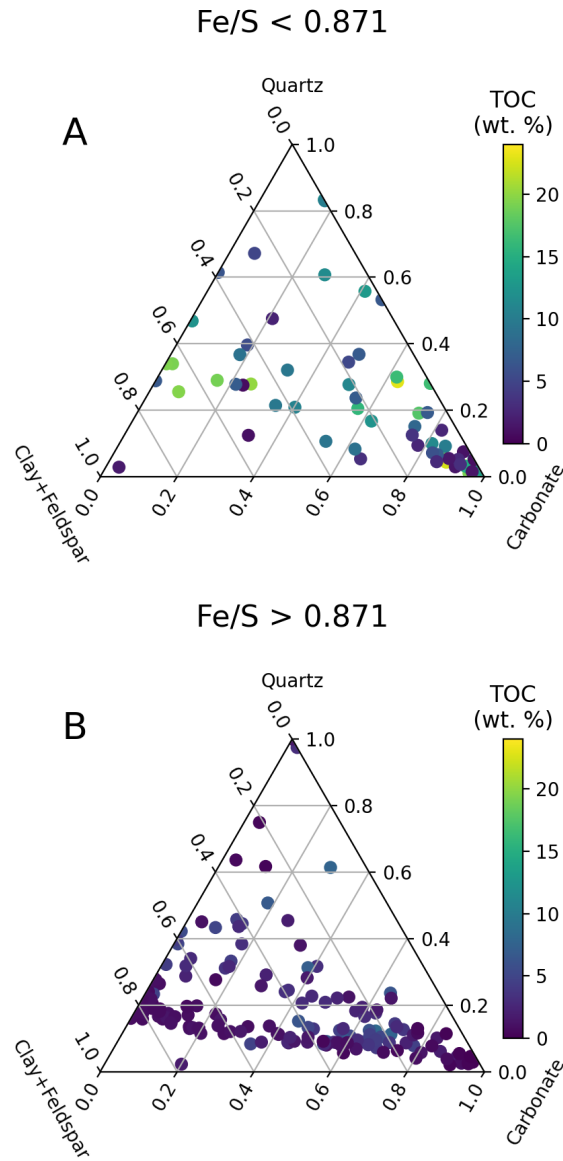


Figure 5: Two ternary diagrams showing interrelation of bulk compositions (quartz or SiO_2 , clay+feldspars, and carbonates), comparing the composition of sediments with high Fe/S bulk ratio (Fig. 5A) vs. those with very low Fe/S bulk ratio (Fig. 5B) where the cutoff value is the pyrite line (0.871).

1. If $\text{Fe/S} \sim 0.871$, then effectively all of Fe and S is in pyrite
2. If $\text{Fe/S} > 0.871$, then iron is present in two or more mineral species/phases
3. If $\text{Fe/S} < 0.871$, then there is notable Type II-S kerogen/petroleum due to sulfurization

In the case of $\text{Fe/S} \approx 0.871$, the values should be about a horizontal line that has a mean of 0.871 because the Fe/S ratio is a constant for stoichiometric pyrite. For $\text{Fe/S} > 0.871$ where iron is present in more than one mineral phase, there would neither be a correlation between the ratios or a clustering about a constant Fe/S value. This could be caused by many minerals and material combination, so $\text{Fe/S} > 0.871$ is not diagnostic or unique of any particular iron-rich mineral. In general, argillaceous mudstones, whether organic-rich or not, are expected to have excess iron relative to sulfur.

What is more interesting is the case where $\text{Fe/S} < 0.871$, where ideally the data points would fall along a logarithmic curve that varies as a function of pyrite/TOC ratio for a given "sulfurization" content of organic matter. This means that for increasing organic sulfur content of kerogen and its petroleum derivatives, the lower the Fe/S ratio is relative to pyrite/TOC ratio because of the excess sulfur residing in organic matter. This would imply a sulfur-rich kerogen that corresponds to a Type II-S (Orr, 1986).

In the spirit of ensuring clear communication, kerogen Type II-S is sometimes just referred to as sulfur-rich kerogen. According to Lewan (1984), this type of kerogen is deposited under what Lewan called Eh-pH regime III. Lewan suggested that this redox regime is typically characterized by $\text{V/Ni+V ratio} > 0.5$ and organic sulfur > 1 wt %. Orr (1986) provides a definition of Type II-S kerogen as $\text{S/C (at)} > 0.04$ which in this note is roughly $\text{S/TOC (at)} > 0.04$ (in the case of wt. % this ratio becomes 0.1068) and is why I provide a 4 wt. % organic sulfurization line in Figs 3. This "regime III" can be understood as a low Eh conditions that is strongly reducing, resulting in sulfate reduction to H_2S and thus nickel is preferentially in sulfides leaving vanadium preferentially accumulating in sulfurized organic matter.

Also, as Fig 1 and 2 show, if the Pyrite-TOC-Fe-S data plot along a logarithmic line, then the sulfur/TOC ratio can be estimated. The ambiguity is that since the non-pyrite mineral-bound sulfur is not accounted for, this ratio could be conservative if other assumptions hold.

6 CAVEATS

Keep in mind that I am not advocating the use Fe/S as a method for calculating TOC, although for formations and fields that are well-studied and calibrated it might give reasonable estimates. It should be noted that for Type II-S kerogen to be detected both TOC and sulfurization levels need to be sufficient to be detectable relative to pyrite, which is why this method may serve as a useful screening criterion for formations suspected of containing sulfurized TOC. As listed under the Model section, the model has at least 9 assumptions that might hold for many formations, but any practitioner that that wants to use Fe/S should be aware of the following issues and check for:

1. Notable covariance between chlorine and sulfur. This would imply that the sulfur is precipitation from pore fluids of dissolved salts and sulfates as the core or rock sample dries out. If covariance of sulfur and chlorine is detected from handheld XRF, I would suggest it might indicate a permeable zone with brine where the brine is slowly releasing from formation and forming precipitates on drill core surface. On the other hand, if one is interested in mineral-bound and organic sulfur and NOT in the sulfur from the aqueous fluids, then it is important to clean and scrub the drill core and samples appropriately.
2. If sulfate minerals are present, then Fe/S ratio could be unexpectedly low. However, if gypsum and anhydrite are dominant, it might be that a cross-plot of Ca and S reveals a covarying trend of $\text{S/Ca} \sim 0.80$, however the other potentially significant sulfate minerals are barite and possibly celestine. Often the presence of gypsum/anhydrite is visibly evident or in petrography; XRD obviously could settle this question if available.
3. Notable covariance between barium and sulfur (by implication sulfate). In the case of this observation being made from drill cuttings, this would be a red flag that probably drilling mud is getting mixed with the cuttings and if any cleaning took place, it was insufficient to remove the drilling mud. Obviously, the use of barium sulfate drilling mud could be verified from examining the well log header or consulting the drillers. In the case of drill core, it could either be related to a permeable zone that was saturated with drilling or actual barite nodules could be present in the core. An examination of the core should discriminate between these possibilities.
4. I would be very cautious about interpreting Fe/S ratio data from outcrop samples because of weathering can easily oxidize pyrite and greatly alter the pyrite/TOC ratio and the Fe/S ratio less so. In the compilation of Eagle Ford Group public data for this study, I plotted data from Chevrot (2019) such like in Fig. 3. The Fe/S ratio is low but the pyrite/TOC ratio seems too low rendering this dataset not usable for this study. The author believes that probably much of the pyritic sulfur was incorporated into gypsum (which was reported up to 10 wt. % in the thesis from XRD results) due to weathering effects.
5. A possibility, which was not observed in the data reviewed for this note, is the significant presence of other sulfide minerals besides pyrite. Sulfide minerals to look out for (even in sedimentary rocks) are pyrrhotite (which has a non-stoichiometric proportion of iron and sulfur, greatly in favor of iron), sphalerite, galena, bornite, and chalcopyrite. Pyrrhotite can be

- easily detected by its magnetism while the others are visibly different. These are more relevant in economic mineral mining, exploration, and extraction. Thin sections, XRD and similar methods could resolve this question if available.
6. The extremely high TOC-rich sediments plot in a region of Fe/S - Pyrite/TOC compositional space that appears to be relatively insensitive to sulfurization estimates because all sulfurization curves tend to converge asymptotically as $\text{Pyrite/TOC} \rightarrow 0$.
 7. Something that does not get discussed or widely reported is the presence of H_2S in shale formations. The presentation of [Xia and He \(2017\)](#) reported that in Eagle Ford oils, H_2S can be 1 % of the produced natural gas by volume. The presence of trapped H_2S if detected by XRF could in theory account for some of "excess" sulfur but it seems that the mobility of H_2S under standard atmosphere conditions makes this improbable. As an aside, a paper by [DuBois et al. \(2014\)](#) reports H_2S concentrations in Eagle Ford petroleum production up to 4 wt. % but it is unclear if those levels of H_2S are actually present natively to the Eagle Ford Group sediments or as the authors suggests are leaking into the horizontal boreholes through faults that intersect both Eagle Ford and the much deeper Edwards Formation. The author has personally experienced the odor of H_2S when drill core is broken in a laboratory setting, suggesting that this may not be a trivial issue.
 8. Lastly, just because $\text{Fe/S} > 0.871$ and has high TOC does not prove that the organic matter is not sulfurized, just merely cannot be demonstrated through this ratio.
 9. The rock samples should not be matured or over matured, as in diagenesis, as experiments (i.e. [Lindsey et al. 2018](#)) suggests that iron increases relative to sulfur during the maturation process of organic matter in sediments, implying sulfur tends to be volatilized. Maturation process involves both increasing pressure and temperature (P-T). The implication being that diagenesis and low-grade metamorphism reduces Fe/S ratio and thus tends to remove past evidence of former low Fe/S ratios.

One factor for which I have seen little published data on, but have had discussions with a mineralogist regarding the mismatch of XRF with XRD based on simplified mineralogy, which I suggested could be resolved if some of the illite/micas detected by XRD is iron-rich and I was aware of an example where we observed glauconite in the thin-sections but the XRD data results did not show glauconite. An end-member case is glauconite, which probably is difficult to distinguish from illite when in low concentration or mixed with other clay and mica minerals with similar crystallographic properties. I suspect that glauconite and chlorite are underreported from the rock record, particularly in organic-rich mudstones, but if present in any notable amount, it would complicate interpretation of the Fe/S data.

7 DISCUSSION

7.1 Eagle Ford Group

So back to the original question of whether the "excess" sulfur as shown by Fe/S ratios lower than 0.871 (Fe/S ratio of pyrite) is organically bound, it appears likely that the low Fe/S ratios documented in this study reflect significant organic sulfur content in the organic-rich mudstones, as I had originally proposed from the dataset of my own study of Eagle Ford Group sediments in west Texas ([Wehner, 2017](#)). The Fe/S ratio for samples from wells north of the San Marcos Arch are usually much in excess of 0.871 and generally do not meet the criteria for using Fe/S conditional proxy, although that should not be misconstrued as proving the kerogen type for Eagle Ford Group in East Texas Basin is not sulfurized. However, it may only be somewhat sulfurized because of high clay content (perhaps Fe-rich clays) and the published results of [Little et al. \(2012\)](#) suggests that the $\text{S}_{\text{org}}/\text{C}$ ratio (3 samples) in East Texas is low, between 0.022 and 0.031, which supports the hypothesis that kerogen from Eagle Ford of East Texas Basin is not be expected to be sulfurized enough to be considered type II-S kerogen. There is supporting evidence for the high organic sulfur content of Eagle Ford Group sediment in south and west Texas ([Bryndzia and Macaulay, 2018](#); [Sun et al., 2016](#); [Little et al., 2012](#); [Edman and Pitman, 2010](#)). The cross-plot of $\text{S}_{\text{org}}/\text{C}$ and Fe/S for kerogen (Fig 7), from data reported by [French et al. \(2024\)](#) for USGS Gulf Coast #3 (abbreviated as GC #3) in Maverick Basin of Texas, demonstrates a very linear relation for $\text{S}_{\text{org}}/\text{C}$ and Fe/S, confirming my hypothesis in [Wehner \(2017\)](#). This suggests that for sediments where the Fe and S are mostly present in pyrite and kerogen, the Fe/S is a good proxy (also confirmed for GC #3 by crossplot of $\text{S}_{\text{org}}/\text{C}$ vs. bulk Fe/S) for sulfurized organics. It appears that the sulfurization rate for GC #3 samples is about 0.10 which broadly is consistent with computed median estimates for c_{su} (ca. 0.08-0.12 for Maverick Basin wells as in Table 2). These values are consistent with a classification of the kerogen as Type II-S (as already observed by [Sun et al. 2016](#), as well by [Little et al. 2012](#); postulated by [Edman and Pitman 2010](#) based on oil analysis). Furthermore, at least for south and west Texas, it appears that the kerogen of Lower Eagle Ford may be more sulfurized than those from Upper Eagle Ford (based on data from [Sun et al. 2016](#) and [Little et al. 2012](#)).

So, while it has been known for a while that Eagle Ford kerogen of south and west Texas was sulfurized and qualify to be considered as Type II-S, the dataset released by [French et al. \(2024\)](#) provides the clear link between Fe/S bulk conditional proxy with kerogen analyses (Fig. 8). Interestingly, I found two geochemical studies ([Núñez-Useche et al., 2016](#); [Mesa-Rojas, 2022](#)) for Eagle Ford in Mexico, both in the state of Coahuila. For both, the median Fe/S value approximated between 1.1 and 1.3 while in both minimum values were about the pyrite ratio. The author's impression is that despite the Eagle Ford Formation of central Coahuila being TOC-rich (like 2-7 wt. %), it does not have the characteristic low Fe/S ratios indicative of Eagle Ford Formation samples from south and west Texas.

USGS GC #3 sulfurization

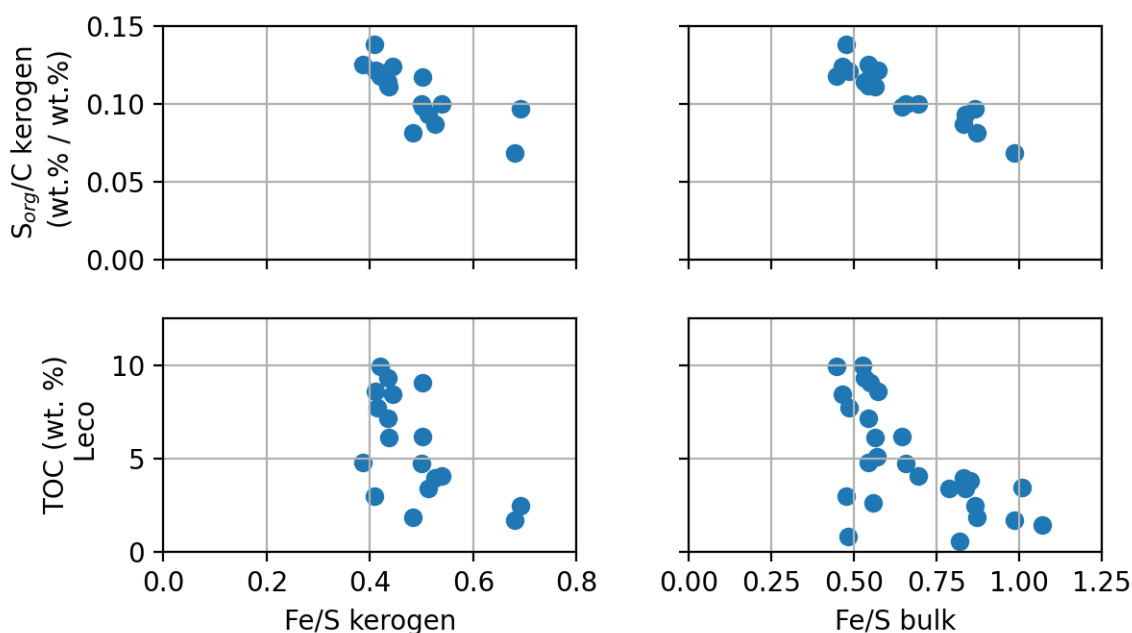


Figure 6: This matrix plot is from the published dataset of [French et al. \(2024\)](#), which is from USGS Gulf Coast #3 and contains mostly just Lower Eagle Ford Formation and is in south Texas. This dataset is important because it clearly shows the relationship of bulk values of Fe/S with the kerogen measurements. Figure 6A, clearly shows that within kerogen, the S_{org}/C increases for decreasing Fe/S of kerogen; Figure 6B, the linear relationship still holds when Fe/S of kerogen is swapped out for bulk Fe/S (the latter still less than 0.871), which is surprisingly linear; Figure 6C shows TOC vs. Fe/S bulk, which seems to have more scatter than in other subplots; Figure 6D, TOC vs. Fe/S bulk seems to similar scatter as Fig 6C, perhaps reflecting variation in kerogen sulfurization.

Another line of evidence that seems to support the observation that the organic matter in Eagle Ford (particularly in the Lower Eagle Ford) is the high DBT/P ratios as measured by gas chromatography of extracts [Sun et al. \(2016\)](#), which they attributed to presence of Type II-S kerogen. DBT/P stands for dibenzothiophene/phenanthrene ratio. For the Lower Eagle Ford in the Iona #1 well of Val Verde County, Texas, [Sun et al. \(2016\)](#) reported DBT/P ratios in excess of 1, which according to [Hughes et al. \(1995\)](#) are associated with sulfur-rich marine carbonates, while [Sun et al. \(2016\)](#) made the suggestion that in the case of Eagle Ford, it might correlate with increase of sulfur-reducing bacteria as indicated by similarity of DBT/P curve and aryl isoprenoid curves. It turns out that the gas chromatography results of [French et al. \(2019\)](#) in their Figure 8 shows DBT/P slightly in excess of 1 for Lower Eagle Ford in USGS GC #1 which may be consistent with the interpretation of [Sun et al. \(2016\)](#).

7.2 Other Formations

The use of Fe/S bulk as a conditional proxy should have utility wherever there are source rocks and unconventional petroleum resources that meet the criteria of the conditional proxy in Table 1. A literature survey (shown in Table 3) suggests that it should be valid for formations like Monterey Shale and Niobrara Formations in the USA. While the data for Niobrara Formation from [Nakamura \(2015\)](#) suggests it is a sulfurized, organic matter rich formation, I am aware of data reported by [Dean and Arthur \(1989\)](#) that suggests most sulfur is in pyrite since the Fe/S ratio in the Fe-TOC-S ternary diagram in their Fig. 10 is pyritic. Globally, it appears to be valid for at least the following: Gordondale Member (Fernie Group) of Alberta, Canada, the various oil shales of Israel and Jordan (Ghareb Formation, Mishah Formation, and Belqa Group). Table 3 was a summary of studies, so it slightly obscures the fact that some formations are poorly sampled (i.e. 1 or 2 samples) and thus it is premature to conclude much on the basis of so few data (for instance, [Abubakar et al. 2022](#), had one or two samples each for 3 formations: Kimmeridge Clay, Monterey Shale, and Whitby formations. The latter is part of the Lias Group of the UK).

7.3 Formations Where Fe/S Seems Not Valid

While it can be shown that Fe/S does have some validity for a range of circumstances, it should be noted that there are some well-known formations for which it does not work. A notable failure is Wolfcamp Formation of Permian Basin, west Texas, USA.

Kerogen sulfurization vs. Fe/S kerogen Ratio

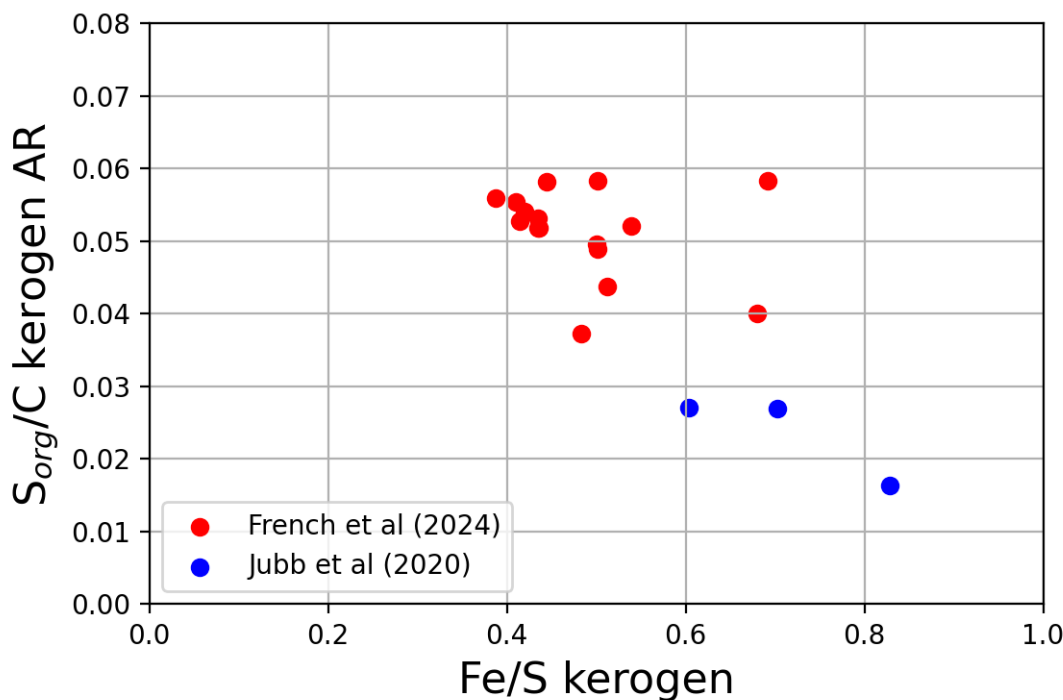


Figure 7: Combines the kerogen data of [Jubb et al. \(2020\)](#) and [French et al. \(2024\)](#) to show an apparent quasi-linear trend of S_{org}/TOC of kerogen vs. the Fe/S of kerogen. This plot is evidence, at least for the Eagle Ford Group sediments, that demonstrates that Fe/S is inversely proportional to of S_{org}/TOC .

It should be noted that this is based on a rather small sampling (this dataset is referenced by [Richards et al. 2023](#) and is from south Midland Basin subbasin of Permian Basin) and probably there are bigger proprietary datasets that could easily lead credence or not to these observations. The author's observation regarding the Wolfcamp Formation is that the bulk Fe/S ratio is not valid because the Fe/S were all very high in excess of 1, making it not useful for assessing sulfurization and thus the “more organic-rich” interval. A review of the XRD data shows, among other things, the presence of ferroan dolomite and/or ankerite, which has a mean of 6 wt. % (roughly 1 wt. % Fe of bulk composition from Fe-dolomite and/or ankerite) from a dataset of 22 samples. In terms of clay content, the mean is 34 wt. % while the pyrite content is low (the pyrite content mean is on the order of 1.5 wt. %). All this seems to add up to characterize the formation as not iron-limited and iron exists in multiple phases besides pyrite. [Wickard et al. \(2016\)](#) noted that dolomite can be allochems in the carbonate debrite/turbidite beds or can be cements and even fracture fill. I suspect that given the relative amount of iron in the carbonate phases and moderate clay content combined with low pyrite content, it does not meet the conditions for the Fe/S conditional proxy.

Another formation that has similar characteristics to Wolfcamp in terms of mineralogy and failure to meet the proxy conditions is the Bowland Shale of the UK ([Emmings et al., 2019](#); [Waters et al., 2020](#)). It appears that the Pennsylvanian-aged shales of the U.S. Midcontinent (mostly, Forest City Basin and Illinois Basin across Nebraska, Kansas, Missouri, Iowa, and Indiana) does not meet the condition for the Fe/S conditional proxy, despite being very high in TOC (up to 40 wt. %) and unusually high concentrations of paleo-redox sensitive elements (Mo, U, Zn, and P) apparently indicating extreme anoxia or even euxinia ([Schultz and Coveney, 1992](#)). A quick check of the elemental geochemistry dataset of [Ardakani et al. \(2026\)](#) suggests that the Montney Shale of Canada has excess iron, so the Fe/S proxy might not work there.

It appears that some well-known Cretaceous formations in central USA (or at least in Colorado) are not candidates for use of conditional Fe/S ratio; these include Carlisle Fm, Graneros Fm, Greenhorn Fm (and its world-famous Bridge Creek Member), and Pierre Shale (examples from Table 4). While the key datasets that contain the required pyrite, TOC, Fe, and S concentrations was provided by [Nakamura \(2015\)](#), there is support from other sources like [Dean and Arthur \(1989\)](#) who only had Fe-S-TOC data and published ternary diagrams for Bridge Creek Member of Greenhorn Formation, and Pierre Shale (and its equivalents, i.e. Gammon Shale). Interestingly, [Hart et al. \(2024\)](#) compared Belle Fourche & Second White Specks formations with Eagle Ford Group to

Table 3: A repeat of Table 1 but uses the 5-number summary approach to avoid making assumptions about the statistical distribution of values. This dataset establishes that the Fe/S conditional proxy does indeed identify intervals that have high TOC content in formations that apparently are characterized by sulfurized kerogen and tend to be contained in either organic-rich marly carbonates or siliceous carbonates. ** is the number of samples that have Fe/S < 0.871

Dataset	Formation	No. **	Fe/S				c_{su} (dec)			
			Q ₁	Median	Q ₃	IQR	Q ₁	Median	Q ₃	IQR
Kothmann #3	Eagle Ford	8	0.54	0.61	0.68	0.14	0.065	0.119	0.307	0.242
USGS GC-1	Eagle Ford	9	0.71	0.79	0.83	0.12	0.009	0.012	0.036	0.028
Harbor 2011	Eagle Ford	30	0.56	0.64	0.71	0.16	0.045	0.083	0.231	0.186
Aristocrat well	Niobrara	9	0.52	0.75	0.84	0.31	0.021	0.052	0.168	0.147
Nordeg Shale	Gordondale	18	0.46	0.58	0.70	0.31	0.061	0.088	0.118	0.057
Belqa Group	Belqa Group	11	0.13	0.19	0.25	0.12	0.135	0.282	0.389	0.254
Dinur et al 1980	Ghareb Fm	5	0.15	0.24	0.45	0.31	0.075	0.080	0.122	0.047
Abubakar et al	3 formations	2	n/a	0.36	n/a	n/a	n/a	0.120	n/a	n/a
Gordondale	Gordondale	6	0.59	0.67	0.73	0.13	0.013	0.016	0.122	0.110
Minster 1992	Ghareb & Mishah	52	0.23	0.46	0.65	0.43	0.017	0.024	0.043	0.026

Table 4: Top row reports the results of data reviewed for the formations listed. These were the datasets that had the required pyrite, TOC, Fe, and S data for testing the hypothesis of whether Fe/S had any validity for assessing organic matter sulfurization. The bottom row represents formations that I make a prediction of whether Fe/S conditional proxy is expected to have some validity for that formation.

	Fe/S	Fe/S NOT valid
Observed	Eagle Ford Group (USA) Monterey Shale (CA, USA) Niobrara Fm. (USA) Woodford Shale (USA) Gordondale Member (Ferne Fm., Canada) Belqa Group (Jordan)	Carlile Fm. (USA) Graneros Fm. (USA) Greenhorn Fm. (USA) Hue Shale (AK, USA) Pierre Shale (USA) Utica Shale (OH, USA) Wolfcamp Fm. (USA) Duvernay (Canada) Bowland Shale (UK)
	Phosphoria Fm. (USA) La Luna Fm. (Venezuela) Neuquen Shale (Argentina) Kimemridge Clay Fm. (UK) Orbagnoux (France) Pantokrator Fm. (Greece) Wealden Shale (Germany) Kaspir Oil Shale (Russia) Ghareb Fm. (Israel-Jordan)	Green River Fm. (USA) Tuscaloosa Marine Shale (USA) New Albany Shale (USA) Athabasca Oil Sands (Canada) Belle Fourche & Second White Specks (Canada) Irati (Brazil) Pumpherson (Scotland, UK) Kukersite (Estonia) Longmaxi Shale (Sichuan, China) Oil Shale of Pahang (Malaysia) Silurian Hot Shale (Libya) Glen Davis (Australia) Montney Shale (Canada)

account for why Belle Fourche & Second White Specks formations was not a successful unconventional play. They noted the excess clay content and somewhat lower oil-generating potential. Notice how this aligns with favorable bulk Fe/S values for Eagle Ford Group versus seemingly unfavorable Fe/S values from Belle Fourche and Pierre Shale, suggesting it can be a first-order screener for higher quality unconventional petroleum resources.

In summary, Fe/S ratio appears to be valid when both TOC content (bulk) and sulfur content (of kerogen and petroleum) are high enough to permit statistically significant values from the pyrite ratio to distinguish between the Fe and S being mostly in pyrite (where Fe/S is at the pyrite line ratio). In very general terms, the conditions of the Fe/S ratio are more likely to be met for organic-rich formations that have low clay content (because sometimes clays contain reactive iron), either high in calcite or silica but for silica it should be biogenic silica not the detrital quartz. It should not have Fe-rich dolomites or strange sulfide minerals typical in hydrothermal deposits investigated for economic grades of metals.

7.4 Formations with sulfurized kerogen

Table 5 contains the 15 datasets that have some kind of elemental analysis of kerogen (i.e. CHNS-type of analysis) which gives an idea of the degree of kerogen is sulfurization. The goal here is to highlight the possibilities of other formations where the Fe/S conditional proxy might be valid. The author did not exhaustively investigate the probability of these formations being good candidates for bulk Fe/S being valid indicators of abundant sulfurized kerogen. However, there are indications that some formations like the Kimmeridge Clay (UK) and Woodford (Midcontinent, USA) formations, based on reported elemental kerogen analyses, may not meet Orr's definition for containing type II-S kerogen but the high level of TOC may still permit the use of Fe/S because for formations with very little sulfur besides those in kerogen and pyrite yet high TOC the Fe/S ratio will reflect the relative proportions of organic sulfur and pyrite. Also, this list is more diverse containing results from Muwaqqar Formation of Jordan, Garau Oil Shale of Iran, Kashpir Oil Shale of Russia, and Pantokrator Formation of Greece. While the author did not attempt an exhaustive search of the entire IODP/DSDP/ODP archives and cross-reference the data types, 3 datasets were found that had elemental kerogen analyses, which shows a detailed search of this massive archive may have fruitful yield. What can be reported that 3 kerogen element datasets were reviewed, spanning the offshore Falkland Plateau (somewhat near the British dependency, Falkland Islands) in the South Atlantic, the Lower Cretaceous in the Straits of Florida (roughly equidistant from Florida, Mexico, and Cuba), and the Plio-Pleistocene sediments in the Gulf of California in offshore Mexico. Of these 3, two had qualified sulfurized kerogen (seemingly kerogen Type II-S). What could not be verified was whether the Fe/S conditional proxy was valid for these datasets. It is reported that La Luna Formation of Venezuela has sulfurized kerogen and early matured hydrocarbons (Baskin and Peters, 1992).

At the last minute after this author wrote this paper that he was made aware of the work of Cohen-Sadon et al. (2025) who published on comparing Tmax parameter for sulfur versus hydrocarbons and utilizing that information in the context of organic matter maturation. It was not until one checks the supplemental data for Cohen-Sadon et al. (2025) that they introduce notation that can be related to Fe/S. In their Table S1, they report $\text{Fe}_R/(\text{S}_{\text{org}} + \text{S}_{\text{py}})$ as molar ratio. In terms of my Py-Fe-S-TOC model, when $\text{Fe/S} = 0.871$, this would be $\text{Fe/S} = 0.5$ molar as Cohen-Sadon et al. (2025). So for $\text{Fe/S} < 0.871$ this would correspond to $\text{Fe}_R/(\text{S}_{\text{org}} + \text{S}_{\text{py}}) < 0.5$ molar. A comparison of their Table S1 with Table 4 of this paper is favorable with one possibly failing the prediction, namely Pumpherston of Scotland, UK, the others seem to be confirmed.

7.5 Implications of Low Fe/S Ratios

From a petroleum exploration standpoint where the explorer is investigating the risks/probabilities of a complete and functioning petroleum system, it is common to use techniques like Rock-Eval and vitrinite reflectance data to assess this. However, it is well known that mineralogy can make Rock-Eval data interpretation problematic like carbonates (one potential host of sulfurous organic matter) because of mixing of organic and inorganic carbon (Katz, 1983; Hart and Steen, 2015). However, sulfur is also known to reduce cracking temperature of bitumen because C-S bonds are easier to break than C-O bonds, which means sulfurized hydrocarbons mature at lower temperature (Yurchenko et al., 2018). So low Fe/S could alert a petroleum explorer that oil was generated at lower temperatures (and probably at shallower conditions) than conventional geologic wisdom would otherwise suggest.

7.6 Possible Causes of Low Fe/S Ratios, Relations of DOP & Fe/TOC and Future Work

There is a body of literature that explores the use of carbon-iron-sulfur proportions for gathering clues about redox or even paleoredox conditions. Initially, there was attention on C/S crossplot (actually $\text{C}_{\text{org}}/\text{S}_{\text{py}}$) since it was thought, based on modern analogues, that it could be used to distinguished normal oxic marine conditions from euxinic bottom-water conditions (Bernier and Raiswell, 1983, 1984; Leventhal, 1983, 1987; Morse and Berner, 1995). Also, ternary diagram of iron, sulfur, and organic carbon (Fe-S-TOC in this manuscript) has been used to make the same distinction as C/S crossplots (Dean and Arthur, 1989; Lyons and Berner, 1992; Arthur and Sageman, 1994). These works often made use of a ternary diagram to diagnose such things as whether the iron-sulfur was approximately the pyrite ratio (i.e. Fig. 9 of Dean and Arthur 1989) or S/TOC trend of about 0.4 that is reported to be the oxic marine trend. From Arthur and Sageman (1994) in their Figure 4, they acknowledge that for $\text{Fe/S} < 0.871$ would imply "excess" sulfur that is not in pyrite and possibly means all iron is reduced and incorporated into sulfides. But published examples of "excess" sulfur, like the data presented in this paper, are somewhat rare (i.e. Fig. 10 of Kolonic et al. 2002 for well S75 in Tarfaya Basin, Morocco). Ross and Bustin (2009) suggested that some of their data from lower Besa River and Muskwa shales (Devonian-Mississippian of Western Canadian Sedimentary Basin, Canada) have a component of sulfurized organic matter but the author of this paper considers their values to be close to the pyrite line. While Raiswell et al. (1988) did warn that significant carbon can be lost from kerogen during maturation, the experiments of Lindsey et al. (2018) also show a shift to iron at expense of sulfur. This consideration limits the value of paleoenvironmental interpretation of Fe-S-TOC data from mature shales. The loss of sulfur relative to iron during shale maturation (which can be somewhat proxied by Ro) would imply that Fe/S ratio would tend to increase. This means that in some cases, sediments that had an excess of sulfur could have Fe/S ratio that increase until it is greater than the pyrite ratio. This would further constitute another assumption for the conditional proxy and a lot of other geochemical proxies which is apparently not well discussed in application papers.

Many works (Raiswell et al., 1988; Leventhal and Taylor, 1990; Schultz and Coveney, 1992) mention a proxy that seems to have some value for paleoenvironmental interpretation is DOP (degree of pyritization). DOP is defined as $\text{Fe}_{\text{py}} / (\text{Fe}_{\text{py}} + \text{FeHCl-soluble})$.

Table 5: This is a collection of elemental kerogen studies (often using CHNS type of pyrolysis on kerogen) from 16 studies that cover an even wider range of formations. These studies did not include data like XRF and XRD to make it into the main dataset of this study. Using Orr (1986) definition for Type II-S kerogen (heavily sulfurized), 10 out of 16 of these datasets contain sulfurized kerogen and may be candidates for formations where the Fe/S conditional proxy is valid.

Dataset	Source	No. Total	No. Type II-S	S _{org} /TOC (AR)	S _{org} /TOC (wt %)	Max S _{org} /TOC (wt %)	Formation, Location	Comments
KOS	Hakimi et al 2024	10	10	0.079	0.211	0.221	Muwaqqar Formation, Lajjun outcrop, Jordan	
Iona #1	Sun et al 2016	4	2	0.053	0.140		Eagle Ford, TX, USA	
Jubb et al 2020	Jubb et al 2020	3	2	0.056	0.149	0.150	Eagle Ford, TX, USA	From 3 wells in Maverick Basin
Qalikuh	Shekarifard et al 2019	4	4	0.054	0.143	0.179	Garau Oil Shale, Iran	Not a kerogen Type II-S deposit
Velez-Arcabuco	Campos et al 2002	6	0	0.008	0.021	0.106	Paja Fm., Columbia	Type study for kerogen Type II-S
Orr's Monterey	Orr 1986	28	18	0.051	0.136	0.176	Monterey Shale, CA, USA	
Naples Beach	Nelson et al 1995	1	1	0.051	0.136		Monterey Shale, CA, USA	
Woodford Study	Craddock et al 2018	7	0	0.009	0.025	0.044	Woodford Shale, OK, USA	
Gorodische outcrop	Riboulleau et al 2000	3	2	0.047	0.125		Kashpir Oil Shale, Russia	
Ionian Zone	Alexandridis et al 2022	9	9	0.057	0.153	0.206	Pantokrator Fm., Greece	
Murray et al 1998	Murray et al 1998	3	2	0.036	0.096	0.150	Kimmeridge Clay	leans more to Type II instead of Type II-S
Froidl et al 2021	Froidl et al 2021	6	6	0.055	0.147	0.422	"Wealden" Shale, NW Germany	
DSDP Hole 71-511	Deroo et al 1983	10	0	0.021	0.055	0.068	Jura-Cret., south Atlantic Ocean	Not a kerogen Type II-S deposit
DSDP Hole 77-535	Herbin et al 1984	12	5	0.057	0.152	0.253	Cret., Gulf of America	Reported to be dark marly limestones
DSDP Leg 64	Kendrick 1982	5	4	0.049	0.130	0.175	Plio-Pleistocene, Gulf of California, Mexico	

What is less discussed is the numerical validity range of this proxy. Basically, DOP has range of 0-1 based on the case of no pyrite (but reactive iron in clays, etc.) all the way to the scenario of all iron is in pyrite (let's be generous and say iron sulfides). This seems straightforward and clear until one plots this data in a Fe-S-TOC ternary diagram where it is clear that it is valid only up to the pyrite line (Fig. 1, 2) and has no meaning for cases where $\text{Fe/S} < 0.871$, implying DOP is only valid for $\text{Fe/S} \geq 0.871$. What is interesting about this is that Fe/S conditional proxy as defined and used in this manuscript is valid for the compositional space where DOP is not, suggesting that DOP and conditional Fe/S may have complementary uses/application/interpretation. At this time, it is a bit risky to postulate what the paleoenvironmental implication is for $\text{DOP} > 1$ and $\text{Fe/S} < 0.871$ but one idea to explore might be shallow-water anoxia (i.e. photic zone euxinia) as that is the paleoenvironment interpretation given to Eagle Ford Group in west Texas (Wehner et al., 2015). Shallow-water anoxia interpretation has already been assigned to some of the formations where conditional Fe/S proxy is known to be valid. These include: Kimmeridge Clay Formation (Wignall, 1991; Raiswell et al., 2001), Woodford and its equivalent Chattanooga (Schieber, 1994; Romero and Philp, 2012). Another factor to review would be basin restriction or stratified water column. Also, I suspect that low deposition rates are important because too much clay overwhelms the sulfur and converts sulfur to pyrite, leaving little to none for sulfurization. Another way to say this might be that the seafloor is iron-limited since the low siliciclastic deposition is overwhelmed by biogenic skeletal debris, like carbonates from microfossils and/or nannofossils, biological silica, etc. (Raiswell et al., 1988). A thorough discussion of this is beyond the scope on this paper.

7.7 Statistical Uncertainty of Fe/S Conditional Proxy

To illustrate the scale of statistical validity, I will use the XRF dataset from one of my study locations, Antonio Creek (further details of locations and data, see Gardner et al. 2013 and Wehner 2017). From the Antonio Creek XRF data, which spans the entire Eagle Ford Group, I analyzed the iron and sulfur data to estimate the uncertainty associated with the Fe/S ratio. Because there is uncertainty associated with the measurement both iron and sulfur in terms of differentiating the signal and background noise, the “error” of the measurements is propagated to the ratio using the following equation:

$$\Delta \frac{Fe}{S} = \frac{Fe}{S} \left(\frac{\Delta Fe}{Fe} + \frac{\Delta S}{S} \right)$$

This is the form of the error propagation formula for multiplicative values like $x \cdot y$ or x/y . It can easily be programmed into Excel (or spreadsheet of choice) or even as a python script (standalone or as plugin for a proprietary software). Formulae like this for error analysis and propagation of errors are easily found and can be verified through references like Bevington and Robinson (2002). For $\text{Fe/S} \approx 0.87$ I found that the 2σ deviation for this particular dataset was ± 0.11 but obviously each practitioner will need to perform their own calculation based on their data, instrumentation, and calibration. A key observation to note is that for data where Fe and S is high compared to detection levels (essentially a high signal-to-noise ratio of each element), the lower this uncertainty is. The goal was to define Fe/S bulk ratio as a conditional proxy so it can be used where it meets the criteria of $\text{Fe/S} < 0.871$ and does not fail the other criteria listed in this note. I provided the modeling and theoretical basis for why this ratio can be indicative of sulfurized TOC in mudstones that have low clay content. I believe this ratio has utility in screening prospective source rocks in new basins. It also can serve as one of the proxies used by the wellsite geologist or mudlogger who runs the XRF or ICP instrument at wellsite or lab; depending on the turn-around time, this data may serve as look-back of nearby wells or even in nearly real-time operations like geosteering (see Tonner et al. 2018 for an example of how this can be done).

8 FURTHER WORK

This work should be considered preliminary since it was partly a literature survey inspired by my own findings; and looking for compatible datasets from the literature proved challenging as it is scattered over a wide range of publication time, variable data quality control, changing technology. So, future work should attempt to make a bigger inventory of data that have a combination of datasets that include quantitative measurements of pyrite, TOC, Fe, and S. This would enable further testing of the utility of Fe/S as a conditional proxy in a wider range of sediments and source rocks. Even more valuable are the datasets that have both the measurements of pyrite, TOC, Fe, and S for bulk composition and elemental analysis of kerogen. The elemental analysis of kerogen allows for more exact measurements of sulfurization of kerogen. As alluded to earlier, it may be that the IODP/DSDP/ODP archive contains records that would fit the objectives of a future project on the utility/use case of the Fe/S conditional proxy. It seems there may be value in comparing with the wider suite of paleo-redox proxies like degree of pyritization (DOP), Mo/TOC, Mo/U, V/(V+Ni), and pyrite framboids.

9 SUMMARY

Based on data from 16 formations and 25 studies (containing pyrite-TOC-Fe-S or elemental data of organic matter) it is proposed that Fe/S bulk ratio can be utilized as a conditional proxy for organic-rich intervals that have TOC content in excess of 1-2 wt. %. This conditional proxy should be valid when its assumptions are met and must be validated in regions where these assumptions have not been verified. Where the conditions are proxy are valid, it is a proxy for richness of sulfurized kerogen. when the amount

of organic sulfur is within an order of magnitude of pyritic iron and other forms of iron. The bulk Fe/S conditional proxy should have some utility in petroleum exploration, source rock studies, and even operations geology (consider for instance, using XRF to land a steer a horizontal well into an unconventional). Data reviewed thus far suggests that the conditional proxy, Fe/S, is valid for Eagle Ford Group (south and west Texas), Niobrara Formation of Colorado, and Monterey Formation of California. Internationally, it is valid for the various oil shales of Israel and Jordan (i.e., Ghareb Formation, Mishah Formation, and Belqa Group), and Gordondale Member of Fernie Group in Alberta, Canada. A list of formations is provided that may be worth a closer inspection.

10 ACKNOWLEDGEMENTS

The seed for this project originated from several discussions with Dr. Mike Pope, retired from Texas A&M, back in 2017 as I preparing the write up of my dissertation and I happened to observe the anomalously low Fe/S ratios in my Eagle Ford dataset for Antonio Creek, Terrell County, Texas. Thanks to those discussions, I hypothesized that it indicated sulfurized organic matter and may be more common with organic-rich carbonates. An early draft benefited from a private critical review by Dr. Eric Peavey of Chevron.

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