Geochemistry of Metasedimentary Rocks in the Hanging Wall of the Greens Creek Massive Sulfide Deposit and of Shales Elsewhere on Admiralty Island

By Craig A. Johnson, Cliff D. Taylor, Joel S. Leventhal, and Katja Freitag

Chapter 8 of

Geology, Geochemistry, and Genesis of the Greens Creek Massive Sulfide Deposit, Admiralty Island, Southeastern Alaska

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Abstract

Metasedimentary rocks in the hanging wall of the Greens Creek massive sulfide deposit span a lithologic range from carbonate-poor shale to nearly pure dolomite, and have organic carbon contents higher than average shale, but lower than average black shale. Rock-Eval analyses of the organic matter reveal that the rocks have undergone heating beyond the oil and gas generation stages, and that carbon-oxygen-hydrogen volatiles have been released. Some hanging-wall samples have sulfur-to-organic carbon ratios and degree-of-pyritization values similar to normal marine shales. These same samples also have base- and precious-metal contents like normal shales but are somewhat enriched in barium. The data are evidence that the depositional history of the hanging-wall sediments included periods where the overlying water column was oxic, with only a slight barium enrichment as possible evidence for venting of hydrothermal fluids to the basin waters. More commonly, hanging-wall samples are high in sulfur, high in metals, and high in degree-of-pyritization, consistent either with (1) sediment accumulation beneath an anoxic water column strongly affected by hydrothermal venting, (2) epigenetic hydrothermal sulfur and metal emplacement, or (3) sulfur and metal release from the underlying massive sulfide body during the Cretaceous regional metamorphism.

The carbon and oxygen isotopic compositions of hanging-wall carbonates appear to have been unaffected by the Cretaceous regional metamorphism, and they are indistinguishable from the isotopic compositions of dolomite in the underlying massive sulfide ores. This observation provides strong evidence that the Greens Creek hydrothermal system continued operating until after the hanging-wall sequence was laid down. The isotopic variations in both the hanging-wall rocks and the ores are consistent with dolomite precipitation from a single carbonate-bearing fluid over the temperature range 200–350°C, or dolomite precipitation from mixed marine and hydrothermal fluids. Carbonate $\delta^{13}C$ correlates positively with organic matter $\delta^{13}C$, which suggests that carbonate precipitation was accompanied by oxidation of the ambient organic matter or organic-matter-derived methane. Carbonate $\delta^{13}C$ correlates negatively with the sulfur content of the rocks, which suggests that organic-matter or methane oxidation was accompanied by reduction of dissolved sulfate to produce hydrogen sulfide. Some sulfate reduction, but not necessarily all, was microbially mediated and took place during early diagenesis beneath the sediment/seawater interface. Limited isotopic data from Hyd Group shales elsewhere on Admiralty Island, which are thought to be distal equivalents of the hanging-wall section, suggest that the same hydrothermal fluid that formed the Greens Creek massive sulfide may also have interacted with basin-floor sediments at distances of several kilometers from the Greens Creek deposit.

Introduction

The metasedimentary rocks in the hanging wall of the Greens Creek massive sulfide deposit have been variously referred to as argillites, calc-argillites, metasiltstones, metashales, and argillaceous limestones (for example, Newberry and others, 1997; Taylor and others, 1999, 2000; Freitag, 2000). Common to all descriptions of these rocks has been the observation that they contain abundant reduced carbon, presumably sedimentary organic matter that has been depleted in hydrogen and oxygen by postdepositional heating. Carbonaceous sediments can be critical to the development of sulfide ores because they can supply metals to ore-forming fluids, or they can supply the reduced sulfur necessary to form sulfide minerals (Tourtelot, 1979; Leventhal, 1993). Simple mass-balance calculations demonstrate that it is not unreasonable to hypothesize that these shales and their distal equivalents were the primary metal source for the Greens Creek hydrothermal system. For example, the zinc content of the presently defined Greens Creek reserve could have been obtained by hydrothermal scavenging from a geologically reasonable volume of shale measuring 5 km^3 if the metal concentration was the same as in average black shale. Carbonaceous sediments can also act to preserve sulfide ores because the anoxic conditions that led to their formation can protect underlying sulfide minerals from destruction by seawater oxidation (Goodfellow and others, 1993; Eastoe and Gustin, 1996).

The purpose of this paper is to report on the organic geochemistry, major and trace-element geochemistry, and stable isotope geochemistry of the hanging-wall rocks at Greens Creek in order to examine their function in the genesis of the underlying ore deposit. Also reported are data from Hyd Group shales collected elsewhere on Admiralty Island, which are presumed to be stratigraphic equivalents of the hanging-wall section (chap. 4), and data from shales that occur lower in the Admiralty Island section, in the Retreat Group (Devonian?), the Gambier Bay Formation (Devonian), and the Cannery Formation (Permian). For descriptions of the Admiralty Island stratigraphy, the reader is referred to chapters 4, 7, and 11. Chapter 7 also gives photographs and descriptions of typical exposures of the rocks.

Sampling and Analytical Methods

Samples

In the immediate mine area hanging-wall rocks were obtained from drill core and from underground workings. An effort was made to obtain a variety of samples from the two main lithologic groups that have been recognized in the mine area: massive argillite and slaty argillite (chap. 6). Petrographic observations have indicated that the massive argillites are characteristically richer in dolomite with abundant included organic matter (the field term that is used for this material is graphite), whereas the slaty argillites are richer in quartz and feldspar (up to 50 volume percent) commonly with rhombic dolomite overgrowths. Samples were taken from (1) core GC1136, which intersected a 275-foot section of wall rock overlying the Lower Southwest orebody; (2) core GC1530, which intersected a 675-foot section of wall rock overlying the Northwest orebody; (3) core GCPP173, which was collared on the 350 level and intersected a 150-foot section of wall rock above the Lower Southwest orebody; (4) core GCPP177, which was also collared on the 350 level and intersected a 280-foot section of wall rock above the Lower Southwest orebody; (5) cores PP–198 and PP–204, which were collared on the 170 level above the Lower Southwest orebody; and (6) core PS–50, which was collared at the surface due south of the South zone of the East orebody. Hand specimens were collected on the 350 level in the 2650 crosscut from rocks overlying the Lower Southwest orebody (96GC prefixes in table 1, on CD–ROM), and from the exposure at the 920 portal (GCPF–1).

The hanging-wall samples included specimens with varying degrees of veining, shearing, and fracturing and also specimens showing none of these features. In all cases, the entire sample was crushed and ground for geochemical analysis. The reasons for this are threefold. First, in most cases it is not clear from the textures whether chemical transport to or from veins occurred on length scales exceeding the size of a typical hand specimen (none of the analyzed samples approached 100 percent of what was clearly vein material). Thus, analysis of entire samples may be a more appropriate measure of original whole-rock compositions than analysis of material between veins. Second, any longer range remobilizations that did occur during either a protracted hydrothermal history or later metamorphism/deformation event were thought to be best characterized by comparing whole-rock analyses of veined or fractured samples with those of unveined samples. Third, analysis of entire samples has been the common practice in geochemical studies of sediment-hosted mineralization at other similar deposits (Williams, 1978, and references therein); thus, comparisons to other occurrences are best made using data that include samples with textural evidence of remobilization.

Shales and related sedimentary rocks also were sampled elsewhere on Admiralty Island from surface exposures of the Retreat Group (Devonian?), Gambier Bay Formation (Devonian), Cannery Formation (Permian), and Hyd Group (Triassic). Sample locations are given in table 1. In all cases efforts were made to obtain fresh rock minimally affected by weathering, but some samples probably experienced pyrite oxidation and sulfur loss, as noted below.

Chemical Analysis

For whole-rock chemical analysis, samples were analyzed either by a protocol referred to as U or by a protocol referred to as A, depending on the analytical services that were available at the time of sample collection. In the U protocol, 50–100 mg of rock was passed through a jaw crusher and then through a pulverizer equipped with ceramic plates. Splits of the resulting powders were decomposed in a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids, and the solutions were analyzed for Ag, Al, As, Au, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Eu, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Sc, Sn, Sr, Ta, Th, Ti, U, V, Y, Yb, and Zn by inductively coupled plasma atomic emission spectrometry using procedures described by Arbogast (1996). Some minerals are known to resist dissolution in the acid mixture, including barite and chromite. Because the shales studied here may contain these two minerals, the results reported for barium and chromium may be too low. Apart from this potential difficulty, the analytical results are considered on the basis of data reported in Arbogast (1996) to be accurate to within ±10 percent of the amount of the element present, except for beryllium, molybdenum, and phosphorus, which are considered to be accurate to within ±20 percent. As part of this same protocol, gold was analyzed by fire assay, mercury was analyzed by vapor extraction using a Leeman PS200 analyzer, carbonate carbon was analyzed by coulometric titration after digestion in perchloric acid, and total carbon and total sulfur were analyzed by high temperature (LECO) combustion. Analyses of standard materials indicate that these methods give results that are generally accurate to within ±10 percent (Arbogast, 1996).

In the A protocol, rock samples were crushed and passed through a pulverizer equipped with steel plates. Splits of the resulting powders were analyzed by instrumental neutron activation (INAA) for Au, As, Ba, Ce, Co, Cr, Eu, Fe, Hg, La, Na, Nd, Sc, Sn, Ta, Th, U, W, and Yb. Splits also

were dissolved in a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids, and the resulting solutions were analyzed by inductively coupled plasma mass spectrometry (ICP–MS) for Al, Ag, Be, Bi, Ca, Cd, Cu, K, Mg, Mn, Mo, Ni, Pb, Sr, Ti, V, Y, and Zn. Incomplete dissolution of the acid-resistant minerals barite and chromite would have no effect on the barium and chromium values reported for these samples because only the INAA results were used. However, the ICP–MS results for strontium might be low for samples containing barite. As part of this same protocol, carbonate carbon was analyzed by acid digestion, and total carbon and total sulfur were analyzed by high temperature (LECO) combustion. Analyses of standard materials indicated that these methods give results that are generally within ±10 percent of the accepted concentrations, except for silver, cadmium, nickel, and vanadium, which have greater uncertainties. Results for these latter elements are not tabulated in this paper, but correlations among them are noted assuming that the relative concentrations were determined more accurately than the absolute concentrations.

For some hanging-wall samples there is evidence that the carbonate carbon values were erroneously low, probably due to the presence of dolomite which is known to be more resistant to acid digestion than calcite. Thus, the carbonate carbon results given for hanging-wall rocks in table 1 should be considered minima. For the Hyd Group, Cannery Formation, and Gambier Bay Formation samples, carbonate is present at lower concentrations, and the carbonate mineral is probably calcite. The carbonate carbon results for these rocks are believed to be accurate due to the greater reliability of the coulometric titration method for calcite. For these samples, organic carbon was determined by taking the difference between total carbon and carbonate carbon (table 1).

Degree of Pyritization

Degree of pyritization (DOP), which is defined as

$$DOP = Fe_{pyrite} / (Fe_{pyrite} + Fe_{reactive}),$$

was determined using methods that have been described by Leventhal and Taylor (1990). The parameter Fe_{pyrite} was calculated from the measured sulfur contents of the samples after correcting for sulfur contained in sphalerite, galena, and chalcopyrite using the equations

$$S_{pyrite} = S_{total} - 0.490\ (Zn) - 0.155\ (Pb) - 1.009\ (Cu),$$

and

$$Fe_{pyrite} = 0.871\ (S_{pyrite}).$$

In some rocks, sulfur is also contained in barite. However, the barium contents of the samples analyzed in this study are low enough that the correction to S_{pyrite} for barite sulfur is insignificant (table 1). The parameter $Fe_{reactive}$ was determined by measuring the amount of iron leached from the samples by a 1N HCl solution at room temperature in a 24-hour period (Leventhal and Taylor, 1990).

Rock-Eval

Rock-Eval analyses were carried out using the standard pyrolysis procedure (Tissot and Welte, 1984), and the results were used to calculate total organic carbon content (TOC), the parameter T_{max}, the hydrogen index (HI), and the oxygen index (OI). Because the organic matter in the rocks is mature and possibly graphitic (see Rock-Eval results, and the conodont color alteration indices reported in chapter 11), the pyrolysis reactions may have been incomplete, resulting in erroneously low values for total organic carbon content. However, prior experience with similar types of samples (J.S. Leventhal, unpub. data, 2001) suggests that the underreporting is no more than 5–10 percent. Conclusions that will be drawn herein from the total organic carbon data are insensitive to errors of this magnitude.

Stable Isotope Analysis

Carbonate minerals were converted to carbon dioxide for isotopic analysis by treating whole-rock powders with phosphoric acid as described by McCrea (1950). All samples were reacted for 2 days at 25°C to ensure that yields were complete whether the carbonate mineral was dolomite or calcite. Isotopic compositions of the gases were determined using a Finnigan MAT 252 isotope ratio mass spectrometer equipped with a dual viscous inlet system. The acid fractionation factor for dolomite was used to calculate the oxygen isotopic compositions (Friedman and O'Neil, 1977). For samples containing calcite, which probably include the Hyd, Cannery, Retreat, and Gambier Bay samples, this has resulted in $\delta^{18}O$ values that are 0.8 permil too low. This potential error is small enough to have no effect on our conclusions. Carbon isotopic compositions determined by the phosphoric acid method do not depend on carbonate mineralogy.

For isotopic analysis of organic matter, powders were treated with 6N HCl to remove all carbonate carbon and then rinsed in deionized water. The solid residues were combusted in an elemental analyzer to convert the remaining carbon to carbon dioxide gas, which was admitted directly to a Micromass Optima mass spectrometer for determination of isotopic compositions by the continuous flow method.

Isotopic data are reported in δ-notation relative to Vienna Standard Mean Ocean Water (VSMOW) for oxygen and Vienna Pee Dee belemnite (VPDB) for carbon. Reproducibility was typically ±0.1 permil or better for $\delta^{13}C$, and ±0.2 permil or better for $\delta^{18}O$.

Results

Major-Element Chemical Compositions

The hanging-wall samples span a wide range of chemical compositions corresponding to lithologic variation from carbonate-free shale to nearly pure carbonate rock (table 1). Elements normally found in detrital silicates or clays, such as aluminum, potassium, and sodium, generally show inverse

relationships with elements normally found in carbonate minerals, such as calcium, magnesium, and carbon. An example is shown in figure 1 where aluminum and carbonate carbon are shown to span the entire range from typical shale or black shale to silicate-poor carbonate. Also evident in figure 1 are samples low in both aluminum and carbonate carbon, presumably due to an abundance of quartz or chert (silicon was not analyzed in this study). The calcium:magnesium ratios for many samples are within analytical error of the dolomite ratio (fig. 2), which is strong evidence that dolomite is the predominant host mineral for these two elements. Organic carbon in samples analyzed by Rock-Eval ranges from 0.5 to 5.0 percent, averaging 1.9 percent (table 2). This is higher than the values that have been proposed for average shale (Blatt and others, 1972; Krauskopf, 1979) but lower than the 2–10 percent range characteristic of black shales (Tourtelot, 1979). The dark appearance of the Greens Creek rocks probably reflects the graphitization of the organic matter due to heating rather than a particularly high organic content (Leventhal, 1993).

Chemical compositions are more restricted for other shale units on Admiralty Island, and the data are summarized as averages in table 2. The Cannery and Gambier Bay samples have major element compositions within the ranges characteristic of shales (Blatt and others, 1972), but the Hyd Group and Retreat Group samples are lower in aluminum. The carbonate carbon values are no higher for these units, so we infer that they contain a greater proportion of quartz or chert relative to feldspars and clay minerals. This inference conflicts with observations made during field mapping (chap. 4) that the Hyd Group is less siliceous than the Cannery Formation. However, other observations from field mapping are borne out by the chemical data. The observation that the Hyd Group is more pyritic than the Cannery Formation is confirmed by higher sulfur contents (1.7 versus 0.7 wt%), and the observation that the Hyd Group is more graphitic than the Cannery Formation is borne out by higher organic carbon (1.9 versus 0.7 wt%).

Rock-Eval

Rock-Eval results for hanging-wall samples are given in table 3. The HI and OI values are generally low, and the T_{max} values generally are greater than 500, indicating that the samples are overmature with respect to oil and gas generation, having been heated to temperatures exceeding 150°C. For comparison, black shales from unmetamorphosed localities elsewhere typically display HI values of 300–500, OI values of 50–100, and T_{max} below 460 (Leventhal, 1998).

Carbon-Sulfur-Iron Relationships

Most hanging-wall samples have sulfur:organic carbon ratios well above the value of ~0.36 that is characteristic of normal marine shale (for example, Berner and Raiswell, 1983)

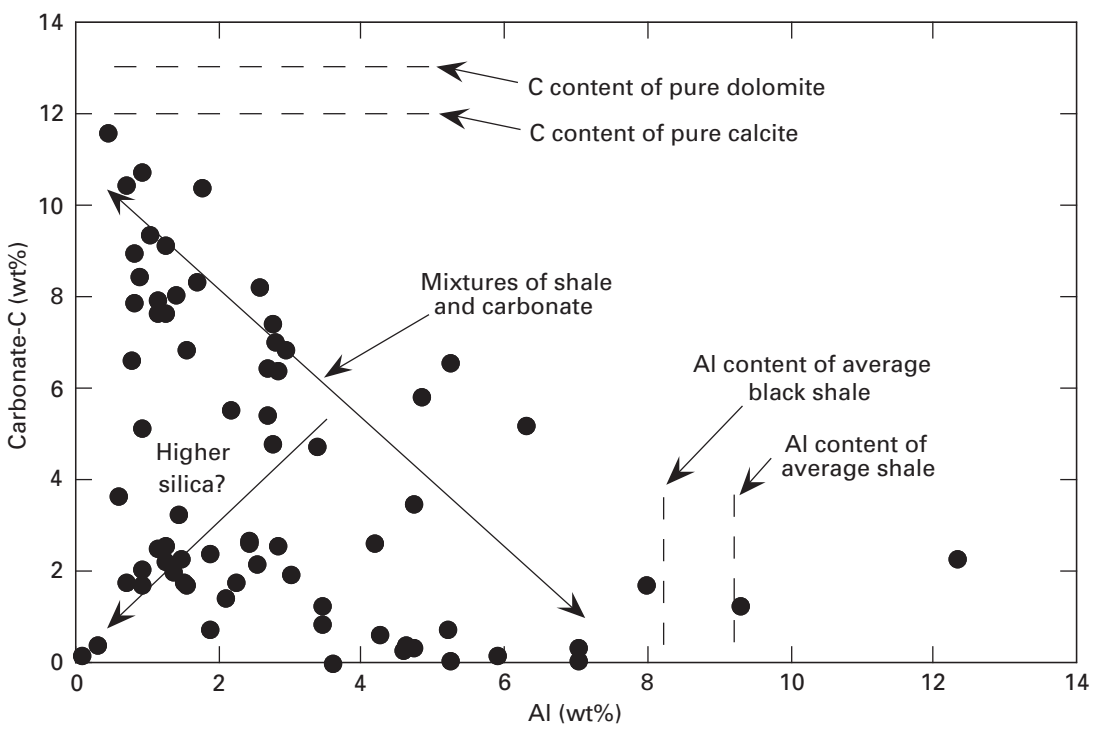

Figure 1. Plot of aluminum compared to carbonate carbon illustrating that the metasediments in the Greens Creek hanging wall span a broad lithologic range from carbonate-poor shale to nearly pure carbonate, and exhibit variable contents of quartz or chert. Aluminum (Al) contents of average shale and average black shale are from Krauskopf (1979) and Quinby-Hunt and others (1989), respectively. wt%, weight percent.

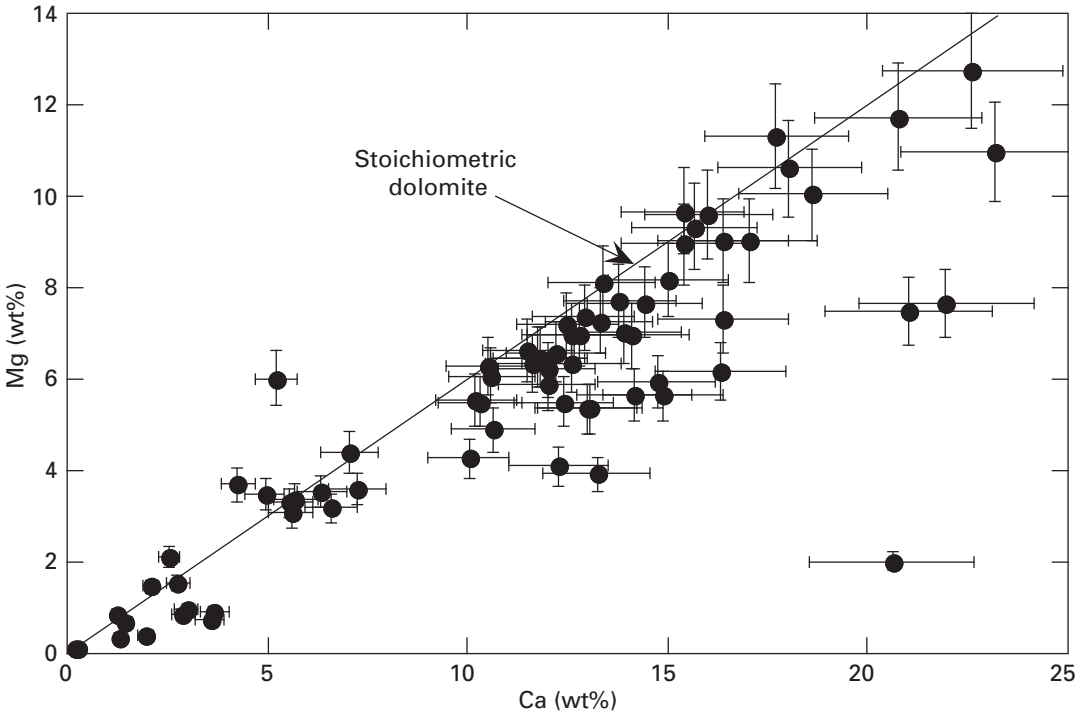

Figure 2. Comparison of the calcium and magnesium contents of hanging-wall samples with the ratio characteristic of dolomite. The close correspondence suggests that dolomite is the dominant host mineral for these elements. Ca, calcium; Mg, magnesium; wt%, weight percent.

in which diagenetic sulfide has been formed in anoxic sediment overlain by an oxic water column (fig. 3). The high ratios could be a consequence of organic matter loss during postdepositional heating, but the sulfur contents of many samples would require organic contents far higher than ordinary marine shales. Sulfide precipitation within an anoxic, hydrogen sulfide-bearing water column could also explain the high sulfur content of the rocks, but this typically preserves a positive- or zero-slope correlation between organic carbon and sulfur (Leventhal, 1983; Raiswell and Berner, 1985), a feature that is not apparent in the hanging-wall data. Epigenetic introduction of sulfur is a third mechanism that can lead to high sulfur:organic carbon ratios (Leventhal, 1995). The very high degree-of-pyritization values determined for many hanging-wall samples (table 1) is consistent with this process.

The Hyd Group and Cannery Formation samples also span wide ranges of sulfur:organic carbon (fig. 4). However, the very low sulfur contents and very low DOP values (less than 0.2, see Leventhal, 1993) displayed by many samples (fig. 5) are strong evidence that the chemical compositions of Admiralty Island surface outcrops have been affected by weathering. The fact that a few Hyd Group and Cannery Formation samples extend to high sulfur contents and high DOP values (figs. 4 and 5) suggests that at least some experienced substantial sulfur addition. Whether epigenetic sulfur addition is widespread in these units cannot be determined from the limited number of fresh samples that were available for this study.

Metals

For most of the listed metals, the agreement between Hyd Group samples analyzed by the A protocol and Hyd Group samples analyzed by the U protocol is reasonably good (table 2). However, for chromium and barium the results obtained using the A protocol are higher, possibly reflecting incomplete dissolution of chromite and barite in the U protocol, or chromium contamination from steel pulverizer plates in the A protocol.

The hanging-wall rocks show extremely broad ranges of metal contents (table 1). For samples that are true shales, which is defined here as samples containing less than 15 percent carbonate, the concentrations of iron and cobalt are the same as average black shale, copper and zinc are the same or slightly higher than in average black shale, and lead, gold, barium, and arsenic are higher than in average black shale (fig. 6*A*).

A comparison of metal concentrations in the hanging-wall shales with concentrations in their stratigraphic equivalents, the Hyd Group shales, is shown in figure 6*B*. The concentrations of cobalt, iron, and molybdenum are similar in the two units, and for each of the other elements the hanging-wall analyses overlap the Hyd average and extend to higher concentrations. No strong evidence exists in the data for metal depletions in the exposed Hyd Group rocks, as might be expected if this unit were the main metal source for the Greens Creek massive sulfide deposit.

With regard to chemical variations within the entire hanging-wall shale + carbonate package, cobalt, chromium, nickel, and vanadium were found to correlate with organic

Table 2. Average chemical compositions of Admiralty Island shales compared with average shale and average black shale.[#]

[<, less than; - , no data; Gp., Group; Fm.; Formation; Ave., average]

Element	Hyd (A) Gp.	Hyd (U) Gp.	Cannery Fm.	Gambier Bay Fm.	Retreat Gp.	Ave. shale[@@]	Ave. black shale[^]
Al_2O_3	7.6	-	11.4	16.8	8.3	17	15.5
CaO	0.8	-	1.0	0.1	0.01	3.5	2.4
FeO[*]	3.6	-	4.8	4.4	2.0	6.0	4.7
K_2O	1.6	-	2.0	3.4	2.2	3.0	3.6
MgO	1.5	-	2.2	1.5	2.0	2.3	1.7
Na_2O	1.0	-	1.6	0.9	0.03	1.2	0.7
TiO_2	0.3	-	0.5	0.6	0.4	0.8	0.7
S	1.7	1.1	0.7	0.9	0.01	0.25	1
C_{org}[**]	1.9	-	0.7	2.3	0.5	0.8	3.2
U	4	-	-	-	-	3.5	15.2
Mo	6	14	7	<2	<2	2	65
V	-	196	206	181	82	130	500
Ni	-	35	36	38	13	80	50
Cu	20	31	37	25	17	50	70
Cr	130[@]	43[***]	36	68	16	100	111
Co	5	8	9	5	<2	20	17
As	23	-	-	18	<10	10	29
Pb	32	16	18	29	9	20	20
Ba	2,078	1,539[***]	2,327	810	4,083	600	1,120
Zn	81	85	119	81	49	90	310
Ag	-	<2	<2	<2	<2	0.1	0.1
Cd	-	<2	<2	<2	<2	0.3	-
P	-	570	717	500	233	750	-
Mn	-	191	479	97	189	850	383
no. samples	9	33	17	1	3	-	-

[#]Oxides in percent, elements in parts per million.

[*]Total iron as iron (II) oxide.

[**]Organic carbon from Rock-Eval for mine argillite, from difference between total carbon and carbonate carbon for all others.

[@]May be high by this method (see text).

[***]May be low by this method (see text).

[@@]Krauskopf (1979), except for organic carbon which is from Leventhal (unpub. data, 2001).

[^]Quinby-Hunt and others (1989), except for lead, organic carbon, nickel, copper, which are from Vine and Tourtelot (1970), and sulfur and silver, which are from Leventhal (unpub. data, 2001).

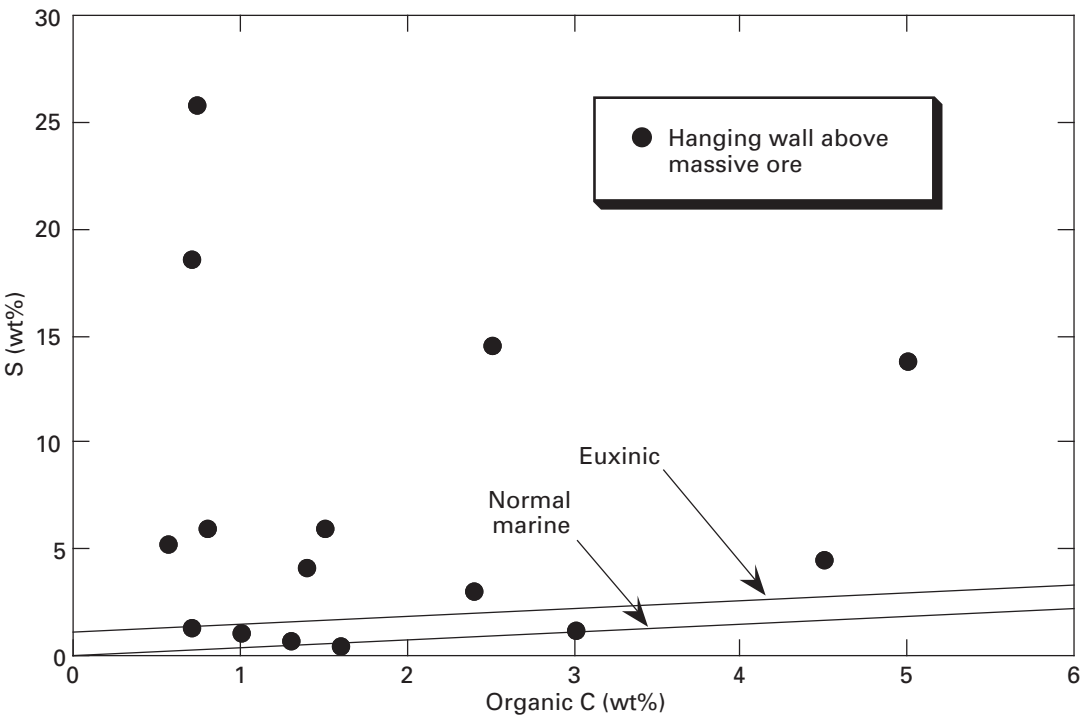

Figure 3. Plot of organic carbon (C) (determined by Rock-Eval) compared to sulfur (S) for hanging-wall samples. The lines marking normal marine sediments and sediments deposited in euxinic environments were taken from Leventhal (1995). wt%, weight percent.

carbon with R-values of around 0.7 (fig. 7). Silver, As, Au, Cd, Cu, Fe, Mo, Pb, and Zn were found to correlate only weakly with organic carbon (R-values less than 0.4), but more strongly with sulfur (R-values of 0.4–0.5 for cadmium, silver; 0.5–0.6 for copper, molybdenum, lead; about 0.7 for gold, arsenic, zinc; 0.9 for iron) (fig. 7). Figure 8 illustrates that samples with intermediate degree-of-pyritization values have lead and zinc contents that are typical of shale or black shale, but samples with higher degree-of-pyritization values have substantially higher metal contents. Barium falls in neither of the two suites of metals shown in figure 8, displaying a fair correlation with organic carbon, but no correlation with sulfur. This may imply that barium was added during sedimentation or diagenesis.

Stable Carbon and Oxygen Isotopes

The stable isotopic compositions of carbonates and total organic carbon are given in table 4. Hanging-wall carbonates have an average $\delta^{18}O$ of 18 permil and an average $\delta^{13}C$ of –6 permil. Both values are significantly lower than marine limestones and dolomites of Triassic age (Veizer and others, 1999). Organic carbon isotopic compositions are –25.9±0.9 (1–σ) permil, which is intermediate between the compositions characteristic of the two kerogen types found in Phanerozoic sedimentary rocks (Lewan, 1986). Thermal maturation can cause an upward shift in organic matter $\delta^{13}C$ values of as much as 3 permil (Schidlowski, 1987). Thus the hanging-wall organic matter may originally have had isotopic compositions resembling *l* (italic "el")-amorphous kerogen (Lewan, 1986). The isotopic fractionations between carbonate carbon and organic carbon are 19.9±0.8 (1–σ) permil across a wide range of organic carbon:carbonate carbon ratios (fig. 9*A*).

Fewer analyses were made of the Cannery Formation and Hyd Group shales (fig. 9*B*). The isotopic compositions of Hyd carbonates resemble those of the hanging-wall carbonates, whereas three Cannery samples have compositions spanning a wide $\delta^{13}C$ range of –13 to –2 permil. Organic carbon $\delta^{13}C$ values for the Hyd Group and Cannery Formation are very similar to the hanging-wall samples, although two Hyd samples extend to significantly higher $\delta^{13}C$ (fig. 10). Of note is the low carbonate $\delta^{13}C$ value and the small carbonate-organic carbon fractionation in Cannery sample Ard–02, which suggest that there may have been isotope exchange between carbonate minerals and organic matter during a postdepositional heating event. The fact that isotopic exchange is apparent in this Permian unit, but neither in the mine argillite nor in the Hyd Group, both of which are Triassic, may mean that the exchange was a consequence of the Early Permian low-grade metamorphic event that affected some areas on Admiralty Island (Haeussler and others, 1999; Karl and others, 1999).

On a plot of $\delta^{18}O$ and $\delta^{13}C$ (fig. 11) the hanging-wall carbonates display a broad linear trend with a regression slope of 0.6. The Hyd samples conform closely to this trend, but two Cannery samples do not. This observation may imply a genetic

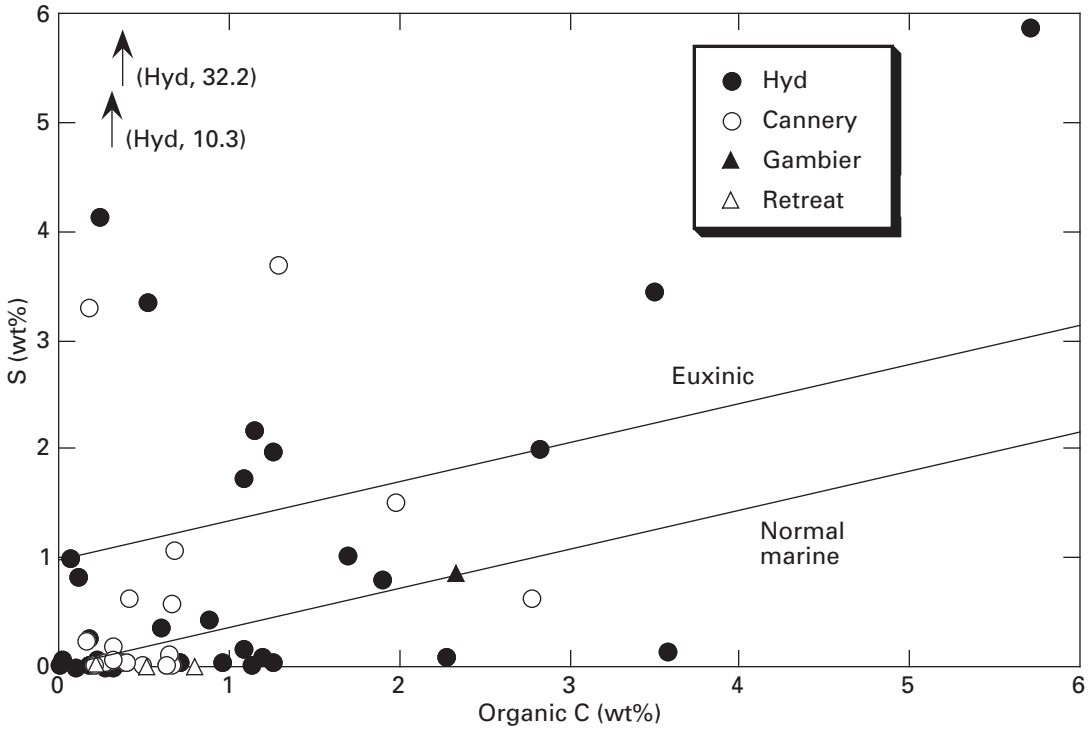

Figure 4. Plot of organic carbon (C) (total carbon minus carbonate carbon) compared to sulfur (S) for Hyd Group, Cannery Formation, Gambier Bay Formation, and Retreat Group samples. wt%, weight percent.

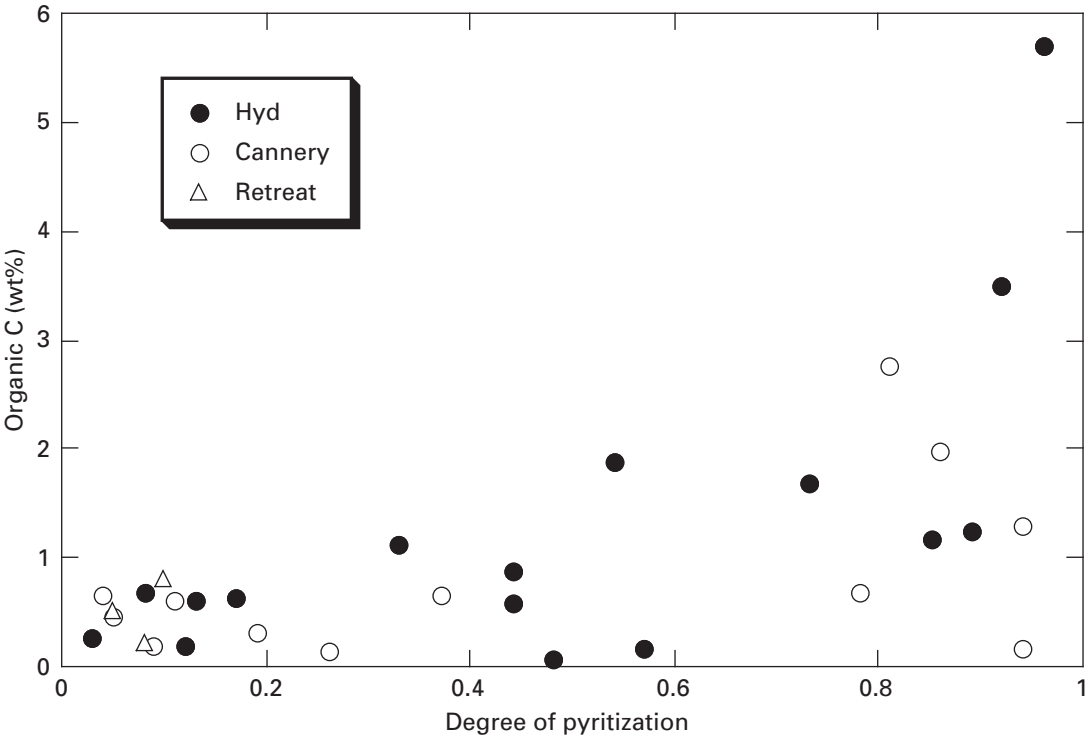

Figure 5. Plot of degree-of-pyritization compared to organic carbon (C) for Hyd Group, Cannery Formation, and Retreat Group samples. wt%, weight percent.

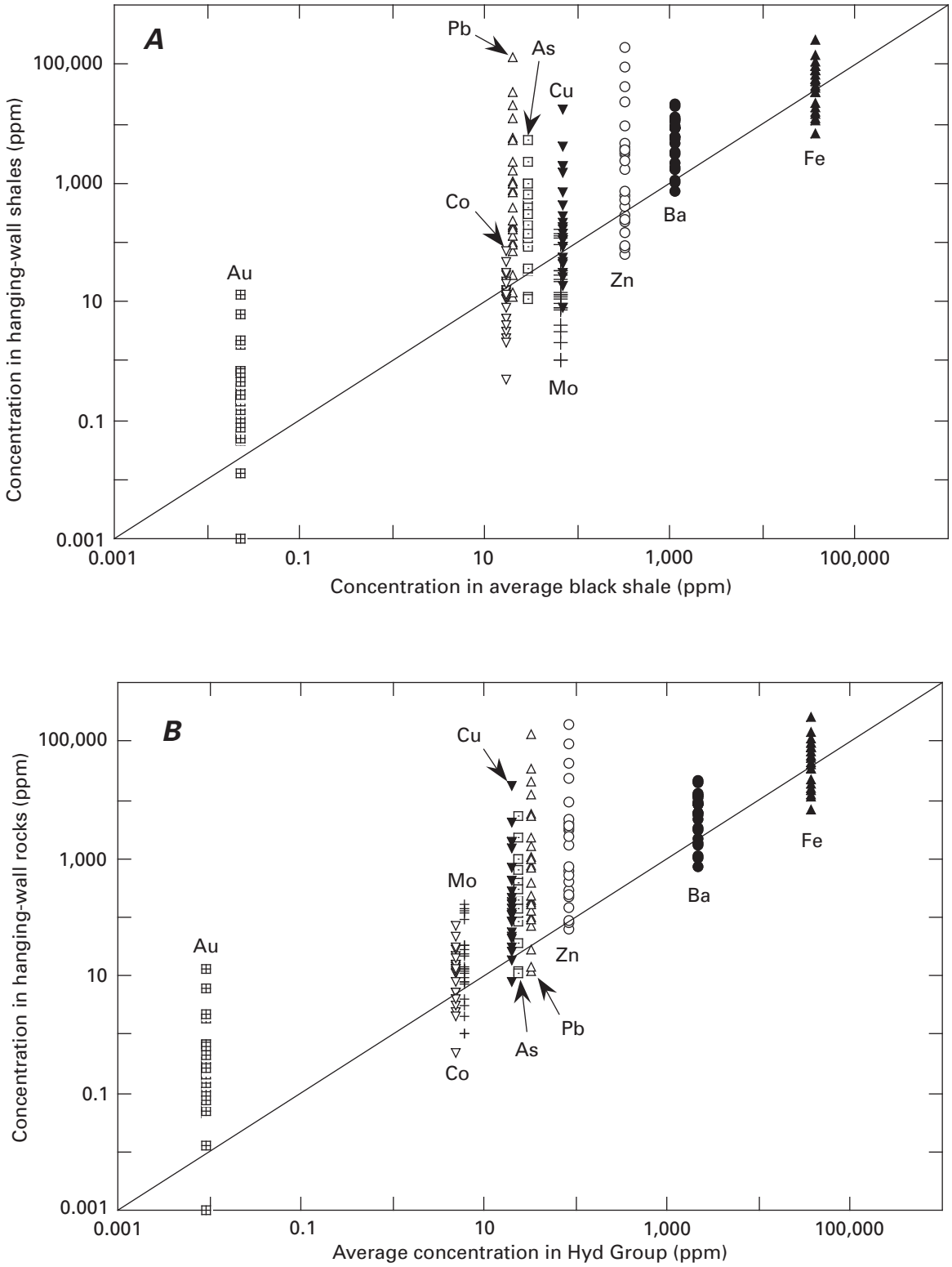

Figure 6. Concentrations of several metals in hanging-wall shales (only those samples that contain less than 15 percent carbonate) compared with the concentrations in (*A*) average black shale (Quinby-Hunt and others, 1989) and (*B*) average Hyd Group shale (table 1). The Hyd average includes only those samples analyzed by the same protocol used for the hanging-wall samples (see text). ppm, parts per million.

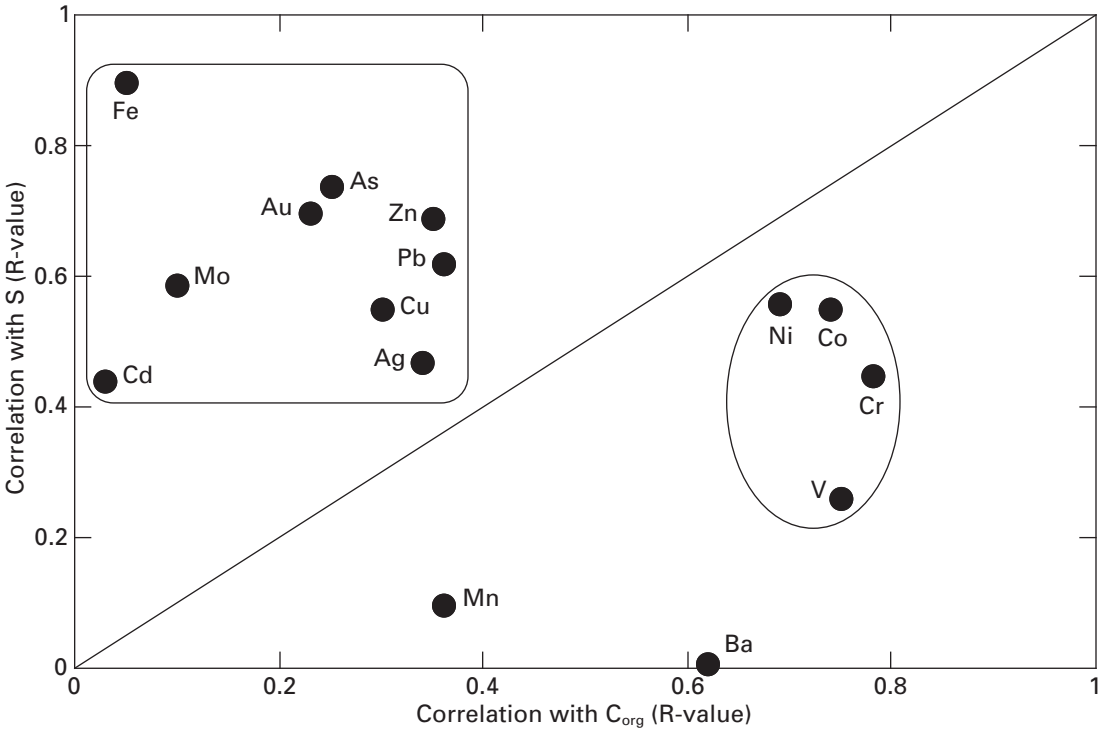

Figure 7. Correlations in hanging-wall samples of various elements with organic carbon (C_{org}) compared to the correlations of the same elements with sulfur (S), expressed as correlation coefficients (R-values). Base metals, precious metals, iron, molybdenum, and arsenic show a higher correlation with sulfur than with organic carbon, and the reverse is true for cobalt, chromium, nickel, and vanadium, suggesting that different processes were responsible for the emplacement of these two groups of elements.

link between the carbonate minerals in the hanging-wall rocks and those in Hyd Group rocks found several kilometers to the northwest near Hawk Inlet (see succeeding discussion).

Effects of Cretaceous Regional Metamorphism

The regional metamorphic-deformation event that affected Admiralty Island in Cretaceous time could have caused significant changes in the hanging-wall rocks, and it is important that any such changes be considered so that primary features can be discriminated from any secondary metamorphic features. In underground exposures and in drill core, there is clear textural evidence for remobilization of metals and sulfur, including crosscutting sulfide veinlets, and fractures and shears with sulfide minerals dispersed along them. Whether these remobilizations were caused by a protracted hydrothermal event or by the Cretaceous metamorphism-deformation is uncertain, in much the same way that remobilization textures within the underlying massive sulfide bodies are of uncertain origin (chap. 9).

Volatile species would very likely have been released from the hanging-wall section during regional metamorphism. Kerogen is known to lose methane starting at around 120°C (Tissot and others, 1974), and clays begin to dehydrate at 100–200°C (Fyfe and others, 1978). The Rock-Eval results (table 3) are consistent with these types of prograde reactions because they indicate carbon-oxygen-hydrogen volatile loss at temperatures greater than 150°C. On the other hand, any pre-Cretaceous heating event, including the metal-depositing event itself, could also explain the Rock-Eval data. The production and movement of fluids during low-grade metamorphism could have led to redistribution of volatile species within the rocks and may be partly responsible for the wide variation in sulfur:organic carbon ratios observed in the hanging-wall samples (fig. 3). Because the metamorphic event was regional, the same phenomenon might also explain the wide variation in sulfur:organic carbon ratios observed in the Hyd Group and Cannery Formation rocks. The fact that the hanging-wall rocks have systematically high degree-of-pyritization values indicates that aqueous sulfide or hydrogen sulfide was abundantly available at some time during the history of these rocks, possibly during the Cretaceous metamorphism when hydrogen sulfide-bearing fluids may have been released from the nearby massive sulfide bodies. For the Hyd Group and Cannery Formation, the wide range in degree-of-pyritization values indicates that reduced sulfur was abundantly available at some locations but was never available at others, presumably due to heterogeneity of flow paths and bulk permeability.

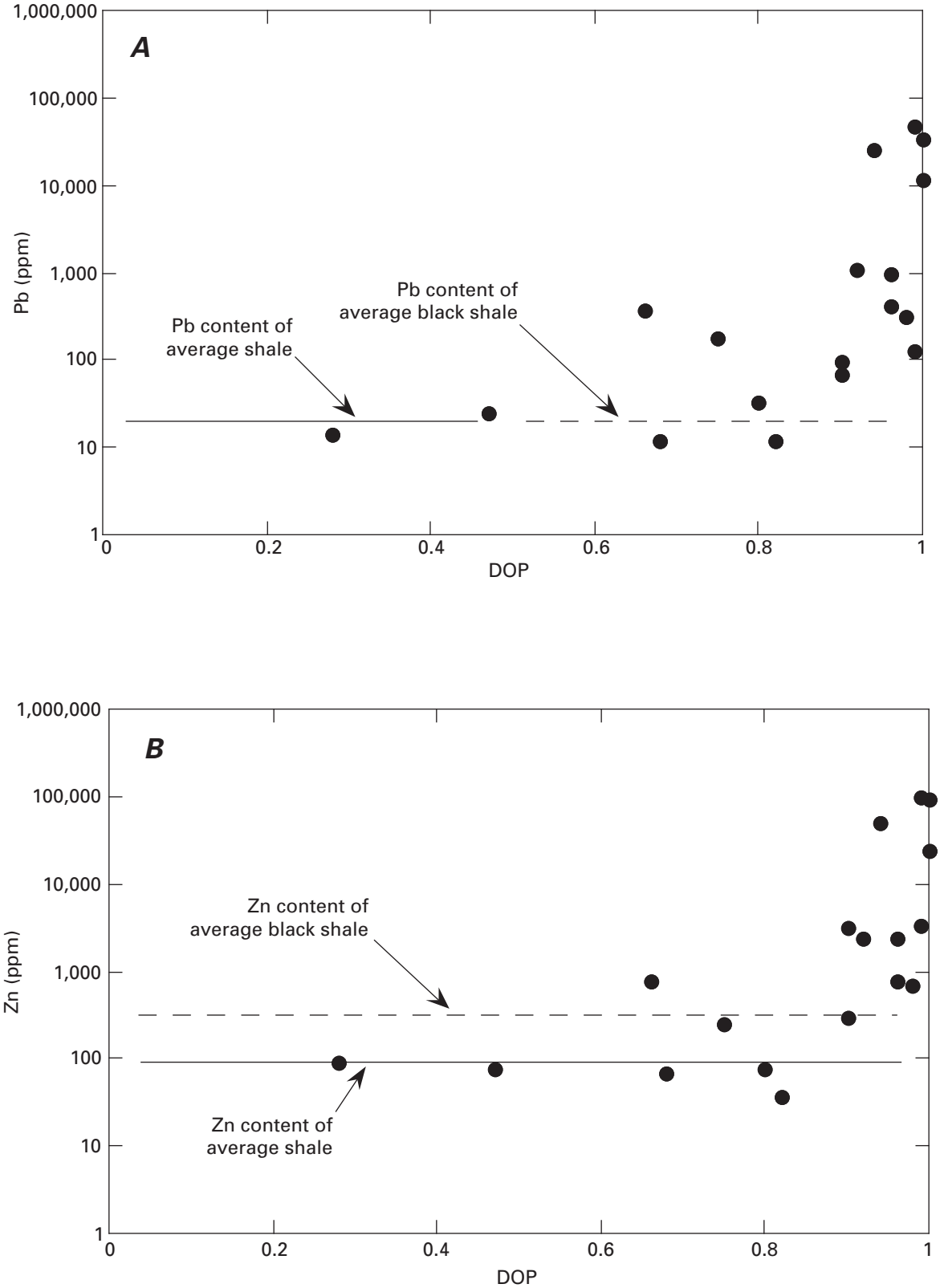

Figure 8. Plots of degree-of-pyritization (DOP) compared to (*A*) lead and (*B*) zinc (Zn) for hanging-wall samples. ppm, parts per million.

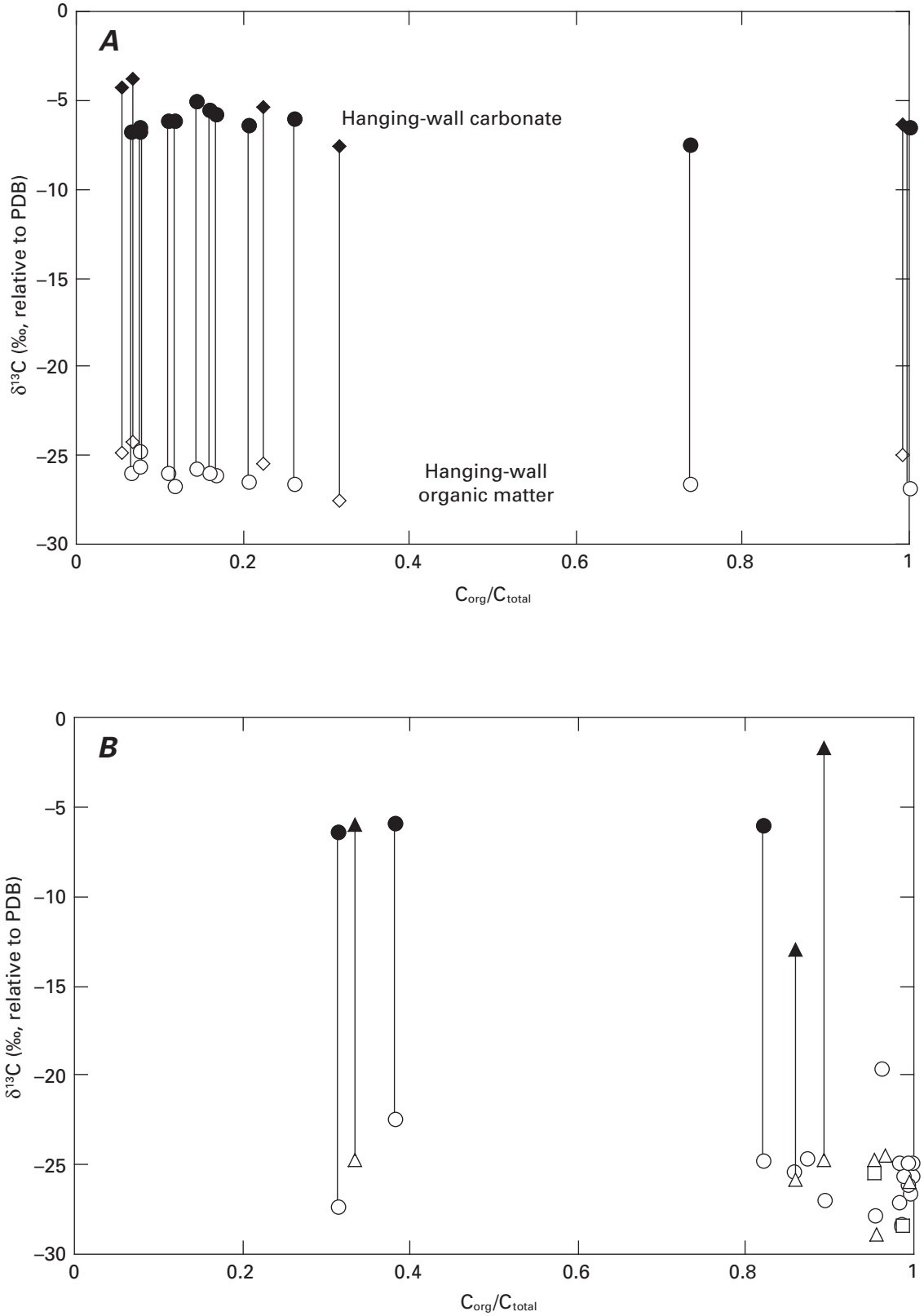

Figure 9. (A) The carbon isotopic compositions of coexisting carbonate (filled symbols) and organic matter (open symbols) in hanging-wall samples. Diamonds indicate samples for which organic carbon was calculated by difference and could be erroneously low. (B) The carbon isotopic compositions of Hyd Group (circles), Cannery Formation (triangles), and Retreat Group (squares) samples. PDB, Pee Dee Belemnite.

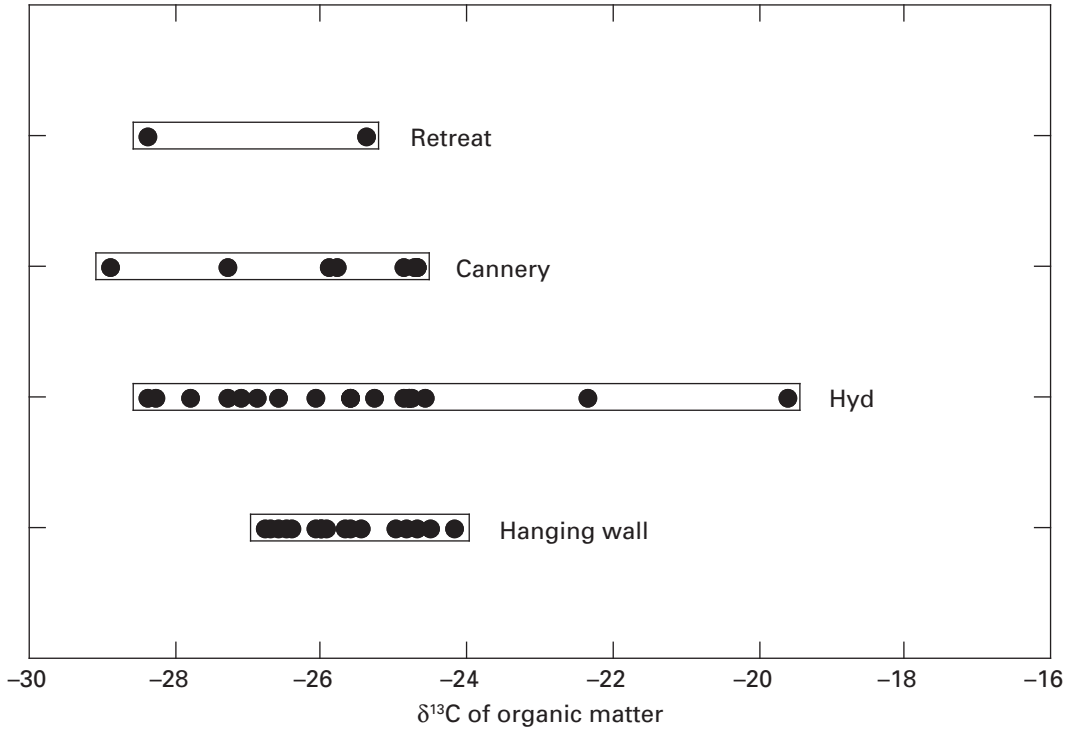

Figure 10. Carbon isotopic compositions of organic matter.

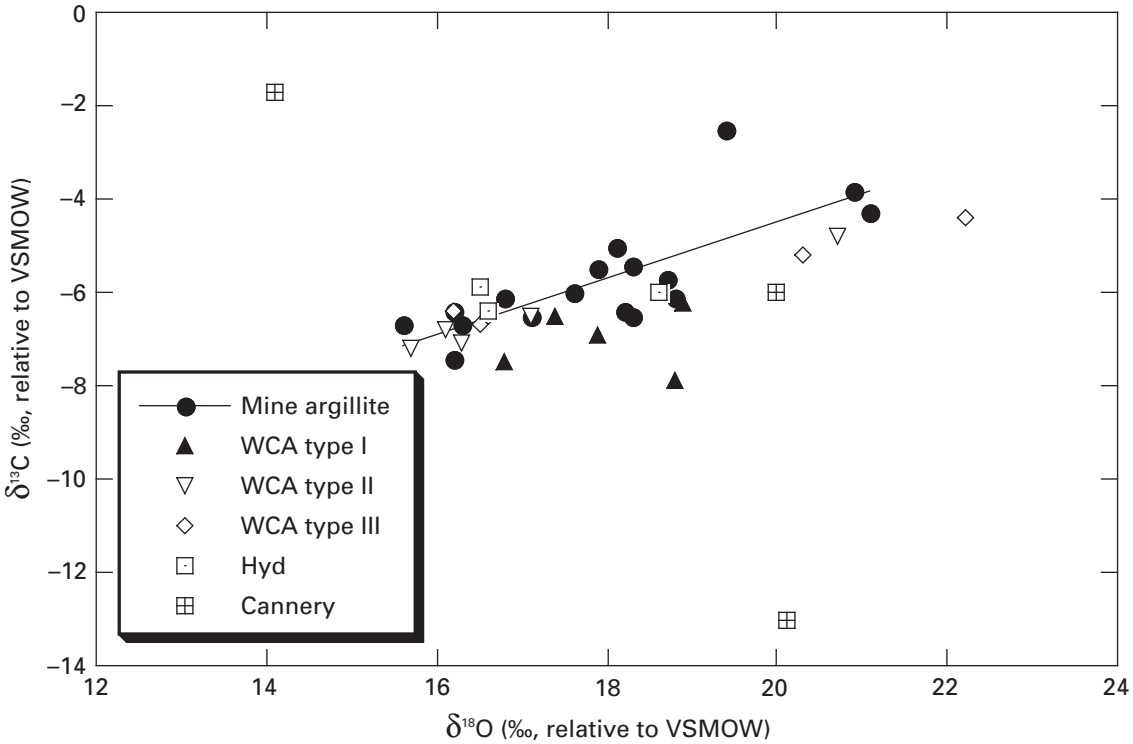

Figure 11. The carbon and oxygen isotopic compositions of carbonate minerals in hanging-wall rocks, white carbonate-rich ore, Hyd Group, and Cannery Formation samples. VSMOW, Vienna Standard Mean Ocean Water.

Table 3. Rock-Eval analyses of hanging-wall samples.

Sample	T_{max}*	TOC**	HI	OI
1136–4	519	3.01	6	3
1136–5A	501	1.62	3	12
1136–8	533	5.04	2	0
1136–12	494	4.48	2	1
1136–26	564	1.02	2	12
1136–27	502	0.75	4	36
1136–13	566	0.7	7	20
1136–16	583	1.26	4	10
96GC–5	527	1.41	2	14
96GC–7	521	2.4	4	6
96GC–9	571	2.48	12	2
96GC–14	514	1.53	9	8
96GC–28	546	0.8	41	36
96GC–37	496	0.56	62	30

*T_{max} is an instrumental, not geologic, temperature. T_{max}<420 is immature relative to petroleum generation (geologic less than about 70°C), T_{max}=420–440 is oil generation (geologic 80–100°C), T_{max}=440–460 is gas generation (geologic 100–150°C), T_{max}>460 is anthracite rank coal equivalent proceeding to amorphous graphite with higher temperature.

**Total organic carbon.

Metamorphic heating also could cause exchange of carbon isotopes between organic matter and carbonate minerals, and this phenomenon could be argued to explain the low carbonate $\delta^{13}C$ values in the hanging-wall rocks compared with typical marine carbonates of Triassic age. However, low-grade metamorphism does not always cause significant exchange (Kitchen and Valley, 1995) due to differences in the duration of heating or to variable exchange kinetics from one locality to another. The work of Himmelberg and others (1995) in the Juneau area on the same metamorphic event that affected the Greens Creek area (their M_1 metamorphism) suggests that the event was characterized by rapid burial, limited duration of heating, and rapid uplift, all of which would have minimized isotope exchange among coexisting minerals.

Two observations suggest that isotope exchange was not important for the Greens Creek rocks and that the carbonates have retained their premetamorphic compositions. First, the carbonate carbon–organic carbon isotopic fractionations are very uniform, quite different from the wide variability observed in other low-grade metamorphic localities reflecting different degrees of isotopic reequilibration from one hand specimen to another (for example, Arneth and others, 1985). The second observation is that the carbonate carbon–organic carbon fractionation does not vary with the relative proportions of the two carbon reservoirs, as would be required by isotope mass balance in systems approaching isotopic equilibrium (Gregory and others, 1989).

Table 4. Stable isotopic compositions of carbonate minerals and organic matter.

Sample	Unit	$\delta^{18}O_{carb}$	$\delta^{18}C_{carb}$	$\delta^{18}C_{org}$
96GC–5	hanging wall	18.7	–5.7	–26.1
96GC–7	hanging wall	17.6	–6.0	–26.5
96GC–14	hanging wall	16.2	–6.4	–26.4
96GC–28	hanging wall	15.6	–6.7	–24.7
96GC–37	hanging wall	16.3	–6.7	–26.0
GC1136–4	hanging wall	18.2	–6.4	–25.0
GC1136–5	hanging wall	18.1	–5.0	–25.7
GC1136–8	hanging wall	16.2	–7.4	–26.6
GC1136–12	hanging wall	17.1	–6.5	–26.8
GC1136–13	hanging wall	18.3	–6.5	–25.6
GC1136–16	hanging wall	18.8	–6.1	–26.0
GC1136–26	hanging wall	17.9	–5.5	–26.0
GC1136–27	hanging wall	16.8	–6.1	–26.7
PP204–01	hanging wall	18.3	–5.4	–25.5
PS50–01	hanging wall*	19.0	–7.6	–27.8
PS50–02	hanging wall	21.1	–4.3	–24.9
PS50–03	hanging wall	20.9	–3.8	–24.2
GCPF–1	hanging wall	19.4	–2.5	–24.5
96ADM7	Hyd			–26.9
96ADM19	Hyd			–28.3
97ADM27	Hyd	16.6	–6.4	–27.3
Brd–01	Hyd	18.6	–6.0	–24.8
Brd–02	Hyd			–24.6
Brd–03	Hyd			–19.6
Brd–04	Hyd	16.5	–5.9	–22.4
NAD T9–1	Hyd			–27.8
NAD T9–6B	Hyd			–28.4
NAD T16–7	Hyd			–26.6
NAD T17–3	Hyd			–24.8
97LG11	Hyd			–25.3
97LG14	Hyd			–26.1
97LG57	Hyd			–25.6
97LG60	Hyd			–25.6
97LG65	Hyd			–24.9
97LG66	Hyd			–24.8
97LG75	Hyd			–27.1
97ADM6	Cannery	14.1	–1.7	–24.7
Ard–02	Cannery	20.1	–13.0	–25.8
Ard–03	Cannery	20.0	–6.0	–24.7
Ard–01	Cannery			–24.9
Ard–04	Cannery			–28.9
96ADM13	Cannery			–25.9
97LG25	Cannery			–24.7
97ADM22	Retreat			–28.4
97LG76	Retreat			–25.4

*This sample is from what may be a separate lithologic unit overlying the hanging-wall unit.

That premetamorphic isotopic compositions might be preserved is somewhat surprising given the ladder veins of quartz and carbonate evident in many hanging-wall rocks (chap. 7) that formed by mobilization of chemical constituents into tension fractures during Cretaceous time (the F2 folding event described in chap. 7). The preservation of isotopic compositions may be due to the sample-selection protocol that was used for the carbonate isotopic work in which rocks with abundant carbonate veining were generally avoided. However, the isotopic results for sample 96GC–37, which did contain megascopic carbonate veins, were indistinguishable from those for other hanging-wall samples (table 4), which suggests that the ladder veins may have been local redistributions (compare Ramsay, 1980; Hobbs, 1986) that did not significantly alter the $\delta^{13}C$ value of the carbonate.

It is noteworthy that the smallest observed carbonate carbon–organic carbon isotopic fractionations are in a Hyd Group sample collected 6 km west-northwest of the mine site (Brd–04) and a Cannery Formation sample collected 10 km northwest of the mine site (Ard–02) (table 4). If these fractionations reflect exchange between organic matter and carbonate minerals on heating, then the highest temperatures (whether hydrothermal or metamorphic), or the longest duration of heating, or the most favorable exchange kinetics were not in the vicinity of the mine but rather to the west and northwest nearer Hawk Inlet.

Implications of Whole-Rock Chemical Compositions

The overall high sulfur:organic carbon ratios and high degree-of-pyritization values found for many hanging-wall samples are strong evidence for epigenetic sulfur addition in much of the section, and the close correlation of lead, zinc, and other metals with sulfur is evidence for epigenetic metal addition as well. However, there are hanging-wall samples that were collected in close proximity to ore that have sulfur:organic carbon ratios and degree-of-pyritization values characteristic of normal marine sediments. In these samples (table 5), the concentrations of zinc, gold, and silver are no greater than in average black shale or average shale, and lead is higher than in average black shale or shale in only one of five samples. Barium is systematically high at about twice the average black shale value. Thus, for at least part of the depositional history of the hanging-wall section, the accumulating sediment appears to have been overlain by an oxic water column with dissolved metal contents that were for the most part like normal seawater. The twofold enrichment in barium suggests enhanced barite precipitation in the water column, which could have been a consequence of elevated barium. This might reflect a hydrothermal fluid flux to the basin producing a geochemical fingerprint in the sediment similar to that observed in the barite-rich, precious metal-rich, base metal-poor, earliest stages of massive sulfide mineralization (chap. 6). Thus, there is some evidence, albeit weak, for hydrothermal venting to the basin waters during the most normal marinelike periods of sediment accumulation. A substantial hydrothermal flux, or a standing brine pool, at the Greens Creek vent site is ruled out during sedimentation of these samples (table 5).

On the other hand, during deposition of the more common metal- and sulfur-rich samples, a hydrothermal brine could have been a significant component of the overlying water column. Many hanging-wall samples show very strong enrichments in sulfur, lead, arsenic, and gold with respect to normal black shales, but these same samples are not enriched in cobalt, nor, for the most part, in copper and zinc (fig. 6*A*). Thus, even if the accumulating sediments were overlain by a brine pool or a hydrothermally impacted water column, evidence is lacking for the basaltic or ultramafic metal source that influenced the metal abundances of the underlying massive sulfide deposit and its alteration envelope in the footwall phyllites.

Implications of Carbonate Isotopic Compositions

Isotopic data from hanging-wall carbonates are compared with data from dolomite in white ore (Freitag, 2000) in figure 11. The hanging-wall compositions are indistinguishable from the compositions of Freitag's (2000) dolomite types I, II, and III. Textural evidence indicates that dolomite types II and III

Table 5. Chemical analyses of hanging-wall samples with low sulfur:organic carbon (C_{org}) and low degree-of-pyritization (DOP) values.[#]

[<, less than; -, no data; S, sulfur; Ba, barium; Pb, lead; Zn, zinc; Au, gold; As, arsenic]

Sample	DOP	C_{org}	S	S:C_{org}	carbonate C	Ba	Pb	Zn	Au	As
96GC1136–3	-	3.00	1.19	0.39	2.31	3,500	142	222	31	15
5	0.68	1.60	0.48	0.30	1.74	1,200	12	68	13	11
16	0.82	1.30	0.69	0.53	2.59	2,200	12	37	40	17
PS–50–01	0.28	-	0.36	-	1.29	1,900	14	93	<2	3.9
PS–50–03	0.47	-	1.14	-	6.42	1,700	25	78	19	11
Average black shale	0.6	3.2	1	0.3	-	1,120	20	310	23	28.8
Average shale	0.5	0.8	0.25	0.3	-	600	20	90	3	10

[#]C_{org}, S, and carbonate C in percent; Ba, Pb, Zn, and As in parts per million; Au in parts per billion.

filled open spaces and that type III coprecipitated with sphalerite, galena, and silver sulfosalts (Freitag, 2000). The isotopic similarity is strong evidence that the carbonate contained in the hanging-wall rocks precipitated from the same fluid that deposited metals in the underlying massive sulfide deposit. Thus, hydrothermal activity at Greens Creek must have persisted until after the hanging-wall sediments had been laid down, a finding which is consistent with the sulfur isotopic evidence that the main sulfur source for the massive ores was bacterial reduction of pore-water sulfate in overlying anoxic sediments (chap. 10).

There are two possible explanations for the carbonate isotopic data shown in figure 11. The first is that the trend reflects variable mixtures of two different carbonate types. One possible end-member is any marine carbonate that may have been present during hydrothermal activity. Evidence for the existence of such an end-member is the platform carbonate rocks that occur discontinuously on Admiralty Island at the same stratigraphic position as the Greens Creek massive sulfide deposit (chap. 2). Triassic marine carbonates would be expected to have $\delta^{18}O$ values of about 30 permil and $\delta^{13}C$ values of about 2 permil (Veizer and others, 1999), compositions which lie along the upper extension of the hanging-wall array shown in figure 11. The low-$\delta^{18}O$, low-$\delta^{13}C$ end-member might reasonably be hypothesized to be a hydrothermal precipitate.

The second possible explanation for the isotopic trend is that it reflects carbonates precipitated from a single hydrothermal fluid over a range of temperatures. Shown in figure 12 are two curves that define the isotopic compositions of dolomite precipitated from two different hypothetical fluids at temperatures ranging from 150 to 350°C, a range that includes the temperatures inferred for sulfide precipitation in the massive sulfide body (chap. 15). Both fluids were assigned a $\delta^{18}O_{H2O}$ value of 10.4 permil on the basis of visual best-fit. The upper curve corresponds to a fluid in which the carbon species is carbonic acid (H_2CO_3) with a $\delta^{13}C$ value of –4.2 permil, and the lower curve corresponds to a fluid in which the carbon species is also H_2CO_3, but with a $\delta^{13}C$ value of –6.2 permil. These $\delta^{13}C$ values were chosen so that the curves would enclose the majority of the hanging-wall and ore data. The development of the dolomite curves follows Rye and Williams (1981), to which the reader is referred for the underlying details and assumptions.

The slope of the model curves corresponds quite well to the trend of the data (fig. 12). Variation of the fluid $\delta^{13}C$ value from –4.2 permil to –6.2 permil could be explained by

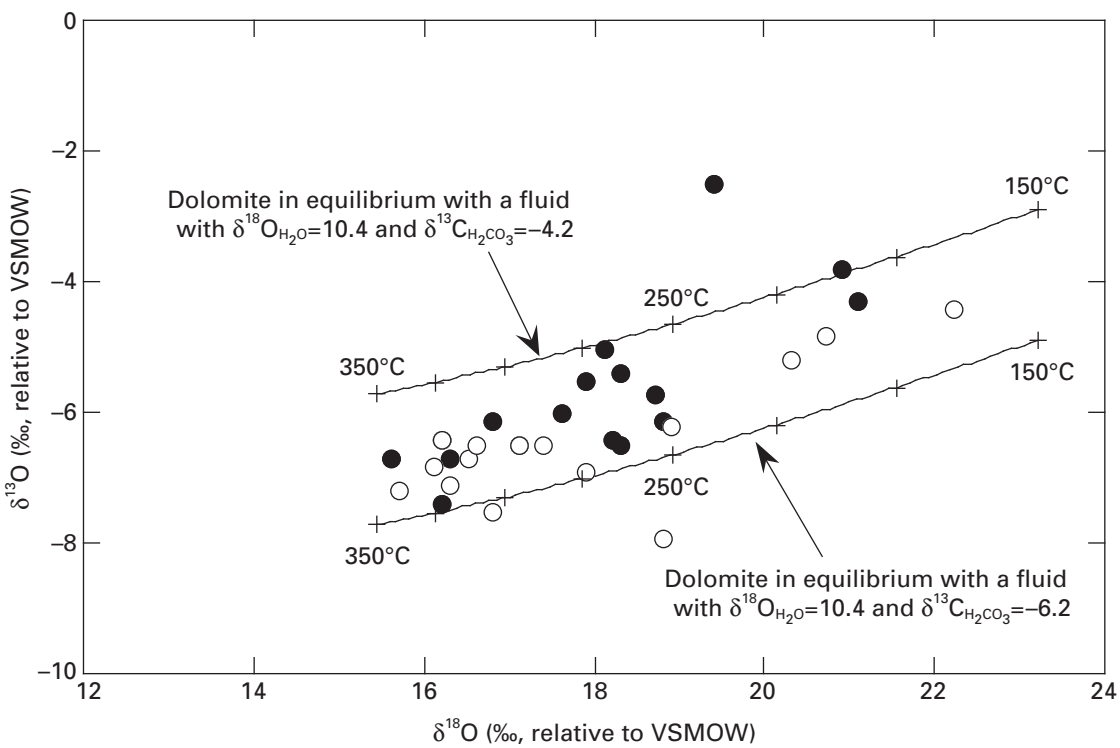

Figure 12. Comparison of the isotopic compositions of carbonate in the hanging-wall rocks (filled circles) with dolomite in white carbonate-rich ore (open circles, Freitag, 2000). Freitag's (2000) tabulated $\delta^{18}O$ values have been reduced by 0.8 permil to correct for the difference between the acid fractionation factors for calcite and dolomite (Friedman and O'Neil, 1977; Rosebaum and Sheppard, 1986; Swart and others, 1991). Also plotted are curves showing the dolomite compositions that would be predicted for precipitation from a hydrothermal fluid with $\delta^{18}O_{H2O}$ value of 10.4 permil and $\delta^{13}C_{H2CO3}$ value of either –4.2 or –6.2 permil over a temperature range of 150–350°C, the same range that has been inferred for formation of the underlying massive sulfide deposit. VSMOW, Vienna Standard Mean Ocean Water; ‰, permil.

progressive precipitation of dolomite, which would have the effect of depleting the fluid in the heavy isotope and driving the $\delta^{13}C$ value of dissolved H_2CO_3 downward over time, or by oxidation of organic matter or methane, which would contribute isotopically light carbon also driving the $\delta^{13}C$ value of H_2CO_3 downward (Rye and Williams, 1981).

Two observations suggest that oxidation of organic matter or methane was an important process during deposition of the hanging-wall section. The first is that the $\delta^{13}C$ values of carbonate and organic matter are correlated (fig. 13), consistent with carbonate production by oxidation of ambient organic carbon or of methane produced by thermal maturation of organic matter. The fact that the carbonate $\delta^{13}C$ values are much higher than the organic carbon $\delta^{13}C$ values implies that organic matter or methane oxidation was a minor carbonate source compared with higher $\delta^{13}C$ marine carbonate rocks or marine fluids. The second observation suggesting that organic matter or methane oxidation was important is that carbonate $\delta^{13}C$ values and sulfur contents of the hanging-wall rocks are correlated (fig. 14). This relationship suggests that hydrogen sulfide was produced from sulfate by reaction with low-$\delta^{13}C$ reduced carbon compounds by chemical pathways such as:

$$2CH_2O + SO_4^{2-} \longrightarrow H_2S + 2CO_3^{2-} + 2H^+, \text{ or}$$

$$CH_4 + SO_4^{2-} \longrightarrow H_2S + CO_3^{2-} + H_2O.$$

The subsequent reaction of hydrogen sulfide with iron or other metals then caused the reduced sulfur to become fixed in the sediments.

The links illustrated in figures 13 and 14 between sulfide sulfur and carbonate carbon, and between carbonate carbon and organic carbon are strong evidence that sulfide minerals formed, at least in part, during early diagenesis beneath the sediment/seawater interface. Whether any of the hanging-wall sulfides represent true syngenetic accumulations on the ancient sea floor cannot be determined from the observations made in this study.

Also uncertain is the relative importance of microbially mediated and inorganic reactions during formation of the hanging-wall section. The abundance of framboidal pyrite in many of the rocks (chap. 9) and the low and variable $\delta^{34}S$ values of the hanging-wall pyrite (ave. $\delta^{34}S$ is –17 permil, range is –29 to 1 permil ([n=12], chap. 10) are evidence that microbial sulfate reduction was important during this paragenetic stage, but the ~300°C mineralization temperatures that have been inferred for the formation of the base-metal sulfides within the orebody (chap. 10) is high enough that inorganic sulfate reduction could also have been important (compare Orr, 1974; Kiyosu, 1980; Powell and Macqueen, 1984).

The fluid isotopic compositions implied by the model curves (fig. 12), $\delta^{18}O$=10.4 permil and $\delta^{13}C$=–5.2±1 permil, should be viewed as approximate. They are within the isotopic ranges expected for fluids that had undergone isotopic exchange with the shale + carbonate + basalt stratigraphic package in which the Greens Creek deposit sits, but they do not rule out magmatic fluids associated with the Triassic mafic/ultramafic magmatism in the region.

The isotopic data for Hyd Group and Cannery Formation carbonates are compared with the hanging-wall data in

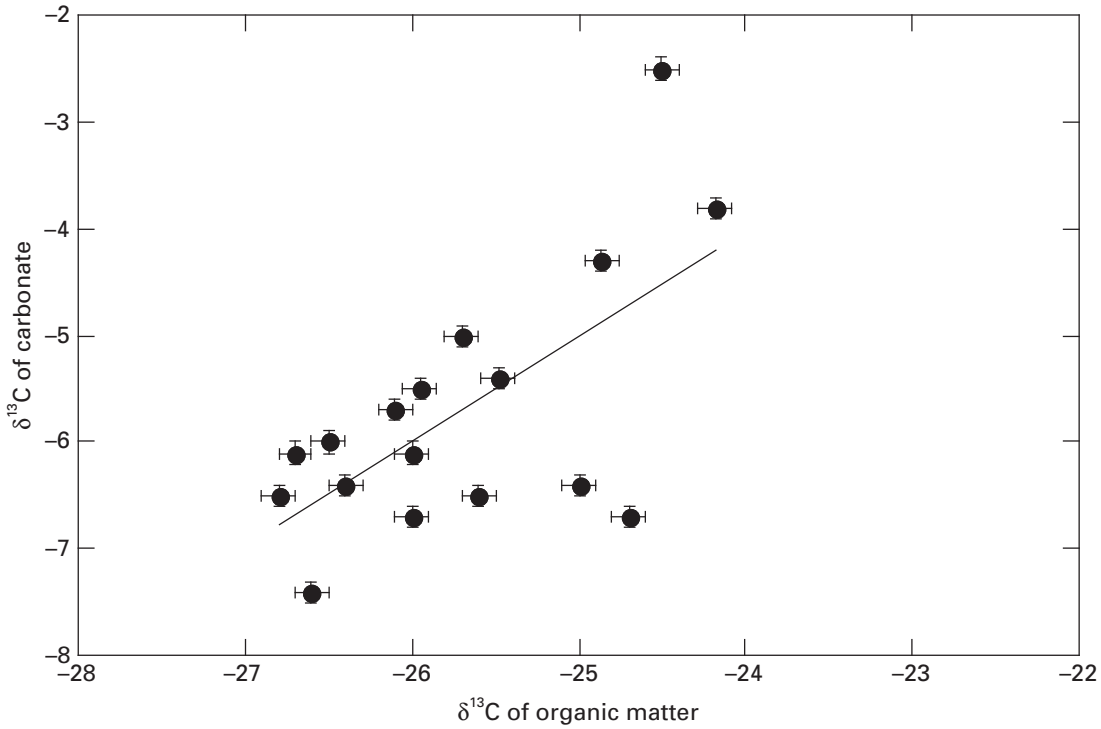

Figure 13. Plot of the carbon isotopic composition of coexisting carbonate and organic matter in hanging-wall rocks. The two parameters show a weak but significant positive correlation (R=0.64).

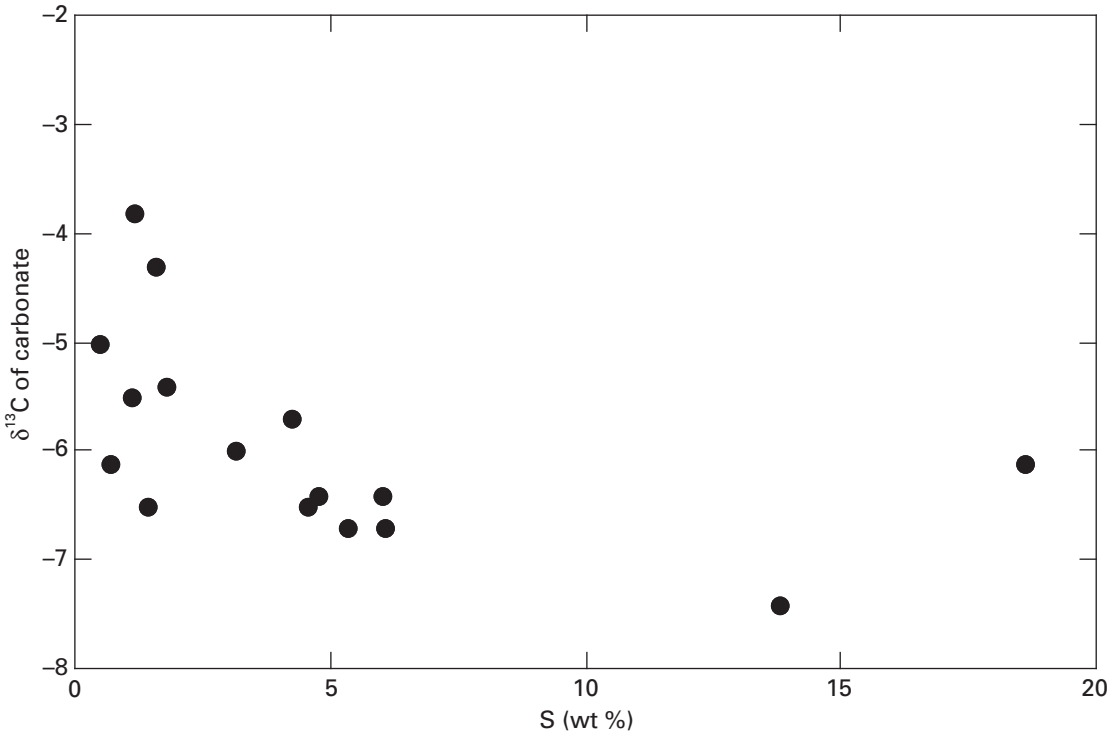

Figure 14. Plot of the carbon (C) isotopic composition of carbonate relative to the sulfur (S) content of hanging-wall rocks. The negative correlation is evidence that the reduction of sulfate to form hydrogen sulfide, which subsequently combined with metals to form sulfide minerals, was accompanied by oxidation of low δ^{13} C organic matter or methane. wt%, weight percent.

figure 11. The Hyd samples conform quite well to the hanging-wall array, but the Cannery Formation samples do not. The implication of the hanging wall–Hyd Group correspondence is that both units were exposed to the same fluid over approximately the same temperature range. This finding is consistent with hydrothermal metal scavenging from the Hyd Group sediments but could also be explained by flushing of Hyd sediments by spent hydrothermal fluids after metals had been precipitated. The absence of obvious metal depletions in the Hyd Group occurrences analyzed for this work would seem to favor the spent hydrothermal fluid alternative. The poor correspondence between the hanging-wall and Cannery data suggests that the hydrothermal fluid did not encounter the Cannery section. The Cannery results also support our conclusion that the carbonate isotopic compositions of Admiralty Island shales were not significantly affected by the Cretaceous metamorphism because the three analyzed samples show neither similar isotopic compositions nor a consistent isotopic trend as they might if isotopic exchange had occurred among minerals or between minerals and fluids during regional prograde heating.

Conclusions

Several conclusions arising from this study have implications for the genesis of the Greens Creek ores. First, large volumes of the hanging-wall sediments experienced epigenetic sulfur addition with associated addition of Ag, As, Au, Cd, Cu, Fe, Mo, Pb, and Zn. However, Co, Cr, Ni, and V show no evidence for similar addition; their abundances appear to be related to the syngenetic accumulation of organic matter.

Second, for at least part of the time that the hanging-wall sediments were accumulating, the overlying water column was oxic, with evidence for possible water column hydrothermal enrichment only in barium. For the remainder of the accumulation history, a hydrothermal component in the overlying water column is neither proved nor disproved. Whatever the exact nature of the overlying water column, there is no clear evidence in the hanging-wall sediments for the basaltic or ultramafic metal source that appears to have been important for the underlying massive sulfide deposit and its alteration envelope in the footwall phyllites.

Third, the isotopic variations of carbonate minerals in both the hanging wall and the white ores are consistent with precipitation from a single hydrothermal fluid over a temperature range of 200 to 350°C, essentially the same temperature range that has been inferred from other observations for formation of the underlying massive ores, or with precipitation from mixed marine and hydrothermal fluids. Whatever the exact dolomite formation mechanism, the close similarity of the compositions in the hanging-wall metasediments and in the white carbonate-rich ores implies deposition from the same fluid by the same mechanism and thus provides strong evidence that hydrothermal

fluid flow at Greens Creek persisted until after the hanging-wall sediments were laid down. The carbonaceous sediment cap may have been an important feature that protected the underlying massive sulfide body from destruction by seawater oxidation.

Fourth, carbonate precipitation was accompanied by, and perhaps driven by, oxidation of organic matter or organic-derived methane. These same reactions resulted in reduction of sulfate to hydrogen sulfide which then reacted with iron and other metals to form sulfide minerals. During growth of framboidal pyrite, sulfate reduction was probably microbially mediated. During formation of base-metal sulfides, sulfate reduction could have proceeded inorganically. Thus, some sulfide minerals, but not necessarily all, formed during early diagenesis beneath the sediment/seawater interface.

Fifth, Hyd Group sediments several kilometers west and northwest of the Greens Creek deposit may have been exposed to hydrothermal fluids either before sulfide mineral precipitation, in which case the fluids may have scavenged metals from Hyd sediments, or after sulfide precipitation from hydrothermal fluids that were spent. The absence of obvious metal depletions in these Hyd rocks suggests that the fluids were spent. Older Cannery Formation shales do not appear to have been exposed to these fluids, although the number of Cannery samples that were studied is too small to exclude this possibility on a regional basis.

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