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SCIENTIFIC COMMENT

Carbon-sulfur plots to show diagenetic and epigenetic sulfidation in sediments

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Abstract—Organic carbon vs. sulfide sulfur plots are now being used regularly by many geochemists to help understand recent and ancient depositional environments and diagenetic processes. Usually, these plots are useful to recognize nonmarine vs. marine environments or oxic vs. anoxic vs. euxinic depositional environments. However, C vs. S plots can also indicate diagenetic and epigenetic events that produce "excess" sulfide. Four new examples are presented and discussed.

INTRODUCTION

Carbon vs. sulfur plots have proved useful in characterizing modern and ancient sedimentary depositional environments. Plots of organic carbon and sulfur (sulfide or total) from modern marine settings (normal, oxic water column) were first presented by Berner (1970) and Sweeney (1972), and summarized in Goldhaber and Kaplan (1974). The same type of C vs. S plots were subsequently used (Leventhal, 1979a, 1983, 1987) to show data for ancient environments and to define a "euxinic" (anoxic-sulfidic water column) field with enhanced S/C ratios and positive S intercept. The latter was based on results from the Black Sea and also applied to ancient black shales in the literature for which C and S data were available. Berner (1984), summarized the modern C-S data including the S-poor freshwater sediment field. Figure 1 summarizes these fields on a C-S plot.

Since then, many workers have used C-S plots to help characterize ancient depositional environments (e.g., Anderson et al., 1987; Leventhal, 1987; Aplin and Macquacker, 1993; Suits et al., 1993; Pratt and Davis, 1993; see Lyons and Berner, 1992, for additional references). Some problems were noted in using C vs. S plots when Fe was limiting (Raiswell and Berner, 1985; Calvert and Karlin, 1991; Lyons and Berner, 1992), because in Fe-poor rocks, such as carbonates and sandstones, the complete sulfidation of Fe may limit the total solid-phase sulfide content of the rock. Other problems in C-S plot interpretations can arise if the system is (metabolizable) organic carbon limited (Raiswell and Berner, 1985), organic matter has been lost by heating (Raiswell and Berner, 1986), or unusual water chemistry is present (Tuttle and Goldhaber, 1993).

To augment the interpretation of C vs. S plots, particularly their value in discerning paleo-redox conditions, Fe-S relationships have also been investigated. These studies have reported Fe vs. S plots (Leventhal, 1979b) and degree of pyritization (DOP) (Berner, 1974, 1984; Raiswell and Berner, 1985; Anderson et al., 1987; Raiswell et al., 1988). DOP is the ratio

$$\mathrm{Fe_{pyrite}}/[\mathrm{Fe_{pyrite}} + \mathrm{Fe_{reactive}}]\ ,$$

and is determined by several acid extraction methods (Berner, 1970, 1974; Canfield, 1988; Huerta-Diaz and Morse, 1990; Leventhal and Taylor, 1990; Lin and Morse, 1991; Raiswell et al., 1994), based on Fe removal from samples by leaching with HCl. Another measure, degree of sulfidation (DOS), has also been proposed (Boesen and Postma, 1988) and ternary plots of Fe, S, and C have also been used (Dean and Arthur, 1989).

However, over the years, I have found suites of samples that plot in a field of high S (generally $>1\%$) and low C (generally $<1\%$) that do not fit the "usual" explanations for C-S plots. (Williams, 1978, noted this for samples from an Australian Pb-Zn deposit.) I will show here that this is because these sediments have a late diagenetic sulfidation overprint due to changing environmental conditions *or* an epigenetic addition of sulfide that is related to ore mineralization. (Williams, 1978, also showed this high S/C ratio for an Australian ore deposit.) In this communication, several examples and explanations of these C-S data plots will be presented.

RECENT EXAMPLE

Black Sea Unit 3

Figure 2 shows a plot of organic C and S data from Hirst (1974) for samples from unit 3 (Ross and Degens, 1974; layer c, Neoeuxinian, in the terminology of Hirst, 1974) of the Black Sea. This layer generally occurs at a sediment depth greater than 100 cm, below Recent unit 1 (representing the last few thousand years) and unit 2 (representing several thousand to approx. 7000 y BP (Emery and Hunt, 1974; Hay et al., 1991). Unit 3 (D of Calvert et al., 1987) represents the time before 7000 or 10,000 years ago (depending on whether you adopt the varve or C-14 chronology, Degens et al., 1980) when the Black Sea was isolated from the Mediterranean Sea because of lowered sea level and exposure of the Bosporous sill (strait) that prevented the flow of seawater into the basin. (Raiswell and Berner, 1985, have noted that the S data of Hirst, 1974, are high relative to those of Rozanov et al., 1974, and Berner, 1974. However, examination of the plots of the Rozanov et al., 1974, data by Raiswell and Al-Biatty, 1993,

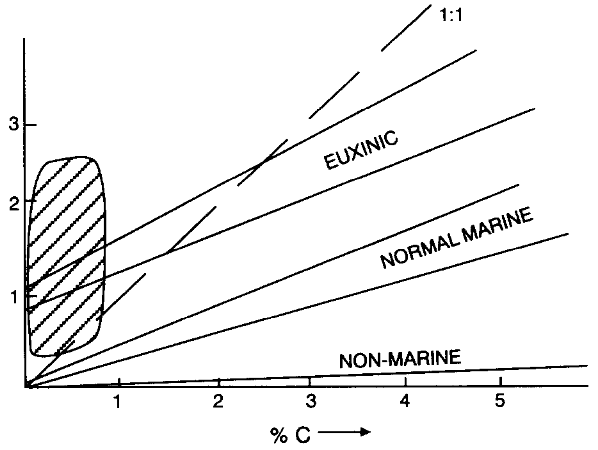

FIG. 1. Carbon-sulfur plot showing fields for syngenetic and diagenetic sulfide formed by bacterial sulfate reduction and reaction of sulfide with reactive Fe. Commonly recognized fields for normal oxic (modern and ancient) marine depositional setting, euxinic water column and freshwater are indicated. Euxinic but Fe-limited sediments would plot in a horizontal trend from the S-axis to high C values and would in-part fall in the region of interest, however the flat trend of these should make them recognizable as a special case (Raiswell and Berner, 1985). Dashed line is the 1:1 relationship; pre-Devonian sediments often plot between the normal marine field and this line. The S-rich, organic-C-poor (enclosed-hatched region) is the subject of this report.

and new data by Calvert et al., 1987, Calvert and Karlin, 1991, Lyons and Berner, 1992, and J. S. Leventhal, unpubl. data, also shows the high S/C ratios and S intercepts for much of the data. Thus, the S/C plots still give the same interpretations.)

During unit 3 deposition, the Black Sea was a large inland freshwater lake (Ross et al., 1970). The lake was not salinity stratified but had a strong thermal stratification, probably mixed to some degree, and may have had some oxygen mixed to its bottomwater at some times of the year (Emery and Hunt, 1974). As a result of this mixed lacustrine setting, the amounts of organic matter preserved were not much above 1%, either due to lower productivity or lower preservation or both. In addition, because of a lack of sulfate in this freshwater lake, little iron sulfide was formed in the bottom sediments. With Holocene sea level rise and incursion of marine waters (containing sulfate) and subsequent stratification, the Black Sea depositional environment changed drastically (Degens and Ross, 1972; Emery and Hunt, 1974; Middelburg et al., 1991).

The observed C and S data in unit 3 can be explained as follows: In the time just after unit 3 deposition, the enhanced production of sulfide in the bottom sediments and water column promoted sulfidation of the underlying reactive Fe species (in unit 3) by downward diffusion of sulfide and sulfate. At this time, unit 3 sediments would have been largely unconsolidated, uncompacted and still contained >80% water. This sulfidation ultimately resulted in high S (as FeS or FeS_2) with only low amounts of indigenous organic C. A similar interpretation of depositional history, using organic C, S, ^{34}S, and metal content, has been given by Middelburg et al. (1991).

A geologically younger example of this postdepositional (diagenetic) sulfidation using DOP data is presented by Lyons et al. (1993) for the movement of the H_2S-O_2 interface at the basin margin of the Black Sea about 250–300 years ago. Another example, the postdepositional sulfidation of freshwater sediments of Kau Bay, Indonesia, is reported by Middelburg (1991). However, these sediments have higher amounts of organic C (2 to 6%) and would not have appeared as anomalous on a C-S plot but Middelburg (1991) has pointed out that "before applying the C/S method to alternating marine and freshwater sediments, one should be certain that diffusion of H_2S has not resulted in sulfur enrichment." The details of postdepositional sulfidation in response to changing environmental conditions have been explained by Middleburg et al. (1991).

ANCIENT EXAMPLES

Creede

The first ancient example is a suite of samples from sediments from the Miocene Creede (Colorado, USA) caldera moat that consist of altered volcanic materials including silica, clays, and carbonates. These samples are from two cores recovered as part of the US Continental Scientific Drilling Program (Bethke, 1988; Campbell et al., 1993). The lake in the Creede caldera probably fluctuated from fresh to brackish (by addition of sulfur species after volcanic eruptions) and was probably 15 to 70 m deep (Crossey and Larsen, 1994). This 13 km diameter caldera was also part of the hydrologic system responsible for the Creede epithermal Ag-Au mineralization located 5 km to the north (Bethke and Rye, 1979). The relatively high-S contents measured in these sediments (Fig. 3) cannot be explained by the small quantities of indigenous organic C. Thus, most of the sulfide is a result of the later passage of ore-related sulfide-bearing solutions associated with the hydrothermal/epigenetic mineralization. DOP values vary from 0.23 to 0.75; however, this is only indirectly related to mineralization (J. S. Leventhal, unpubl. data). It is not clear if the sulfide minerals result from local or regional thermochemical (abiological) sulfate reduction or bacterial sulfate

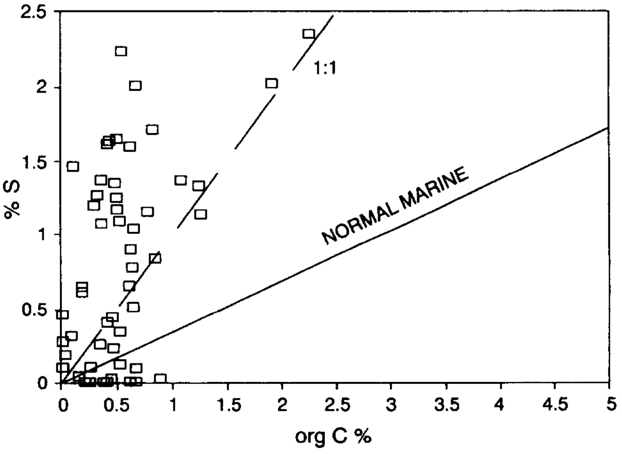

FIG. 2. Plot of data from Black Sea unit 3 (layer c data from Hirst, 1974). Lines are normal marine and 1:1 C-S ratio.

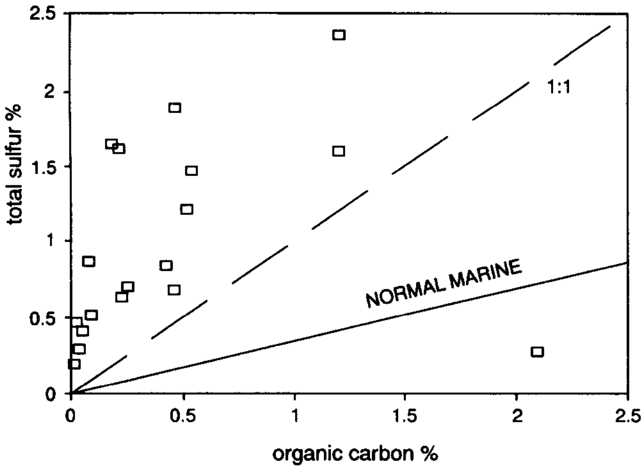

FIG. 3. Plot of data from Creede caldera moat sediments (J. S. Leventhal, unpubl. data). Lines are normal marine and 1:1 C-S ratio. Representative samples from drill cores were analyzed for organic C and total S by methods outlined in Stanton et al. (1983) and Leventhal et al. (1986).

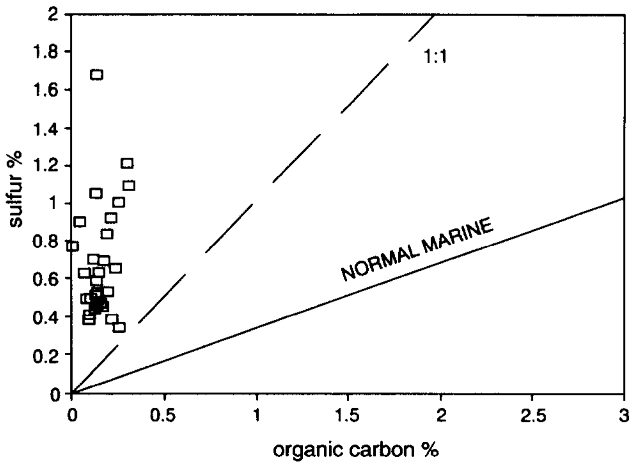

FIG. 4. Plot of data from Davis shale samples in vicinity of Buick Pb-Zn mine (J. S. Leventhal and S. V. Panno, unpubl. data). Samples from ore deposits analyzed by usual methods (Stanton et al., 1983; Leventhal et al., 1986). Lines are normal marine and 1:1 C-S ratio.

reduction (McKibben et al., 1994) or igneous sulfide (Ilchik and Rumble, 1994), however, indigenous microbiological sulfate reduction appears unlikely to be able to account for all the sulfide because the organic carbon content is so low.

MVT Deposits

Williams (1978) showed a number of C-S plots for shales and compared these to plots for two Australian "concordant" ore deposits (H.Y.C. and Concordant Ridge II). He pointed out that these deposits show large excesses of sulfide relative to organic C (S/C ratios of 25, wt%/wt%) that he explains as due to epigenetic sulfate reduction. The next suite of samples is from the Cambrian Davis shale and associated carbonate sediments in the vicinity of the Viburnum trend Mississippi-Valley type (MVT) Pb-Zn mineralization in Missouri (Anderson and Macqueen, 1982). Here, fluids with sulfide may have been generated by thermochemical sulfate reduction (Barton, 1967; Leventhal, 1990) either locally or regionally (Goldhaber, 1993). However, this sulfide generation and ore deposition took place nearly 150 my after sedimentation of the Late Cambrian ore host rocks, probably during Pennsylvanian time (Leach and Rowan, 1986, and references therein). Fluid inclusion temperatures (80–120°C; Rowan, 1987) and Rock-Eval T_{max} (420–440°C; J. S. Leventhal and S. V. Panno, unpubl. data) values are only moderate and no large loss of organic C should have occurred (as is of concern to Raiswell and Berner, 1986). Samples of Davis shale collected within several kilometers of the Buick Mine (Panno et al., 1988; Panno and Moore, 1994) have been analyzed for C and S (J. S. Leventhal and S. V. Panno, unpubl. data) and show S-C ratios (Fig. 4) that are far above those expected for normal marine sediments (compare Fig. 1).

Several authors have reported atypically high S-C ratios (relative to modern and ancient marine sediments) of more than 0.4 up to 1 for pre-Silurian (pre-land plant) sediments (Raiswell and Berner, 1986; Murty et al., 1962; Leventhal, 1979a,b; Berner, 1984; Donnelly et al., 1988; Strauss et al., 1993), perhaps due to a less well-oxygenated ocean or lack of (less metabolizable) lignin. However, the results presented on Fig. 4 are well above the previously reported S-C ratio of 1. Thus, the epigenetic effects of hydrothermal fluids that are related to the formation of MVT Pb-Zn deposits are responsible for a sulfide enrichment (sulfidation path or halo?) in the adjacent sediments.

Jerritt Canyon

The final sample suite characterized by anomalously high S and low C values (Fig. 5) derives from the Jerritt Canyon sediment-hosted-disseminated ("Carlin-type") gold deposit located northwest of Elko, Nevada, USA. This deposit formed when ore bearing solutions containing $Au(HS)_2^{-1}$ encountered reactive Fe, sulfidized the Fe to form pyrite and precipitated the Au (Hofstra et al., 1991). These rocks have been heated extensively and there is evidence of migration (but not necessarily loss) of organic matter. However, the S-C ratios

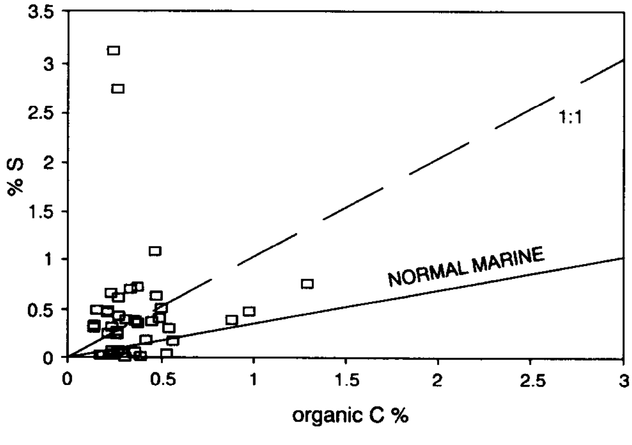

FIG. 5. Plot of data from Jerritt Canyon district (J. S. Leventhal and A. H. Hofstra, unpubl. data). Lines are normal marine and 1:1 C-S ratio.

are still anomalous, even if half of the organic matter has been lost from the system. The marine deposited Ordovician and Devonian carbonate/shale host rocks locally have high DOP values associated with ore mineralization (Leventhal et al., 1990). The ore deposition took place during the Miocene (A. H. Hofstra, unpubl. data) several hundred million years after the sediments were deposited. This is another example of epigenetic sulfidation, but in this case, it is directly related to the gold deposition/mineralization process.

Other Examples—A Caution

Diverse depositional environmental conditions sometimes result in problems in interpretation of C-S relationships and plots, for example:

1) The high C-S data reported by Pandali et al. (1991) for pre-Cambrian shales of India appear to be due to a special case of very low sedimentation rate and massive pyrite (15–30%) and are probably synsedimentary-syngenetic.
2) Roll-type uranium deposits in sandstone host rocks (often a problem in C-S plots due to low Fe and low C contents) in Texas and Wyoming, USA, give mixed results for C-S plots with some showing very high amounts of epigenetic sulfide relative to only small amounts of organic carbon (Goldhaber et al., 1979; Harshman, 1974), a situation similar to the epigenetic sulfidation reported here. But other roll-type uranium deposits (at least in Wyoming) associated with coal beds do not consistently show greatly enhanced levels of S (Leventhal and Santos, 1981), although some of the S is certainly epigenetic.
3) Caution is urged when interpreting data sets involving carbonate or sandstone units because they generally contain only small amounts of Fe (iron limited) and can be completely sulfidized.
4) As mentioned earlier, also beware of losses of organic C due to thermal effects (Raiswell and Berner, 1986) and unusual water chemistry (Tuttle and Goldhaber, 1993).

CONCLUSIONS

The results from these sample suites show that sediments containing high sulfide sulfur (greater than 1%) in association with low contents of organic C (generally less than 1%) that are not sufficient to account for this quantity of sulfide can now be explained. These data are interpreted to result from later diagenetic or epigenetic addition of HS^{-1} that combines with available reactive iron to form pyrite. This postdepositional sulfidation is a process that is relatively common in the natural environment and is sometimes related to the evolution of euxinic or silled basins and/or migration of epithermal or hydrothermal fluids associated with ore deposits. It is also possible that anomalously high S/C ratios in sedimentary rocks with low organic C (<1%) can, in certain situations, be used as a prospecting method or assessment tool for nearby mineralization, when evaluated in conjunction with sulfur isotope and textural/paragenetic trends.

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