≡USGS
science for a changing world

PRELIMINARY SCIENTIFIC RESULTS OF THE CREEDE CALDERA CONTINENTAL SCIENTIFIC DRILLING PROGRAM

P.M. Bethke, Editor

Open-File Report 94-260-K

2001

CARBON-SULFUR PLOTS AND DEGREE OF PYRITIZATION DETERMINATIONS TO SHOW DIAGENETIC AND EPIGENETIC SULFIDATION IN CREEDE CALDERA CORES

By

Joel Leventhal
U.S. Geological Survey, Denver, CO

INTRODUCTION

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

Since then, many workers have used the carbon-sulfur plots to help characterize ancient depositional environments (for example: Leventhal, 1987; Aplin and Macquacker, 1993; Suits and others, 1993; Pratt and Davis, 1993; see Lyons and Berner, 1992 for references). Some problems were noted in using carbon vs. Sulfur plots when iron was limiting (Calvert and Karlin, 1991; Lyons and Berner, 1992); in iron-poor rocks, such as some carbonates, the complete sulfidation of iron may limit the total solid-phase sulfide content of the rock.

To augment the interpretation of carbon vs. sulfur plots in defining the environment of deposition, iron-sulfur relationships have been studied. These studies have reported iron vs. sulfur plots (Leventhal, 1979b) and degree of pyritization (DOP) (Raiswell and Berner, 1986; Raiswell and others, 1988) as determined by a variety of methods (Berner, 1970; Canfield, 1988; Huerta-Diaz and Morse, 1990; Leventhal and Taylor 1990; Raiswell and others, 1994). Ternary plots of iron, sulfur and carbon have also been used (Dean and Arthur, 1989).

In lacustrine systems that are saline (sulfate containing) or are affected by episodic inputs of sulfate or reactive iron, the carbon vs. sulfur plots can be quite irregular and will reflect these episodic events (Tuttle and others, 1990; Tuttle and Goldhaber, 1993). The abundant ashfall beds in the Creede caldera sediments (Finkelstein et al., 1994; Heiken, et al., 1994) may reflect this type of setting with episodic addition of sulfate and reactive iron that might tend to give higher carbon/sulfur ratios and higher DOP and pyrite values (Rye, et al, 1994; M. Tuttle, written commun.) if sufficient organic carbon reductant is present in the sediment. For non-lacustrine settings, I have found suites of samples that plot in a field of high sulfur (generally >1 percent) and low carbon (generally <1 percent) that do not fit the "usual" explanations for carbon/sulfur plots. The possible explanations for these sediments have a late diagenetic sulfidation overprint due to changing environment *or* an epigenetic addition of sulfide that is related to ore mineralization. In this report, an example and explanation of this carbon-sulfur data plot will be presented.

leachable iron (that could be sulfidized to pyrite) plus pyrite iron. Originally, this measurement was applied to recent sediments (Berner, 1970, 1984) but it has also been applied to ancient sediments (Raiswell and others, 1988) and to sediments related to sulfide ore mineralization (Leventhal and Hofstra, 1990; Hofstra and others, 1992). Sediments from normal fresh water (very low in dissolved sulfate) environments show DOP values of >0.2. Sediments from normal oxic water marine (containing abundant sulfate) environments show DOP values of around 0.4 (figure 3). Samples with DOP values of >0.6 are usually considered to be deposited in an anoxic ocean bottom, and those with DOP >0.8 are interpreted to have been deposited below sulfidic bottom waters (Raiswell and others, 1988). In a suite of samples from the same lake of ocean depositional environment, anomalously high DOP values can represent individual sulfidic micro-environments that could be diagenetic or epigenetic. From a changing lacustrine environment, however, this could be due to changing input of sulfate and reactive iron (Tuttle and others, 1990; Tuttle and Goldhaber, 1993; Rye, et al, 1994; M. Tuttle, written communication).

SAMPLES AND METHODS

Representative samples from the Creede caldera cores were analyzed for organic carbon and total sulfur by methods outlined in Stanton and others (1983) and Leventhal and others (1986). DOP methods are reviewed by Leventhal and Taylor (1991).

CREEDE ORGANIC CARBON AND SULFUR PLOTS

The suite of samples from sediments from the Miocene Creede (Colorado) caldera moat consist of altered volcanic materials including silica, clays and carbonates. These samples were analyzed as part of the U.S. Continental Scientific Drilling Program that recovered 2 cores (Bethke, 1988; Campbell and others, 1993). The lake in the Creede caldera probably fluctuated from fresh to brackish after volcanic eruption and was probably 15 to 70 m deep (Larsen and Crossey, 1994). This 13 km diameter caldera was also part of the hydrologic system responsible for the Creede epithermal silver-gold mineralization that is 5 km to the north (Bethke and Rye, 1979). The relatively high sulfur contents (figure 3) measured in these sediments cannot be explained by the small quantities of indigenous organic carbon. Thus, most of the sulfide is a result of the later passage of ore-related sulfide (HS^{-1}) bearing solutions associated with the hydrothermal/ epigenetic mineralization. It is not clear if the hydrothermal sulfur is due to local or regional thermochemical (abiological) sulfate reduction or igneous sulfide (Rye, et al., 1994; Lillis, 1994; Leventhal et al., 1994).

Figure 3 shows a histogram of the DOP values from the Creede core samples (table 1). There is a wide range of values from less than 0.2 to 0.8. The results from both cores CCM-1 and CCM-2 do not appear to be different from each other. The values above 0.3 are not expected for a freshwater lake, and values above 0.5 are unexpected for an oxic, but saline, lake (Raiswell and others, 1988). However, the DOP may be higher in this lacustrine setting because of volcanic sulfate input and because the iron derived from recent volcanism may be more reactive than the iron supplied to many marine settings (M. Tuttle, written communication). The DOP results indicate that a number of the samples show evidence of post depositional (diagenetic or epigenetic) sulfidization. To test the possible influence of DOP and episodic volcanic input of sulfate and/or reactive iron, the depths of the samples and their DOP (table 1) was examined to see which samples are near the volcanic ash and tuff units (Finkelstein and others, 1994). Sample 2R203 is within a meter of an ash layer and its DOP is 0.23; samples 1R56 is within 2 meters of an ash unit and its DOP is 0.15; and sample 1R69 is about 3 meters from an ash unit and its DOP is 0.36. Thus, the samples with close proximity to ash layers do *not* show anomalous high DOP values [I thank Michele Tuttle for suggesting this test]. This may be because of the lack of organic matter reductant for the sulfate. Figure 4 shows that no clear relationship of DOP to (corrected) depth because sulfidation is dependent on the interaction of fluids containing sulfides with the host rock, and this would be controlled by porosity and permeability rather than mainly burial depth. A plot of DOP vs. percent sulfur (not shown) shows some correlation, but it is not a valid plot of independent variables because the sulfur content is used in calculating the DOP value. It would be interesting to determine if the samples with high DOP values have a sulfur isotope value and a distinct sulfide mineral morphology (or reactive iron minerals) relative to the low DOP samples.

CONCLUSIONS

The results from these sample suites show that sediments containing high sulfide sulfur (greater than 1 percent) and low contents (generally less than 1 percent) of organic carbon, that under normal conditions 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 post-depositional sulfidation is a process that is relatively common in the natural environment, frequently related to the evolution of euxinic basins and migration of hydrothermal fluids associated with ore deposits. It is also possible that anomalously high carbon/sulfur ratios in sedimentary rocks with low organic carbon (<1 percent) can, in certain situations, be used as a prospecting method or assessment tool for nearby mineralization where other indicators such as anomalous gold, silver, or arsenic are present.

The results of DOP determination show variable degrees of sulfidation, some that suggest sulfidic events. These results are not related to a particular burial depth

(stratigraphic zone/ depositional event) or only one core. It is likely that the results represent sulfide-rich localized or micro-environments
that can be explained by selective epigenetic fluid pathways controlled by fractures, porosity and permeability.

ACKNOWLEDGMENTS

REFERENCES CITED

Aplin, A.C., and Macquacker, J.H., 1993, Carbon-Sulfur-Iron geochemistry of some modern and ancient marine muds and mudstones. Phil. Trans. Roy. Soc. London, v. 344A, p. 89-100.

Barton, P.B. Jr, 1967, Possible role of organic matter in the precipitation of the Mississippi Valley ores, Economic Geology, Mon 3, p. 371-78.

Berner, R. A., (1970) Sedimentary pyrite formation. American Jour. Sci., v. 268 p. 1-23

Berner, R.A., (1984) Sedimentary pyrite formation: an update. Geochimica et Cosmochimica Acta, v. 48, 605-615.

Berner, R. and Raiswell, R., 1984, Carbon/Sulfur method for distinguishing freshwater from marine sedimentary rocks: Geology. v. 12, p. 365-68.

Berner, R.A., 1984, Sedimentary pyrite formation: an update. Geochimica et. Cosmochimica Acta, v. 48, p. 605-15.

Bethke, P.M., 1988, The Creede Colorado ore forming system, U.S. Geological Survey Open-File Report 88-403, 29 p.

Bethke, P. and Rye, R., 1979, Environment of ore deposition in the Creede mining district, Colo., Economic Geology, v. 74, p. 1832-51.

Calvert, S.E., and Karlin, R.E., 1991, Relationships between sulfur, organic carbon, and iron in the modern sediments of the Black Sea, Geochimica et Cosmochimica Acta, v. 55, p. 2483-2490.

Campbell, W.R. and others, 1993, Research drilling into the "fluid reservoir" of the Creede epithermal vein system: SEG Newsletter no. 13, April, p. 1. and 12-16.

Canfield, D. E., 1988, Sulfate reduction and the diagenesis of iron in anoxic marine sediments. Unpublished Ph.D. thesis, Yale University 248 p.

Canfield, D. E., 1989, Reactive iron in marine sediments, Geochimica et Cosmochimica Acta, v. 53 p. 619-632.

Canfield, D. E., and Berner, R. A., 1987, Dissolution and pyritization of magnetite in anoxic marine sediments. Geochimica et Cosmochimica Acta, v. 51 p. 645-659.

Dean, W. and Arthur, M.A., 1989, Iron-sulfur-carbon relationships in organic carbon-rich sequences. Amer J. Sci., v. 289, p. 708-43.

Donnelly, T., Shergold, J., and Southgate, P., 1988, Pyrite and organic matter in Middle Cambrian age Australia, Geochimica et Cosmochimica Acta, v. 52 p. 259-264.

Finkelstein, D.B., Altaner, S.P., Hay, R.L., and Greenberg, S., 1994, Silicate diagenesis of tuffs in the Creede Formation, U.S. Geological Survey Open-File Report 94-260F, 23p.

Goldhaber, M., and Kaplan, I.R., 1974, The sulfur cycle, in The Sea, v. 5, Marine Chemistry. Goldberg, E.D., ed., John Wiley and Sons, Inc. p. 569-655.

Huerta-Diaz, M. and Morse, J.W., 1990, Quantitative method for determination of trace metal concentration in sedimentary pyrite, Mar. Chem., v. 29, p. 119-144.

Larsen, Daniel, and Crossey, Laura, 1994, Depositional environments and authigenic mineral distributions in the Oligocene Creede Formation, Colorado, USA, , U.S. Geological Survey Open-File Report 94-260E, 77p.

Leventhal, J.S., 1979a, The relationship between organic carbon and sulfide sulfur in recent and ancient marine and euxinic sediments, EOS Trans Amer. Geophys. Union, v. 60, p. 286.

Leventhal 1979b, Chemical analysis and geochemical association in Devonian black shales from Martin Co., KY and Overton Co, TN., U.S. Geological Survey Open File Report 79-1503, 51 p.

Leventhal, J. S., 1983, An interpretation of carbon and sulfur relationships in Black Sea sediments as indicators of environments of deposition, Geochimica et Cosmochimica Acta, v 47 p. 133-137.

Leventhal, J. S., 1987, Carbon and sulfur relationships in Devonian shales from the Appalachian Basin as an indicator of environment of deposition, Am. Jour. Sci., v. 287, p. 33-49.

Leventhal, J.S., Carbon-sulfur plots to show diagenetic and epigenetic sulfidation in sediments, 15 p., 5 figs., submitted to Geochimica et Cosmochimica Acta, June 1994.

Leventhal, J., Daws, T. and Frye, J., 1986, Organic geochemical analysis of sedimentary organic matter associated with uranium, Applied Geochem., v. 1, p. 241-247.

Leventhal, J. and Taylor, C., 1990, Comparison of methods to determine degree of pyritization, Geochimica et Cosmochimica Acta, v. 54 p. 2621-25.

Lin, S., and Morse, J.W., 1991, Sulfate reduction and iron sulfide mineral formation in Gulf of Mexico anoxic sediments, Am. J. Sci., v. 291, p. 55-89.

Lyons T., and Berner, R.A., 1992, Carbon-sulfur-iron systematics of the uppermost deep-water sediments of the Black Sea, Chem. Geol., v. 99, p. 1-27.

Lyons, T.W., Berner, R.A., and Anderson, R.F., 1993, Evidence for large scale pre-industrial perturbations of the Black Sea chemocline, Nature, v. 365, p. 538-40.

Lyons, T. and Raiswell, R., 1993, Carbon-sulfur-iron geochemistry of modern Black Sea sediments: a summary, Geol. Soc. Amer. 1993 Abstracts, v. 25, p. A239.

Pratt, L. and Davis, C., 1993, Implications of Sulfur incorporation and diagenesis in organic rich marine sediments, Geol. Soc. Amer., 1993 Abstracts, v. 25, p. A20.

Raiswell, R., and Berner, R. A., 1985, Pyrite formation in euxinic and semi-euxinic sediments, Am. Jour. Sci., v. 285 p. 710-724.

Raiswell, R., and Berner, R., 1986, Pyrite and organic matter in Phanerozoic normal marine shales, Geochimica et Cosmochimica Acta, v. 50 p. 1967-1976.

Raiswell, R., Buckley, F., Berner, R. A., and Anderson, T.F., 1988, Degree of pyritization of iron as a paleoenvironmental indicator of bottom-water oxygenation. Jour. Sed. Pet., v. 58, no. 5, p. 812-819.

Raiswell, R., Canfield, D.E., and Berner, R.A., 1994, A comparison of iron extraction methods for DOP, Chem. Geol., v. 111, p. 101-110.

Suits, N., Arthur, M., and Dean, W., 1993, Carbon-sulfur-iron systematics in Peru margin muds, Geol. Soc. Amer. 1993 Abstracts, v. 25, p. A199.

Stanton, M., Leventhal, J., and Hatch, J., 1983, Short-range vertical variation in organic carbon and sulfur in Upper Pennsylvanian Stark shale, Kansas, U.S. Geological Survey Open-File Report 83-315, 8 p.

Sweeney, R. E., 1972, Pyritization during diagenesis of marine sediments. Unpub. Ph.D. thesis, U.C.L.A. 184 p.

Tuttle, M.L., Rice, C.A., and Goldhaber, M.B., 1990, Geochemistry of organic and inorganic sulfur in ancient and modern lacustrine environments, in Geochemistry of sulfur in fossil fuels, ed. W.L. Orr and C.M. White, Amer. Chem. Soc., Symposium series 429, p. 114-48.

Tuttle, M.L., and Goldhaber, M.B., 1993, Sedimentary sulfur geochemistry of the Green River Formation and depositional and diagenetic processes: Geochimica et Cosmochimica Acta, v. 57, p. 3023-3039.

FIGURE CAPTIONS

Figure 1. Carbon-sulfur plot showing fields for syngenetic and diagenetic sulfide formed by bacterial sulfate reduction and reaction of that sulfide with reactive iron. Commonly recognized fields for normal (modern and ancient) marine, euxinic water column and fresh water are indicated (Sweeney, 1973; Leventhal, 1983; Berner and Raiswell, 1984). Dashed line is the 1:1 relationship for reference; pre Devonian sediments often plot between the normal marine field and this line. The sulfur-rich, organic-poor (circled-lined region) is the subject of this report.

Figure 2. Plot of data from Creede caldera moat sediments (Leventhal, unpub data). Lines are normal marine and 1:1 reference carbon/sulfur ratio.

Figure 3. Range in degree of pyritization (DOP) values for Creede caldera moat core samples. Figure includes 12 samples from R. Reynolds that are low in organic carbon.

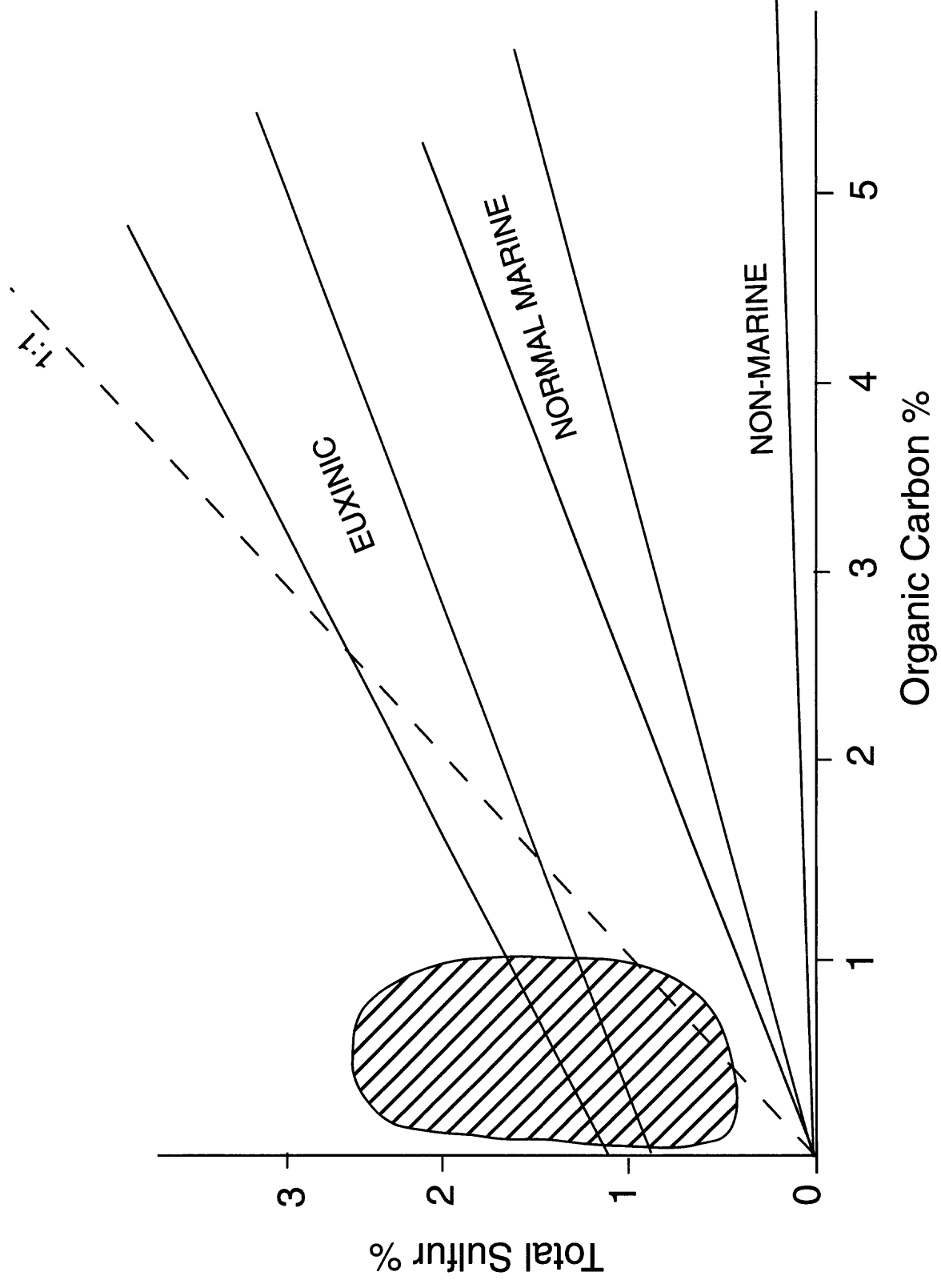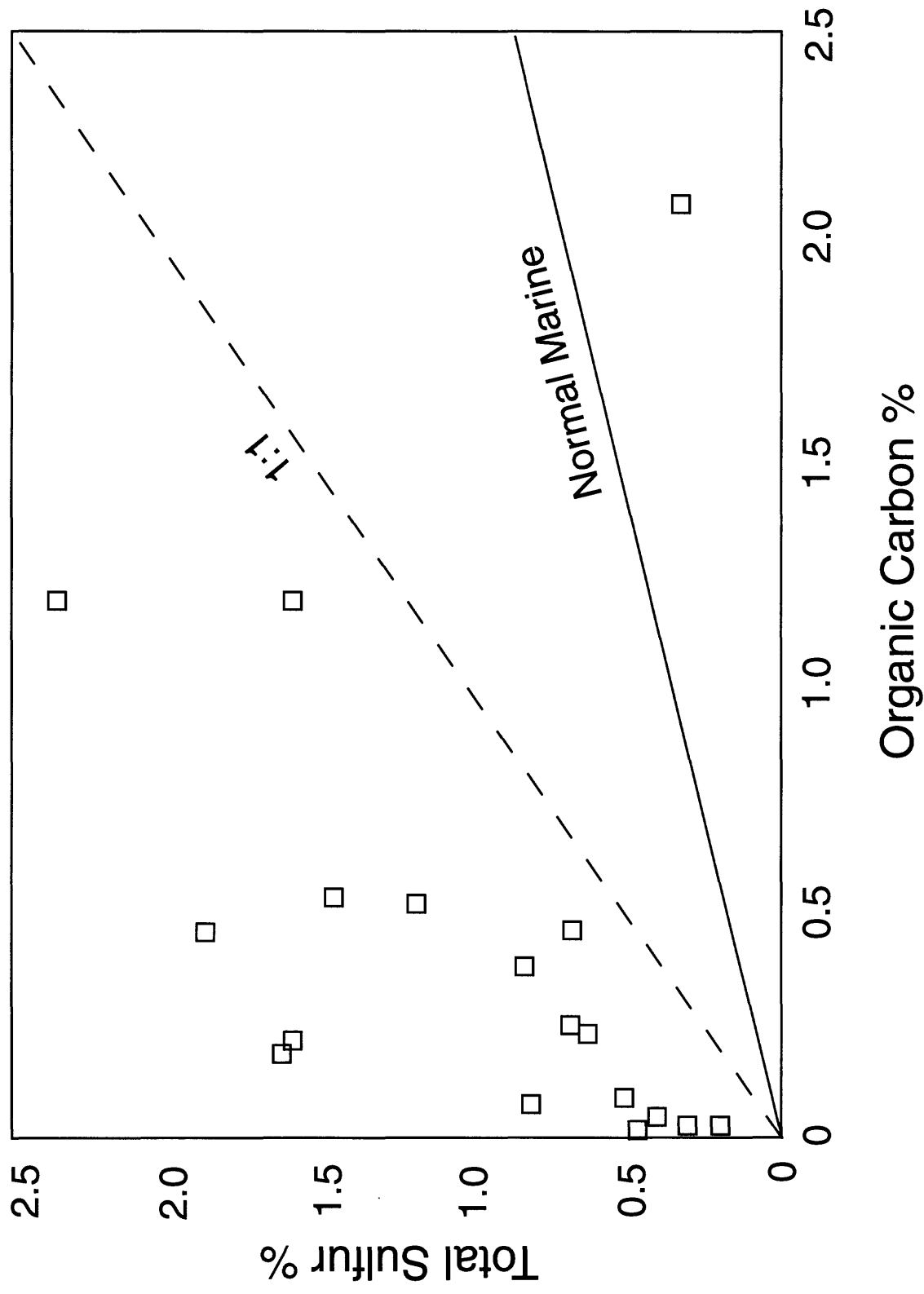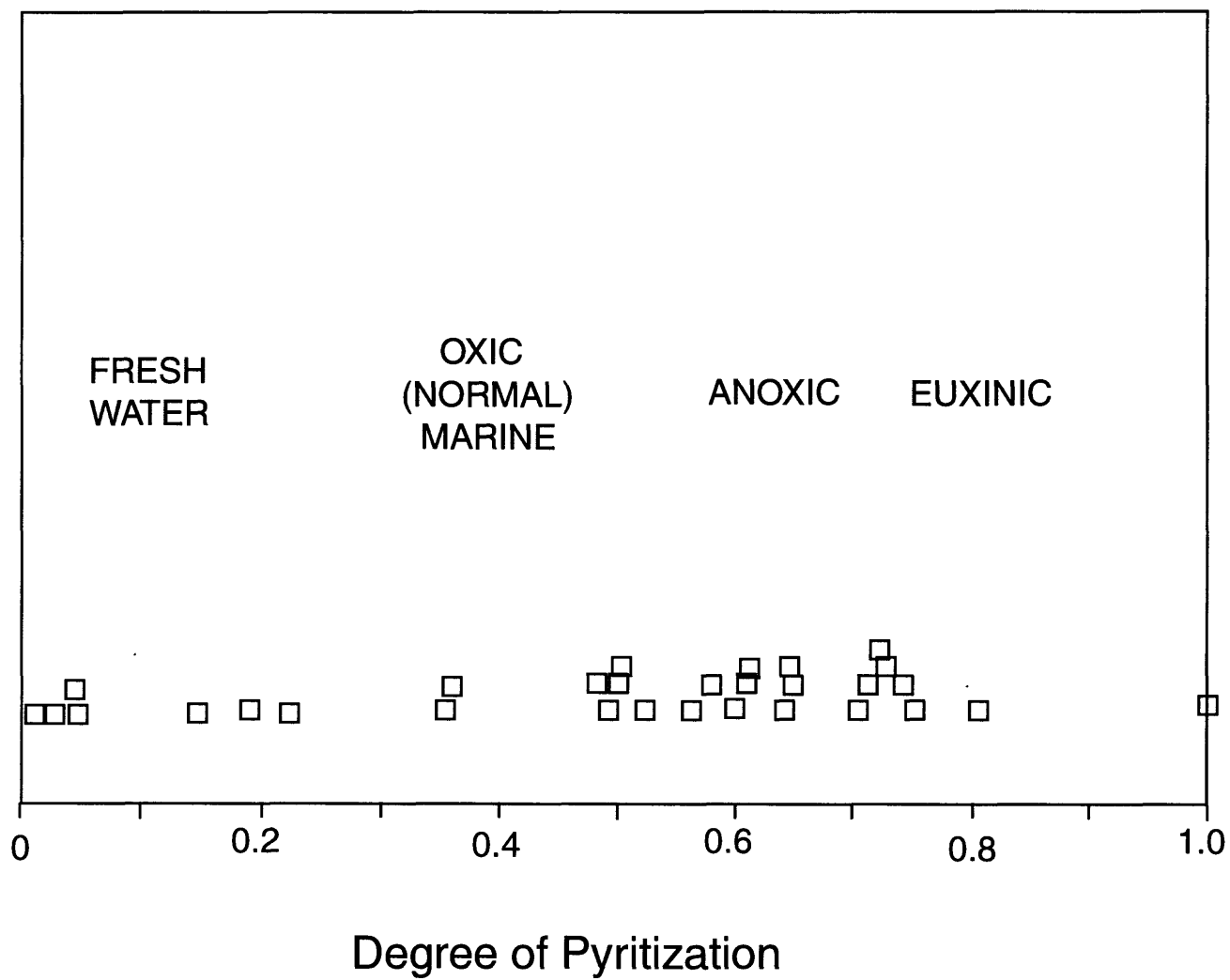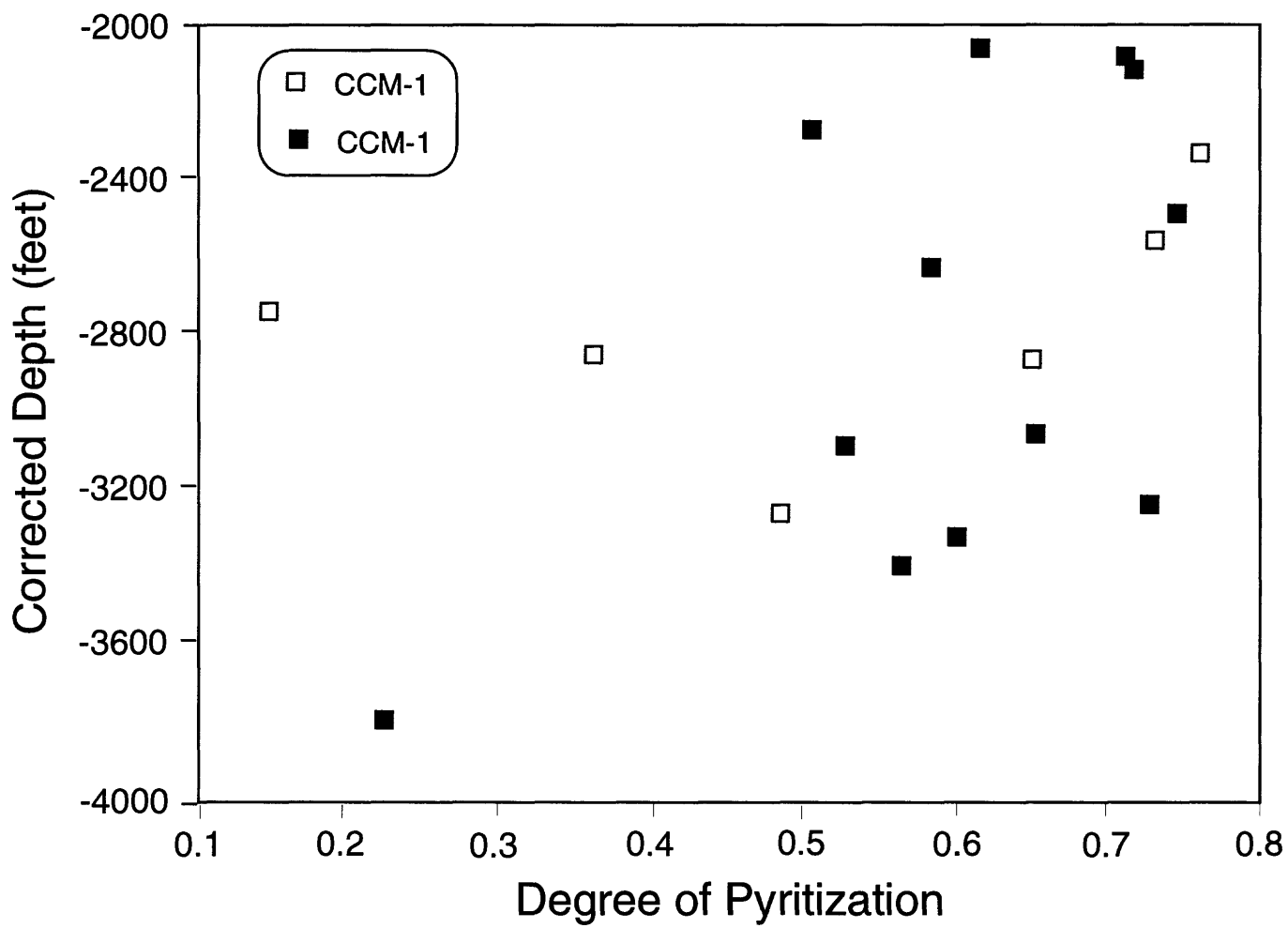Figure 4. DOP vs. corrected depth for Creede core samples.

Figure 1

Figure 2

FRESH
WATER

OXIC
(NORMAL)
MARINE

ANOXIC   EUXINIC

Degree of Pyritization

Figure 3

Figure 4