Strategic and Critical Minerals in the
Midcontinent Region, United States

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Strategic and Critical Minerals in the Midcontinent Region, United States

Edited by WARREN C. DAY and DIANE E. LANE

A. Geology and Mineral Paragenesis of the Pea Ridge
Iron Ore Mine, Washington County, Missouri–Origin of the
Rare-Earth-Element- and Gold-Bearing Breccia Pipes

By LAURENCE M. NUELLE, WARREN C. DAY, GARY B. SIDDER, and
CHERYL M. SEEGER

B. Some Mineralogical and Geochemical Aspects of Middle and Upper
Pennsylvanian Marine Black Shales in Part of the Midcontinent Region

By GEORGE A. DESBOROUGH, JOSEPH R. HATCH, and JOEL S.
LEVENTHAL

C. Mineralogical and Geochemical Analysis of the Metal- and Organic-Rich
Grassy Creek Shale of the New Albany Group (Upper Devonian and
Lower Mississippian) in Hardin County, Southern Illinois

By GEORGE A. DESBOROUGH

U.S. DEPARTMENT OF THE INTERIOR

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Chapter A

Geology and Mineral Paragenesis of the Pea Ridge Iron Ore Mine, Washington County, Missouri— Origin of the Rare-Earth-Element- and Gold-Bearing Breccia Pipes

By LAURENCE M. NUELLE, WARREN C. DAY, GARY B. SIDDER, and CHERYL M. SEEGER

CONTENTS

FIGURES

TABLE

Geology and Mineral Paragenesis of the Pea Ridge Iron Ore Mine, Washington County, Missouri—Origin of the Rare-Earth-Element- and Gold-Bearing Breccia Pipes

By Laurence M. Nuelle[1], Warren C. Day, Gary B. Sidder, *and* Cheryl M. Seeger[1]

Abstract

Breccia pipes containing rare-earth elements (REE) and gold are a potentially significant economic target in the Pea Ridge iron ore mine, Washington County, Missouri. The Pea Ridge deposit is one of eight known volcanic-hosted iron ore deposits in the Middle Proterozoic St. Francois terrane that are similar to the Olympic Dam type of deposits of Australia. The iron orebody is steeply dipping and tabular shaped, and it cuts across the host rhyolite. The footwall of the deposit is zoned from the massive apatite-bearing magnetite core outward to heterolithic breccia, pseudobreccia, a specular hematite zone, and an extensive silicified zone. The hanging wall is zoned from the massive magnetite core outward to heterolithic breccia, pseudobreccia, and an amphibole skarn zone. The REE-rich breccia pipes cut through the various rock types along the footwall at or near contacts. They are typically about 60 m long and 15 m wide, and they extend at least 120 m vertically. The pipes consist of fragments of rhyolite host rock and zones of massive magnetite, specular hematite, and silicified rocks supported in a matrix of rock flour, barite, feldspar, monazite, apatite, chlorite, xenotime, and, locally, gold. Total REE oxide content of samples of the groundmass material, which are not diluted with lithic fragments, average about 20 weight percent. Grades from working faces in the mine are lower, averaging about 12 weight percent. Gold distribution is erratic, but concentrations are as high as 371 parts per million.

The Pea Ridge iron deposit represents an intrusion-type deposit in which the magnetite orebody stoped upward into the host rhyolite and created the various breccia zones around the margins of the deposit. The REE-bearing breccia pipes probably formed from late-stage magmatic-hydrothermal fluids that evolved from the main magnetite orebody. Sanidine phenocrysts (or xenocrysts) in the breccia pipes confirm a magmatic component for their origin. The magmatic-hydro-thermal fluids underwent second boiling and decompression and caused crystallization and release of a volatile phase. Fluid-inclusion evidence of boiling includes a mixed population of vapor-rich fluid inclusions coexisting with liquid-rich inclusions in quartz from the REE-bearing breccia pipes. The concomitant volume increase associated with boiling released significant mechanical energy and caused fracturing and brecciation of the wallrock. The REE-bearing fluid and crystal mixture streamed upward along zones of weakness (faults and contacts), entrained and milled wallrock fragments, and formed the breccia pipes.

The REE- and, locally, gold-bearing breccia pipes associated with the Pea Ridge iron deposit are attractive targets in the midcontinent of the United States for exploration of large deposits of iron, copper, REE, gold, and uranium similar to the Olympic Dam deposit in Australia.

INTRODUCTION

This study of the Pea Ridge mine is part of a 5-year cooperative effort between the Missouri Department of Natural Resources–Geology and Land Survey and the U.S. Geological Survey (USGS) under the USGS Midcontinent Strategic and Critical Minerals Project. One of the overall goals of the cooperative effort is to provide a genetic and predictive model for the possible occurrence of iron, copper, REE, and gold deposits in the midcontinent region that may be similar to the Olympic Dam deposit of Australia (Oreskes and Einaudi, 1990). Initial work centered on the Pea Ridge deposit inasmuch as it offers the most complete lateral and vertical view of this deposit type in the midcontinent region. This report presents observations and hypotheses generated from our mine mapping program. Traverses that cross lithologic contacts and structural features in the mine were selected in order to establish paragenetic relationships and to serve as a base for geochemical and petrographic studies.

GEOLOGIC SETTING

Middle Proterozoic rocks of the St. Francois terrane, which includes rhyolitic ash-flow tuffs, lava flows, and coeval granitic plutons, host Missouri's Precambrian iron ore deposits. Zircon crystals from the granite bodies have yielded U-Pb isotopic ages of 1,480–1,450 Ma (Bickford, 1988). Kisvarsanyi (1980, 1981) recognized three types of granitic rocks in the St. Francois terrane: subvolcanic massifs, ring intrusions, and central plutons (fig. A1). The subvolcanic massifs, which are intrusive equivalents of coeval rhyolitic rocks, are epizonal biotite granite having granophyric and rapakivi textures and containing perthitic alkali feldspar; biotite is the characteristic mafic mineral. Magnetite is a ubiquitous accessory mineral. Ring intrusions, which include intermediate- to high-silica amphibole granite, biotite-hornblende granite, adamellite, and syenite, were emplaced in ring fractures related to caldera collapse and cauldron subsidence. In contrast, central plutons of high-silica, two-mica granite were emplaced in resurgent cauldrons. The central plutons have distinct accessory minerals, such as fluorite, topaz, allanite, monazite, garnet, and cassiterite, and a characteristic trace-element suite that includes elevated abundances of Sn, W, Nb, Y, Be, Li, Rb, Ba, and F. The central plutons have a unique negative magnetic anomaly signature (Kisvarsanyi, 1984; Kisvarsanyi and Kisvarsanyi, 1989). Most authors agree that the magmas were generated from melting of previously accreted crustal material (Nelson and DePaolo, 1985). Kisvarsanyi (1975) proposed that the St. Francois terrane formed in an anorogenic extensional tectonic setting (failed cratonic rift environment), whereas Patchett and Ruiz (1989) suggested that these rocks are not anorogenic, but formed during orogenic-accretionary processes associated with the early stages of the Grenville Orogeny.

The St. Francois terrane hosts eight known magnetite and hematite deposits (fig. A1), which together constitute an iron metallogenic province (Kisvarsanyi and Proctor, 1967; Snyder, 1969). The iron deposits occur as both intrusive and replacement bodies within volcanic rocks of the terrane. The deposits may be genetically related to the host anorogenic rhyolite rocks, as suggested by Day and others (1989) for the Pea Ridge deposit.

The southeastern Missouri iron metallogenic province contains reserves estimated at nearly 1 billion tonnes of iron ore (Arundale and Martin, 1970). Iron ore has been continuously produced from the province since 1815, except for one year during the Great Depression. Until 1963, Precambrian hematite deposits were the major source of iron ore in Missouri; since the opening of the Pea Ridge mine in 1964, all iron ore production has been from subsurface Precambrian magnetite deposits. The Pilot Knob underground mine opened in 1967 and produced slightly more than 9.8 million tonnes of usable iron ore before closing in 1980. Since 1980, the Pea Ridge mine has been the State's
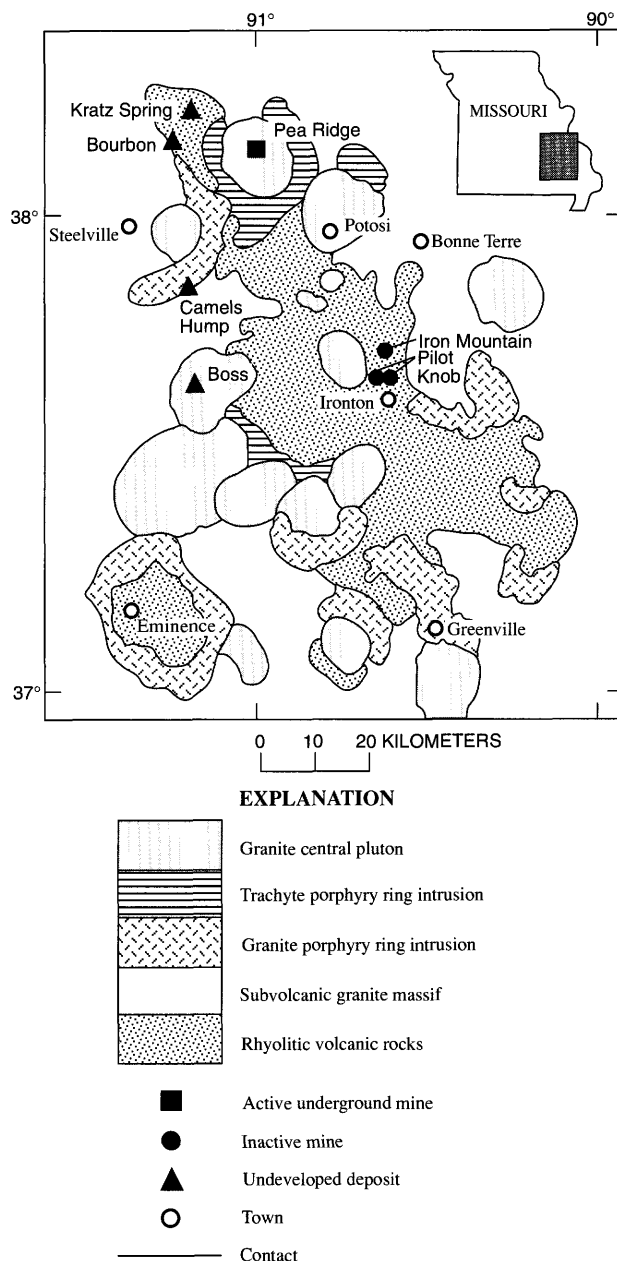
Figure A1. Geologic map of the Middle Proterozoic St. Francois terrane, southeastern Missouri, showing locations of eight known magnetite and hematite deposits (modified after Kisvarsanyi, 1981).

only iron ore producer, and it is the only remaining underground iron mine in the nation. To date, about 41.6 million tonnes of usable iron ore have been produced from the Pea Ridge mine.

GEOLOGY OF THE DEPOSIT

The Pea Ridge magnetite-apatite deposit is a tabular body that is discordant to bedding of the rhyolitic host rocks. The orebody strikes roughly N. 55° E. and dips

75°–90° SE. (Husman, 1989). Xenotime from a quartz vein that cuts the iron ore yielded a U-Pb age of 1.46 Ga (W.R. Van Schmus, University of Kansas, written commun., 1988), which is a minimum age for the deposit; this age is within the age range of 1.45–1.48 Ga for the St. Francois terrane as reported by Bickford and Mose (1975) and Bickford (1988).

Rocks of the Pea Ridge deposit are divided into four zones: (1) the amphibole-quartz zone; (2) the magnetite zone, which is made up of massive magnetite, magnetite-cemented heterolithic breccia, and pseudobreccia; (3) the specular hematite zone; and (4) the silicified zone. Other rock types include magnetite veins, quartz veins, aplite dikes, mafic dikes, and a unique banded rock. REE-bearing breccia pipes cut rocks of the footwall. Figures A2 and A4 present the paragenetic relationships in the deposit, and figure A3 is a geologic map of the 2,275-ft level.

Amphibole-Quartz Zone

The amphibole-quartz zone occurs in both the hanging wall and footwall of the deposit. It consists of massive, coarse-grained actinolite (blades as much as 5 cm long) and interstitial apatite, magnetite, pyrite, chalcopyrite, and calcite. Quartz is present as both interstitial grains and as massive pods 1–50 cm in diameter. From the eastern edge of the deposit westward, the amphibole-quartz zone thins in the hanging wall from massive amphibole-quartz rock into host rock in which fractures are filled with amphibole and have silicified walls (Emery, 1968). Locally, contacts grade into host rhyolite wallrock, which exhibits incipient stages of amphibole replacement. Farther from the contact, veins of magnetite cut massive actinolite. The footwall zone is less brecciated and contains fewer quartz pods than the amphibole-quartz zone in the hanging wall.

This zone represents a skarn alteration front that preceded the emplacement of the magnetite orebody. The protolith of the amphibole-quartz zone is the host rhyolite. Metasomatic replacement of the protolith has partially destroyed obvious textural or chemical evidence of the original rock type. Relict textures of rhyolitic wallrock have been noted in amphibole-quartz fragments along the hanging wall (J.R. Husman, The Doe Run Company, oral commun., 1990).

Magnetite Zone

In previous reports, the magnetite and rhyolite porphyry breccia zones (Emery, 1968) and the magnetite and brecciated wallrock-magnetite zones (Nuelle and others, 1989) were treated separately. However, further mapping and documentation of temporal relations have shown that the massive magnetite orebody and magnetite-bearing breccias were contemporaneous and that it is useful to treat the magnetite orebody as a zone composed of subzones of massive magnetite, magnetite-cemented heterolithic breccia, and pseudobreccia.

Massive Magnetite

Ore faces in the massive magnetite contain as much as 65 volume percent magnetite, with average grades ranging from 47 to 55 percent magnetic iron (Emery, 1968). The texture varies from massive and shiny ore having subconchoidal fracture to finely crystalline and granular. Some ore has a porphyritic texture in which magnetite (or martite after magnetite) and hematite megacrysts are in a massive, fine-grained magnetite groundmass. Gangue minerals in the magnetite ore are predominantly apatite, quartz, pyrite, and monazite, and minor ferroactinolite, biotite, chlorite (after biotite), fluorite, barite, grunerite, and talc (fig. A2). The gangue forms interstitial intergrowths, net-textured veinlets, and pods within the massive magnetite ore.

Magnetite-Cemented Heterolithic Breccia

This breccia is characterized by fragments of host rhyolite, chloritized rhyolite, and rock from the amphibole-quartz zone in a matrix of massive magnetite and (or) hematite. It occurs discontinuously along the margins of the orebody, but is particularly well developed along the hanging wall (fig. A3).

The breccia was formed in a manner similar to an intrusion breccia as described by Laznicka (1988). In situ exfoliation of wallrock fragments, filling of the planes of the exfoliated sheets with magnetite, and the presence of wallrock schlieren suggest that the magnetite ore fluid had rheological properties similar to an intrusive magma.

Pseudobreccia

Laznicka (1988) described one variety of pseudobreccia as being formed by replacement of host rock, which results in a breccialike appearance; the rock fragments are not produced by physical abrasion, nor are they displaced or rotated. The term "pseudobreccia," as used here, is defined as host rhyolite that has been partially to totally replaced by magnetite and (or) hematite along fractures and has a breccialike appearance. The fragments do not appear to have been rotated or mechanically fragmented.

The pseudobreccia has a sharp contact with the magnetite orebody. Along its outer margins, the pseudobreccia grades inward from iron oxide-cemented crackle breccia to iron oxide-cemented mosaic breccia, and then into rubble breccia near the magnetite orebody. Roundness and metasomatic alteration of the rhyolite fragments increases towards the orebody.

	Amphibole-quartz zone	Magnetite zone	Magnetite veins	Specular hematite zone	Silicified zone	Quartz veins	REE-bearing breccia pipes	Quartz veins
Quartz	▬▬▬	▬▬▬		–	▬▬▬	▬▬▬	– – –	▬▬▬
Actinolite	▬▬▬		▬▬▬					
Magnetite	▬▬▬	▬▬▬	▬▬▬			– – –	– –	
Hematite	▬▬▬	▬▬▬		▬▬▬	– – –	– – –	– – – – –	– –
Pyrite	▬▬▬	▬▬▬			– –	– –	– – – –	– –
Chalcopyrite		▬▬▬			– –		– –	▬▬▬
Apatite		▬▬▬	▬▬			– –	– – – – –	– –
Monazite		▬▬▬	– ? –				▬▬▬	
Xenotime						– –	▬▬▬	
Biotite		▬▬▬			– –	– – –	– – – – –	– – –
Chlorite		▬▬▬			▬▬▬	▬▬▬	▬▬▬	▬▬▬
Epidote	– –				▬▬▬	▬▬▬		– –
Muscovite/sericite					▬▬▬	– –		– –
Potassium feldspar					▬▬▬	– –	▬▬▬	– – –
Fluorite		▬			– – –	– –	– – ▬▬	– – –
Barite		▬			– –		▬▬▬	
Tourmaline					– – –		– – – – –	
Rutile					– –		– – – – –	
Calcite	▬	▬			– –	▬▬▬		– –
Grunerite		▬						
Talc		▬						
Anhydrite		▬		–			– – –	

Figure A2. Paragenesis of major and minor minerals in the Pea Ridge mine, Washington County, Mo. Solid line, major deposition; dashed line, minor deposition.

Specular Hematite Zone

The specular hematite (specularite) zone separates the silicified zone from the magnetite orebody along the foot-wall, and rhyolite host rock from the orebody along the eastern edge of the deposit (fig. A3). The width of the zone varies, and it thins with depth (Husman, 1989). Contacts between the specular hematite zone and the magnetite orebody are commonly gradational, and the hematite contains irregularly distributed patches and areas of magnetite. However, the contacts are sharp locally. The specularite is finely to coarsely crystalline, generally platy, compact, and massive. Most of the specularite is an alteration product of magnetite.

Mapping documents that the specular hematite zone in part formed along fault zones and that the width of the
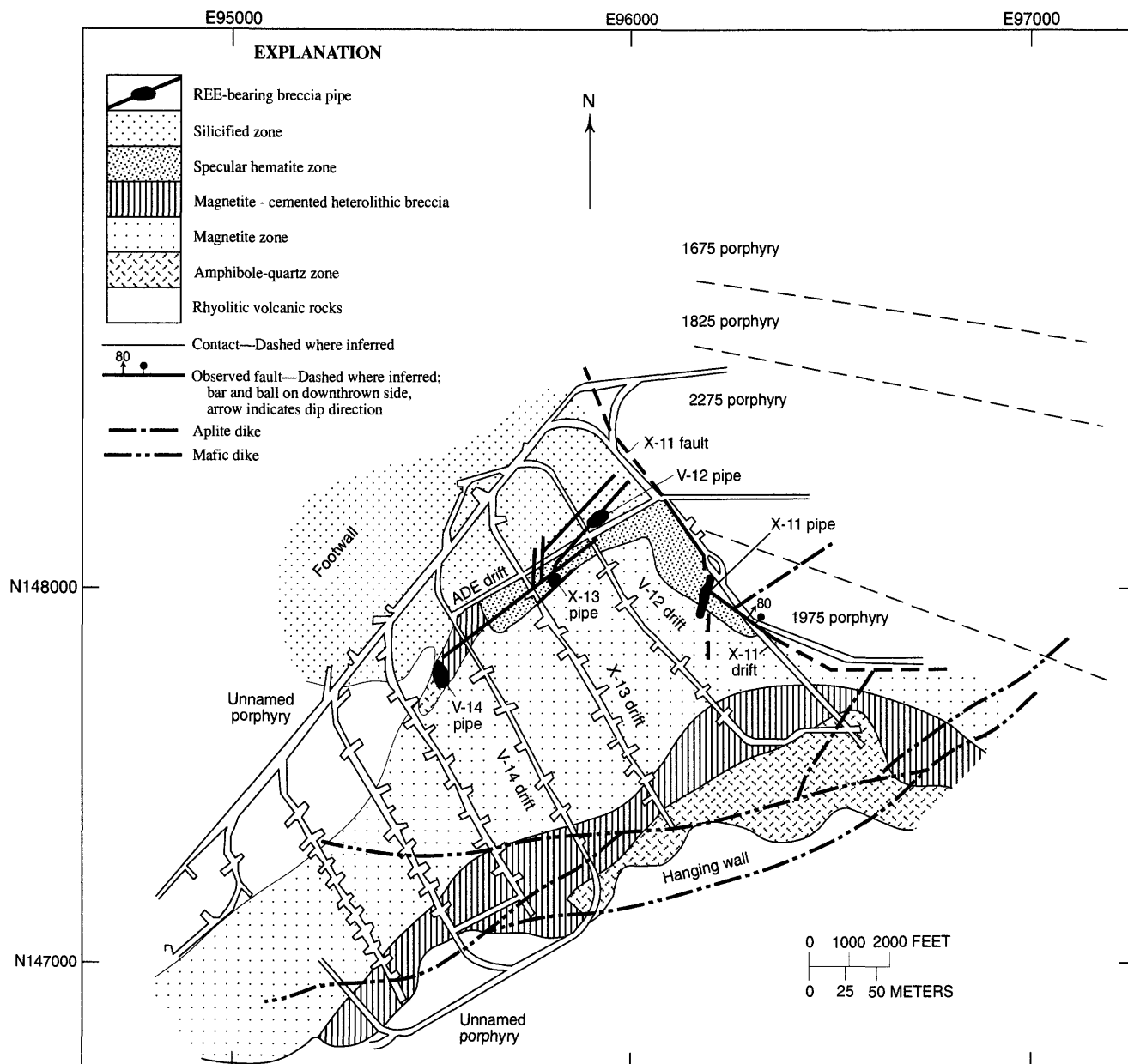
Figure A3. Geologic map of the 2,275-ft level, Pea Ridge mine, Washington County, Mo. (modified after Hussman, 1989).

zone varies proportionally with the width of the fault zones. The specularite is locally sheared and foliated parallel to the orientation of post-ore faults.

Silicified Zone

Silicified wallrock is extensively developed in the footwall (fig. A3). Horizontal underground drilling of the footwall northward away from the orebody on the 2,275-ft level penetrated 120 m of silicified rock without exiting the zone, and surface drill holes more than 400 m north of the
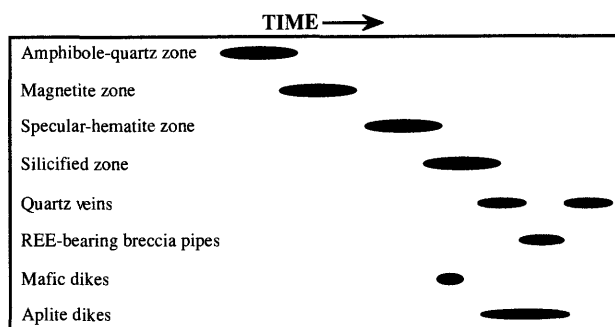
Figure A4. Paragenetic sequence of the rock types in the Pea Ridge mine, Washington County, Mo.

orebody intersected silicified volcanic rock. The silicified zone is characterized by massive, white to light-gray quartz that replaced the host rhyolite wallrock to varying extents; areas that are greater than 75 percent quartz are not uncommon. Potassic alteration associated with silicification included the addition of potassium feldspar to the wallrock. Potassium feldspar flooding converted the grayish or reddish-brown volcanic rocks to bright moderate-reddish-orange rock. Locally, quartz and potassium feldspar form pegmatitic pods and veins. Accessory minerals in the silicified zone include fluorite, muscovite, biotite, tourmaline, chlorite after biotite, epidote, calcite, barite, rutile, pyrite, and chalcopyrite. In addition, Husman (1989) noted monazite, apatite, and topaz.

The silicified zone is a product of both open-space filling and replacement. An increase in the number of fractures from the wallrock into the silicified zone suggests that stockwork fracture systems may have controlled silicification. On the 2,275-ft level, along the X-11 drift, silicification is associated with a high-angle fault. Sericite along fractures and fragment surfaces shows that sericitization accompanied silicification. The silicified zone grades into areas of fracture-fill quartz veins. Silicification also extends several meters into the specular hematite zone. Younger sets of quartz veins cut both the zone and the adjacent wallrock. Relict breccia textures in the silicified zone suggest that brecciated zones were conduits that were later rehealed by silica (Seeger and others, 1989).

Mafic Dikes

Mafic dikes cut across the host rhyolite, the magnetite orebody, and the silicified zone. Contact with the REE-bearing breccia pipes was not observed. The temporal relationship between the mafic and aplite dikes is ambiguous (fig. A4). Emery (1968) observed mafic dikes that are cut by aplite dikes. However, our mapping indicates that a mafic dike also cuts an aplite dike.

The dikes are black to dark greenish gray and have a greasy luster. They range in thickness from less than 1 cm to more than 3 m and occur in two fracture systems. One fracture system strikes N. 60° E. and dips 60°–80° SE., whereas the other strikes N. 85° W. and dips 60°–80° SW. (Emery, 1968).

Pervasive chloritic alteration partially obscures the original composition of the dikes. However, major and trace-element data indicate that the dikes are tholeiitic basalt (W.C. Day, unpub. data, 1990). These dikes are similar to those emplaced throughout the St. Francois terrane during the waning stages of rhyolitic volcanism (Bickford, 1988).

Aplite Dikes

Aplite dikes cut the host rhyolite and the magnetite orebody. Contacts with the REE-bearing breccia pipes are not exposed, and their relative ages are therefore unknown. The mutually crosscutting relation between the aplite dikes and rocks of the silicified zone indicates that their emplacement was coeval (fig. A4).

The dikes have variable dips, and they fill fractures that strike N. 25° W. (Emery, 1968). They consist of potassium feldspar and quartz with minor to trace amounts of biotite, and they have a fine-grained, equigranular (aplitic) to pegmatitic texture. Some dikes grade into quartz veins near their terminations. Some dikes have traces of disseminated molybdenite.

The aplite dikes are alaskitic and are high in SiO_2 (72.0–74.7 weight percent and K_2O (6.7–9.8 weight percent). Geochemical modelling of the trace-element abundances demonstrates that the aplite dikes and the host rhyolite are cogenetic (Day and others, 1989). The crosscutting relations of the aplite dikes with the host rhyolite, the magnetite orebody, and the silicified zone indicate that the magnetite ore was emplaced during the regional Middle Proterozoic igneous activity in the St. Francois terrane.

Banded Rock

Banded rock is a relatively rare rock type in the Pea Ridge deposit. It consists of alternating bands of light-gray and dark-gray minerals. The light-gray bands consist of igneous rock fragments, quartz, and potassium feldspar; the dark bands are martite and chlorite. The bands may represent altered horizons in a bedded volcaniclastic sediment. Beds range in thickness from 1 or 2 mm to several centimeters and exhibit ripple marks and graded beds (Marikos and others, 1989a). The banded rock occurs along the footwall near the contact between the specularite and silicified wallrock. Locally, it has a penetrative fabric, as defined by mineral lineations, and has been deformed by a drag fold along a fault zone (ADE drift, 2,275-ft level; fig. A3). The rock grades into specularite, which suggests that it was part of the host rock sequence that was replaced by magnetite (converted later to martite) during orebody emplacement. The protolith was probably a water-laid pyroclastic airfall tuff deposited as a volcaniclastic intraflow sediment.

REE-Bearing Breccia Pipes

Four REE-bearing breccia pipes have been delineated along the footwall and eastern edge of the 2,275-ft level of the orebody (fig. A3). The pipes are at or near the contacts between the major lithologic zones. The contacts with

rhyolite and rocks of the silicified zone are abrupt and commonly sheeted; those with the specular hematite zone are irregular and embayed. Locally, apophyses of breccia pipes intrude adjacent rocks along fractures.

The pipes dip steeply (>60°) and are elongate to ovoid in plan view. They range in length from several meters to as much as 60 m and have widths as much as 15 m. Their maximum vertical extents are not known, but the X–13 pipe (fig. A3) extends from the 2,675-ft sublevel to at least the 2,275-ft level, a distance of about 120 m.

The breccia pipes contain fragments of rhyolite, magnetite-hematite ore, and rock of the silicified zone in a groundmass predominantly composed of rock flour, feldspar, chlorite, barite, apatite, monazite, quartz, and calcite (fig. A2). The rock-flour consists of milled volcanic wallrock and disaggregated specularite grains. The volcanic rock fragments grade in size from rock-flour to about 0.5 m in diameter. They are reddened, due to potassium feldspar alteration, and have subrounded to angular edges and moderate to high sphericity. The specularite fragments reach several meters in length, are angular, and have low sphericity. Where specularite fragments are prevalent, they form a tight-fitting, fragment-supported breccia having angular voids between fragments. Where wallrock fragments predominate, they are irregularly distributed and are matrix supported.

Most of the breccia pipe material may have been well indurated. For example, the X–11 pipe (fig. A3) has a particularly hard, fine-grained matrix. Other pipes are now friable because of the coarseness and excellent cleavage of potassium feldspar and barite and post-emplacement brecciation.

Geopetal structures within void spaces in one of the REE-bearing breccia pipes indicate that the magnetite deposit has not been tilted significantly since emplacement of the breccia pipes. The geopetal structure on the 2,440-ft level is characterized by horizontally bedded, granulated rock particles that fill the bottom part of the vug and calcite that fills the upper part of the vug.

The relative age of the REE-bearing breccia pipes is poorly constrained. Rhyolite wallrocks, magnetite ore, and rocks of the silicified zone occur as fragments within the pipes. Thus, the breccia pipes were emplaced after formation of the silicified zone. Aplite dikes cut across rocks of the silicified zone; however, relations between the aplite dikes and the breccia pipes have not been observed.

The absolute age of the REE-bearing breccia pipes can be estimated from a U-Pb date on a xenotime crystal in a quartz vein that is cut by a breccia pipe. The xenotime yielded a date of 1.46 Ga (W.R. Van Schmus, written commun., 1988). It occurs both in quartz veins cut by the REE-bearing breccia pipes and in the pipes themselves (fig. A2). Therefore, formation of the REE- bearing breccia pipes was about 1.46 Ga.

Mineralogy and Chemistry

Barite, potassium feldspar, chlorite, monazite, apatite, quartz, and calcite are the most abundant minerals in the pipes; biotite, fluorite, tourmaline, chalcopyrite, and pyrite are accessory minerals. Marikos and others (1989b) reported anhydrite in some pipes. Barite occurs as massive cement and open-space fill; crystals range from 1 mm to as much as 50 cm long. Sanidine and orthoclase are present as fractured and broken euhedral phenocrysts (or xenocrysts) that are as much as 2 cm in diameter. Apatite forms subhedral to euhedral crystals that range in size from 0.5 to 1.0 cm. Quartz forms both rounded and embayed phenocrysts (or xenocrysts) and secondary overgrowths as cement within the groundmass. Areas of broken barite and potassium feldspar record a post-cementation brecciation event.

REE-bearing minerals in the breccia pipes include monazite, xenotime, and rare bastnaesite and britholite(?). Monazite and xenotime occur as 0.5- to 1.0-mm-long crystals in aggregates having a granular texture, as radial crystal aggregates, as acicular crystals that replaced wallrock microfragments, and less commonly as irregular crystals that fill cracks in barite and potassium feldspar.

Swarms of barite and calcite veins and radioactive zones serve as exploration guides to blind pipes. Barite and calcite vein swarms and crackle breccias adjacent to pipes represent extensions of pipe mineralization. The radioactivity results from thorium and uranium associated with the REE-bearing minerals. The breccia groundmass contains notable amounts of thorium and uranium, averaging 3,321 ppm (parts per million) and 189 ppm, respectively (table A1). The thorium-uranium ratio is about 19, whereas the normal crustal ratio is about 4 (Rose and others, 1979).

The breccia pipe groundmass has variable concentrations of the REE. Data listed in table A1 represent grab samples of groundmass material, and as such do not represent average ore grades of the breccia pipes. Total REE oxide concentrations of our samples range from 4.9 to 37.8 weight percent, averaging 20.3 weight percent. In contrast, ore grades determined from bulk samples range from 7 to 25 weight percent and average about 12 weight percent (C.W. Whitten, U.S. Bureau of Mines, oral commun., 1990). The REE-bearing breccias are enriched in the light REE, having a pronounced negative europium anomaly (fig. A5).

Gold is erratically distributed in the breccia pipes. Husman (1989) reported that gold occurs as electrum and sylvanite. Gold concentrations uncommonly exceed 1 ppm, but assays of drill core and chip samples are as high as 371 ppm (Husman, 1989). Our samples have yielded gold values of less than 6 ppb (parts per billion) (table A1). The extremely high concentrations may be due to the "nugget effect," where atypically large grains of gold give a higher assay value than the average for the pipe.

Table A1. Analyses for rare-earth elements (REE), uranium, thorium, and gold in REE-bearing breccia pipes, Pea Ridge mine, Washington County, Mo.

[The REE were determined by the ICP-MS method as outlined by Lichte and others (1987). Uranium and thorium were determined by delayed neutron activation analysis (McKown and Millard, 1987) and gold by graphite furnace (Meier, 1980). <, less than; --, insufficient number of samples above detection limit to calculate meaningful value]

Element	Sample No. (mine level)									Average	Standard deviation
	PR-21 (2,370 ft)	PR-71 (2,370 ft)	PR-72 (2,370 ft)	PR-168 (2,370 ft)	PR-33C (2,440 ft)	PR-33D (2,440 ft)	PR-32 (2,475 ft)	PR-126 (2,675 ft)	PR-127 (2,675 ft)		
					Parts per million						
La	34,000	35,000	22,000	35,000	52,000	18,000	5,700	14,000	12,000	25,300	13,863
Ce	34,000	56,000	33,000	58,000	60,000	29,000	9,500	22,000	20,000	35,722	17,242
Pr	5,400	5,500	3,200	5,800	8,900	2,800	850	2,100	1,900	4,050	2,391
Nd	18,000	19,000	12,000	20,000	31,000	9,700	3,100	7,600	6,700	14,122	8,175
Sm	2,800	2,900	2,100	2,900	4,300	1,500	450	1,200	1,000	2,128	1,140
Eu	420	380	270	360	580	230	51	150	130	286	156
Gd	1,900	1,600	1,700	1,800	2,500	1,200	460	860	680	1,411	622
Tb	360	320	270	350	340	240	68	150	110	245	104
Dy	2,100	1,700	1,500	2,200	1,400	1,700	410	870	630	1,390	594
Ho	400	300	270	450	170	370	86	170	110	258	124
Er	1,200	830	760	1,400	310	1,200	240	530	340	757	409
Tm	190	140	110	240	32	200	33	91	53	121	72
Yb	1,500	990	760	1,800	160	1,600	210	670	390	898	580
U	297	135	192	94	354	284	23	199	121	189	101
Th	4,400	1,940	804	6,160	10,100	2,710	227	1,950	1,600	3,321	2,948
					Weight percent						
RE2O3t*	23.9	29.2	18.2	30.5	37.8	15.8	4.9	11.8	10.3	20.3	10.2
					Parts per billion						
Au	6	<2	<2	2	<4	<4	<4	<2	2	--	--

*Sum of rare earth oxides.

Structure

Faults are a common feature in the mine and appear to have occurred throughout the history of the deposit. Two styles of deformation are present in the deposit. One occurred at the transition between the ductile and brittle deformation regimes, whereas the other was under conditions of brittle deformation. In the former, penetrative fabric defined by mineral lineations, mullions, foliations, and elongation of pseudobreccia fragments is parallel to and within the fault planes. These faults commonly dip at low angles (45° to 60°). Also, on the 2,675-ft sublevel pseudo-breccia fragments are elongated within a fault plane. The ductile-brittle deformation resulted from a transpressional event that affected the host rhyolite, magnetite ore, banded rocks, and mafic dikes.

Brittle deformation is recorded by high-angle faults that produced angular fault breccias and clayey fault gouge along fault planes. An example is the fault on the X-11 drift of the 2,275-ft level (fig. A3), where a high-angle reverse fault roughly parallels the iron ore–wallrock contact. Specular hematite was drag folded and developed foliation parallel to the fault plane.

GENESIS OF THE REE-BEARING BRECCIA PIPES

The REE-bearing breccia pipes are similar to magmatic-hydrothermal breccias related to porphyry-type deposits (Sillitoe, 1985). However, they are not entirely analogous due to the disparity between the two types of ore systems (one is a high-grade magnetite body, whereas the other is a porphyry copper deposit having a low metal content). Nonetheless, the geochemical character and the intimate spatial relation of the REE-bearing breccia pipes with the magnetite ore system implies a genetic link between the two.

Magmatic-hydrothermal breccias are commonly associated with subvolcanic ore deposits. The breccias are a result of fluids that exsolve from water-saturated magmas in subvolcanic or plutonic environments. The exsolved fluids undergo second boiling and decompression as they cool. Burnham (1979, 1985) quantified the process of second boiling as the exsolution of a vapor phase from a water-saturated melt, with the reaction: H_2O-saturated melt = crystals + vapor. The violent rapid expulsion of fluid from magma and the increase of volume due to the expansion and
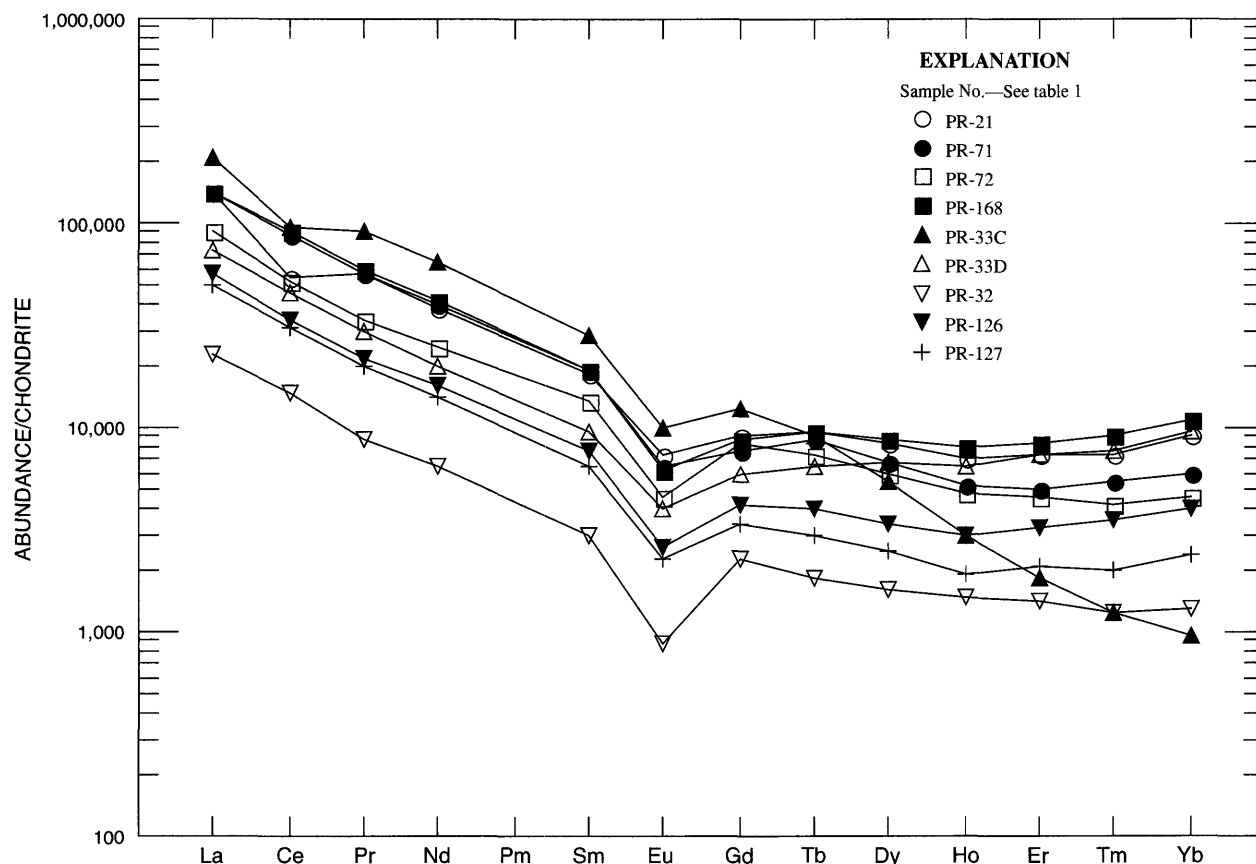
Figure A5. Plot of abundances of rare-earth elements in breccia pipes in the Pea Ridge mine, Washington County, Mo. Abundances normalized to C1 chondrite values of Evensen and others (1978).

subsequent decompression of the vapor phase release sufficient mechanical energy to generate steep tensile fractures in the wallrocks, or reopen existing faults and fractures, and further widen them by hydraulic fracturing of their walls (Burnham, 1985; Sillitoe, 1985). Upward streaming of the magmatic-hydrothermal fluid and vapor results in mixing and milling of fragments, production of rock-flour matrix, and varying degrees of upward transport of material (Sillitoe, 1985).

The REE-bearing breccia pipes were forcefully emplaced into the Pea Ridge magnetite deposit. Rock fragments rounded by abrasion as well as swirl textures of intermixed hematite and rock flour are textural evidence of fluidization during pipe emplacement. Emplacement of breccia pipes appears to have been contolled by lithologic contacts in the footwall along which faults and fractures formed.

According to our proposed magmatic-hydrothermal breccia model, the REE-bearing breccia pipes of the Pea Ridge deposit were emplaced during the waning stages of the magnetite ore system. The magnetite orebody was emplaced as an iron-rich magmatic-hydrothermal fluid. The presence of sanidine phenocrysts (or xenocrysts) confirms a magmatic constituent for the origin of the breccia pipes, and possibly the entire ore system. Late-stage magmatic-

hydrothermal fluids, which exsolved from the iron ore system, were enriched in K, Ba, REE, U, Th, P, SO_2, F, Cl, and Au. The volatile phase released during second boiling provided the mechanical energy for brecciation and fracturing of the wallrocks. The REE-bearing fluids streamed upward into the footwall of the magnetite orebody along fractures, faults, and zones of weakness at lithologic contacts.

The fluids entrained fragments of wallrock, magnetite ore, and rocks of the silicified zone and abraded them during transport. Extreme abrasion resulted in the milling of fragments into rock flour. Some of the pipe-fill minerals may have crystallized during second boiling, including sanidine, orthoclase, barite, monazite, apatite, quartz, and other accessory minerals in the groundmass of the breccia pipes. Evidence for boiling includes populations of both vapor-rich and liquid-rich fluid inclusions coexisting in quartz within the groundmass. Some of the fluids may have circulated in the pipes after boiling and replaced microfragments, cemented rock flour and fragments, and formed crystal-lined vugs.

During formation of the breccia pipes, quartz veins adjacent to the pipes were reopened, and breccia pipe minerals of the same suite were deposited in the reopened veins. In addition, crackle breccias and vein swarms of

barite and calcite formed adjacent to the pipes. Rebrecciated, recemented fragments record more than one brecciation event during the evolution of the magmatic-hydrothermal system.

SUMMARY

The Pea Ridge deposit is a tabular body of magnetite that stoped upward into the host rhyolitic wallrocks. Development of an amphibole-quartz skarn preceded magnetite deposition. The deposit is crudely zoned successively outward from a massive magnetite core to magnetite-cemented heterolithic breccia, to pseudobreccia, and to distal amphibole-quartz skarn. Other rock types include a specular hematite zone along the footwall and eastern edge of the orebody, massively silicified rock of the footwall, banded volcaniclastic rock, aplite dikes, and mafic dikes.

The specular hematite is in part an alteration of magnetite ore and seems to have developed along fault zones. During and after specularite development, the massive silicified zone formed by open-space filling and wallrock replacement; silicification extends into the hematite zone. Fracture-fill veins of quartz continue from the silicified zone into the adjacent altered rhyolite. Potassium feldspar flooding and sericitization accompanied silicification.

Faults occur throughout the orebody. Some faults developed a penetrative fabric that formed in the ductile-brittle transitional regime. A fault zone along the footwall contains two, and possibly three, REE-bearing breccia pipes; another pipe is along a high-angle reverse fault at the eastern edge of the orebody.

Breccia pipes, containing potentially economic concentrations of REE in monazite and xenotime, cut all rock types. The pipes include fragments of volcanic wallrock, silicified rock, and iron ore. Feldspar, quartz, and barite occur as euhedral phenocrysts in chloritic groundmass. Barite also occurs as massive replacement cement and open-space fill. Monazite and xenotime are present as granular crystals in the groundmass, as replacement of microfragments, as radial aggregates of acicular crystals in the groundmass, and as abraded platy grains that appear to have been transported. Total rare-earth oxide content of select grab samples of the breccia pipe groundmass averages 20 weight percent, whereas bulk ore averages about 12 weight percent. Gold is erratically distributed in the pipes; concentrations are not commonly greater than 1 ppm, but assays as high as 371 ppm have been reported.

The REE-bearing breccia pipes formed as magmatic-hydrothermal breccias, which were localized along fractures, faults, and lithologic contacts. Magmatically derived hydrothermal fluids underwent second boiling, during which both vapor-rich and liquid-rich fluid inclusions were trapped in quartz within the groundmass of the REE-bearing breccia pipes. Euhedral crystals of barite and other accessory minerals may have formed during second boiling. The sanidine phenocrysts (or xenocrysts) indicate that the breccia pipes had a magmatic component. Release of the vapor phase during boiling resulted in fracturing at lithologic contacts. Fluidization, coupled with the upward streaming of magmatic-hydrothermal fluids, resulted in the widening of the fractures and faults and in the brecciation of the wallrock. After boiling, some fluids may have circulated in the pipes and replaced rock microfragments and rock flour, cemented the pipes, and formed crystal-lined vugs.

ACKNOWLEDGMENTS

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Chapter B

Some Mineralogical and Geochemical Aspects of Middle and Upper Pennsylvanian Marine Black Shales in Part of the Midcontinent Region

By GEORGE A. DESBOROUGH, JOSEPH R. HATCH, and
JOEL S. LEVENTHAL

CONTENTS

FIGURES

TABLES

Some Mineralogical and Geochemical Aspects of Middle and Upper Pennsylvanian Marine Black Shales in Part of the Midcontinent Region

By George A. Desborough, Joseph R. Hatch, *and* Joel S. Leventhal

Abstract

This study assesses the regional variations in mineralogy and metal content of thin (<1 m) marine black shales of Middle (Desmoinesian) and Upper (Missourian and Virgilian) Pennsylvanian age in the midcontinent region. It can be inferred that the ratios of illite to kaolinite, albite to potassium feldspar, frequency of occurrence of gypsum, and frequency of occurrence of apatite are probably a function of distance from shoreline or are related to proportion of detrital contributions. The distribution of kaolinite, potassium feldspar, and gypsum seem to reflect a detrital origin, whereas the distribution of illite, albite, and iron-rich chlorite indicates an authigenic or diagenetic origin.

Although the relative positions with regard to shoreline are given, it is very well known that these black shales were deposited in deep water during maximum stands of sea level in the midcontinent region; thus those referred to as nearer shoreline were probably several hundred kilometers from the shoreline.

For Middle Pennsylvanian marine black shales the samples from Iowa have lower ratios of illite to kaolinite and a higher proportion of gypsum than do samples from farther south and west, in Missouri, Kansas, and Oklahoma. This is apparently due to the detrital origin of kaolinite and gypsum from a shoreline or nearshore source to the northeast or north of Iowa. The Iowa samples also have a lower ratio of albite to potassium feldspar than do samples from farther south, in Missouri and Oklahoma, because of the detrital origin of potassium feldspar.

The concentrations of both molybdenum and vanadium are much greater in the samples from Iowa than in the samples from the areas to the south and southwest. This is consistent with previous suggestions that these metals tend to be more concentrated in areas closer to shoreline. The concentration of nickel, in most cases, seems to be related more to the content of organic matter than to any other factor.

For the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone, the patterns of ratios of illite to kaolinite and albite to potassium feldspar and the frequency of occurrence of gypsum are similar to the patterns shown by the Middle Pennsylvanian black shales. The average concentrations of both molybdenum and vanadium in the Stark Shale Member are higher in samples from Iowa and northeastern Kansas than in those from western Kansas and in northern Oklahoma.

INTRODUCTION

This study was conducted as part of the U.S. Geological Survey Midcontinent Strategic and Critical Minerals Project. This report is an outgrowth of a study of Middle and Upper Pennsylvanian black shales of the midcontinent selected for their possible nonfuel mineral resource potential. We studied 150 core samples from 12 black shale members of Middle Pennsylvanian (Desmoinesian) and Upper Pennsylvanian (Missourian and Virgilian) age in the midcontinent region to determine their mineralogical and geochemical characteristics (table B1). The general characteristics and environment of deposition of these thin (<1 m), deep-water (maximum submergence of the craton) shales were described by Heckel (1977), who concluded that they were deposited during maximum marine encroachment.

These marine black shales represent 12 "Kansas-type" cyclothems (Weller, 1958) that are present in the region studied. Many of the samples investigated during this study were described previously and their organic geochemical data were reported (Stanton and others, 1983; Hatch and others, 1984).

The purpose of the present investigation is to determine whether (1) mineralogy of the samples can be used to discern subtle differences in depositional environments, (2) what effects diagenesis had on the samples, and (3) whether mineralogical and diagenetic differences might relate to metal content and amount and type of organic matter. Specifically, we wanted to show that such mineralogical and geochemical differences over a large surface area were related to facies differences. Due to extremely small grain size, x-ray diffraction methods were used to quantify the mineralogical contents of the samples. Their finely laminated character results in considerable inhomogeneity of both minerals and organic matter on a fine scale.

In a study of the equivalents of the Mecca Quarry Shale Member of the Carbondale Formation of Illinois (see table B1), Coveney and others (1987) reported distinctive geochemical differences in the nearer shore facies. They reported that the nearer shore facies contains more terrestrial organic matter than did more distal age-equivalent strata, and that the nearer shore facies has a higher concentration of molybdenum, vanadium, uranium, selenium, and antimony. Previous studies of Pennsylvanian black shales have not included systematic study of bulk mineralogy to see if, and how, it relates to metals and organic matter. Mineralogical x-ray diffraction parameters are given in table B2; results are given in tables B3 and B4.

DEPOSITION AND DIAGENESIS

Albite in all the studied samples was formed by authigenic or diagenetic growth. There is no known detrital source (for example, trondhjemite) that could have provided a consistent and sufficient source of albite without the additional supply of significant amounts of potassium feldspar (for example, granitic sources), which was not detected in 55 percent of the samples. The potassium feldspar was either derived from igneous or metamorphic cratonic areas (Canadian shield) or perhaps from reworking of older Paleozoic or Proterozoic clastic rocks to the northeast or from the lower or Morrowan and Atokan parts of the Fountain Formation in Colorado, which is arkosic (for black shales in western Kansas). Thus, the relative proportions of albite and potassium feldspar indicate an authigenic source for albite and a chiefly detrital origin for potassium feldspar.

Both illite and kaolinite are relatively abundant in all samples. Kaolinite in the low-temperature environment is normally developed from weathering in acidic (low pH) environments, such as peat bogs or swamps containing a substantial amount of humic material. In contrast, at low temperatures illite tends to be stable or form in nearly neutral or slightly alkaline environments. Because marine sediments generally undergo diagenesis under nearly neutral or slightly alkaline conditions due to buffering by calcite and dolomite, kaolinite in these strata is probably of

detrital origin, having been transported from humic organic sources near the shoreline and deposited as a flocculent in a marine environment. Illite is presumed to be chiefly diagenetic or an authigenic product developed from alteration of detrital aluminosilicates in a marine environment.

Iron-rich chlorite is not stable under highly oxidizing conditions in low-temperature environments. The occurrence of iron-rich chlorite in more than 90 percent of the samples indicates an environment of reducing, or nonoxidative, conditions; thus, chlorite is a late diagenetic mineral in these strata, taking up the iron that was available after the formation of pyrite.

Because gypsum develops only in relatively oxygenated environments, the presence of gypsum in samples is inconsistent with development in an anoxic environment that contains authigenic and diagenetic pyrite and iron-rich chlorite. The gypsum, therefore, was probably deposited from terrestrial or nearshore marine environments.

Siderite is found chiefly in those shales that Heckel (1977) called "near-shore" shales, although some is found in what he called "offshore" shales. Because siderite occurs in samples that have an anomalously low hydrogen content in the organic matter, it probably developed as a result of methanogenesis (bacterial oxidation of organic matter). In this process the organic matter is converted to methane and carbon dioxide. Whereas siderite is abundant in these strata, pyrite is sparse or absent, and total sulfur is very low because it was oxidized and removed in solution before diagenesis.

DISTRIBUTION OF MAJOR AND MINOR MINERALS IN BLACK SHALES OF THE DESMOINESIAN AND MISSOURIAN PENNSYLVANIAN STRATA IN PART OF THE MIDCONTINENT REGION

Figure B1 shows the localities for 85 upper Middle Pennsylvanian (Desmoinesian) black shale core samples from 10 areas and a summary of some of the mineral ratios and percentages of samples in which gypsum and apatite occur. Only those black shales considered by Heckel (1977) to be "offshore" shales were used for this illustration. Ratios of greatest concentrations of illite to kaolinite (ill/kao), albite to potassium feldspar (albite/Kf), and calcite to dolomite (cal/dol) are given for each of the 10 areas. These ratios are based on the means of each sample set. Examination of the illite- to-kaolinite ratios reveals a significant increase from Iowa south to Oklahoma and western Kansas. In addition, illite-to-kaolinite ratios increase from eastern to western Oklahoma. From this increase we infer that the kaolinite was derived chiefly from a source area north and east of the study area during Desmoinesian time.

Ratios of albite to potassium feldspar are somewhat similar; there is a great increase in the ratio from south-

EXPLANATION

No. of samples/No. of sites

ill/kao ─ % with gypsum
alb/Kf ─ % with apatite
cal/dol

0   100 MILES
0   100 KILOMETERS

IOWA

26/5
1.1 ┬ 58%
2.7 ┼ 92%
1.8

NEBRASKA
KANSAS

COLORADO

2/1
1.9 ┬ 0%
1.7 ┼ 100%
1.5

4/2
1.3 ┬ 50%
7.0 ┼ 75%
6.9

3/1
2.4 ┬ 0%
1.5 ┼ 100%
1.5

6/6
2.0 ┬ 50%
3.6 ┼ 83%
2.5

10/2
1.3│0%
100│90%
1.7

2/1
2.9 ┬ 0%
100│50%
0.7

OKLAHOMA

7/2
1.5 ┬ 0%
16 ┼ 100%
1.2

13/3
1.5 ┬ 0%
26 ┼ 85%
1.9

TEXAS

MISSOURI
ARKANSAS

ILLINOIS

12/7
1.5 ┬ 8%
27 ┼ 83%
1.3
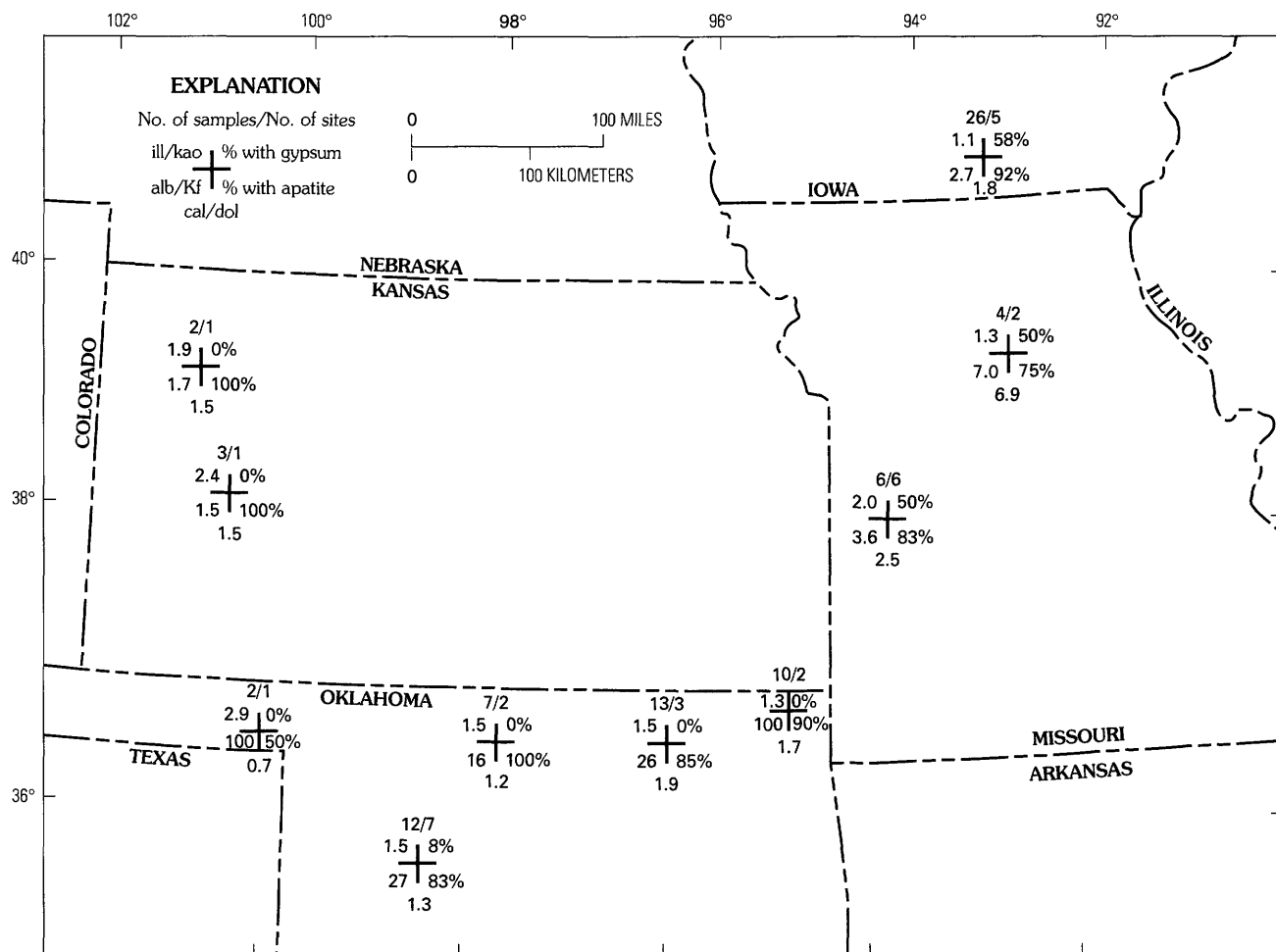
Figure B1. Average ratios of illite to kaolinite (ill/kao), albite to potassium feldspar (alb/Kf), and calcite to dolomite (cal/dol), and percentages of samples containing gypsum and percentages of samples containing apatite for 85 samples of Middle Pennsylvanian (Desmoinesian) marine black shales from 10 areas in southern Iowa, Missouri, northern Oklahoma, and western Kansas.

central Iowa to northern Oklahoma, and in many samples from northern Oklahoma potassium feldspar is not detectable (for these a value of alb/Kf of 100 was arbitrarily assigned). These relations are taken to indicate that the chiefly detrital potassium feldspar was derived from areas north and east of the western interior basin during the Desmoinesian. The intermediate ratios of albite to potassium feldspar in western Kansas may reflect in part contributions of potassium feldspar from the ancestral Rocky Mountain uplift 350 km to the west in Colorado, which shed large quantities of arkosic material (lower part of Fountain Formation) to the east.

The distribution of the percent of samples containing detectable gypsum decreases significantly from Iowa and Missouri to northern Oklahoma and western Kansas; this is consistent with the interpretation that gypsum was detrital and was derived like kaolinite and potassium feldspar from a source to the northeast of the study area.

The percentage of samples containing detectable apatite increases from Iowa and Missouri to western

Kansas, but the differences in the percentages for samples from Iowa and Missouri are not significantly different from some areas of northern Oklahoma. The greater percentages of samples containing apatite in western Kansas and Oklahoma are consistent with deposition in deeper water more remote from shoreline .

Ratios of calcite to dolomite are highest in central Missouri and decrease significantly westward and southward into western Kansas and northern Oklahoma, respectively. This is consistent with an authigenic or diagenetic origin for dolomite in the southwestern midcontinent and a largely detrital origin for calcite in the northeastern midcontinent. The greater ratio of magnesium to calcium at places more distal from shoreline is also consistent with a marine (algal) origin for the magnesium in the dolomite.

These relations are consistent with a northeasterly source of very fine grained detrital material that contributed sediments to the marine environment of the western interior basin during late Middle Pennsylvanian (Desmoinesian) time.
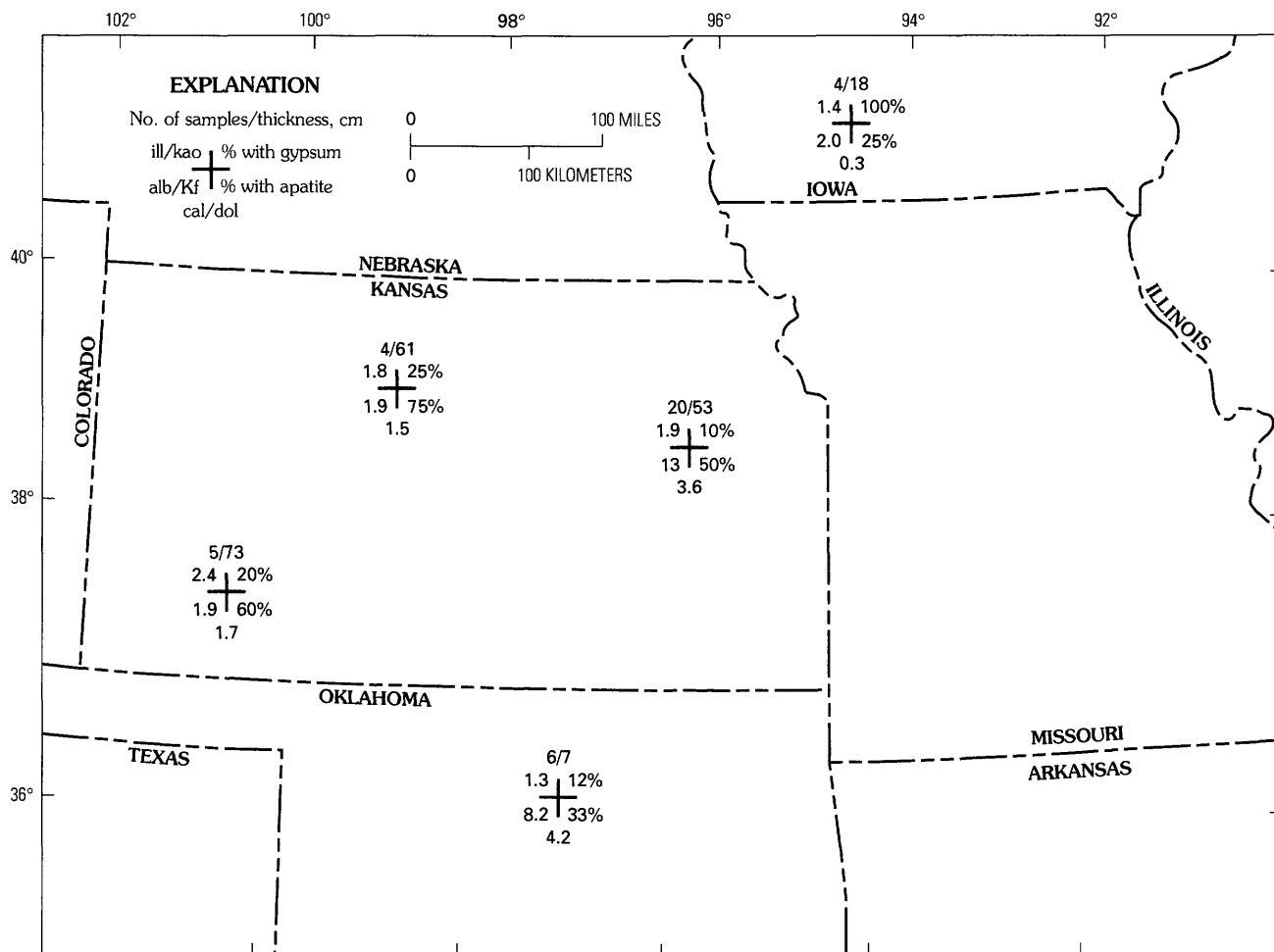
Figure B2. Thickness and average ratios of illite to kaolinite (ill/kao), albite to potassium feldspar (alb/Kf), and calcite to dolomite (cal/dol), and percentages of samples containing gypsum and percentages of samples containing apatite for 39 samples of the Upper Pennsylvanian (Missourian) Stark Shale Member of the Dennis Limestone from six areas in southern Iowa, Kansas, and Oklahoma.

Only 57 samples from the Upper Pennsylvanian Missourian black shales were available for study; 39 of these are from the Stark Shale Member in Iowa, Kansas, and Oklahoma. Figure B2 shows the mean values for mineral ratios, the percentages of samples containing gypsum and apatite, and the thickness of the Stark Shale Member for six drill holes in southwestern Iowa and in Kansas and Oklahoma. The thickness of the Stark Shale Member is about three-fold greater in Kansas than it is in Iowa. The ratio of illite to kaolinite increases substantially from Iowa to southwestern Kansas, but this ratio is lowest in northern Oklahoma. The ratio of albite to potassium feldspar is greatest in eastern Kansas and northern Oklahoma, but it is the same in Iowa and western and northern Kansas. The ratio of calcite to dolomite increases significantly from Iowa to Kansas, and this ratio is greatest in eastern Kansas and northern Oklahoma; these relations are different from those observed for the Middle Pennsylvanian (Desmoinesian)

strata (fig. B1). Gypsum is present in all samples from southwestern Iowa, but it is least abundant in eastern Kansas and northern Oklahoma. The percentage of samples containing apatite increases significantly from Iowa to Kansas; however, the percentage of samples containing gypsum in northern Oklahoma is similar to the Iowa samples.

Only seven samples of the Upper Pennsylvanian Virgilian black shales from three localities in southwestern Iowa were available for study; these included the Larsh Shale Member of the Deer Creek Limestone, Queen Hill Shale Member of the Lecompton Limestone, and the Heebner Shale Member of the Oread Limestone. The maximum thickness of these black shales is less than 15 cm for cores from southeastern Iowa (P.H. Heckel, written commun., 1982). Six of these (86 percent) contained gypsum, five of seven (71 percent) contained siderite, and only one contained apatite, suggesting a nearshore environment.

Figure showing map with data points:

102° 100° 98° 96° 94° 92°

EXPLANATION

No. of samples/No. of sites

Mo, ppm | V, ppm
Cr, ppm + Ni, ppm
C, organic
weight %

0   100 MILES
├──────────┤
0   100 KILOMETERS

NEBRASKA
KANSAS

COLORADO

40°

25/5
170 | 1251
729 + 243
15.1

IOWA

38°

2/1
40 | 465
305 + 131
5.1

3/1
30 | 163
385 + 180
6.9

4/2
40 | 461
381 + 95
16.1

ILLINOIS

5/5
30 | 716
684 + 218
10.0

10/2
27|307
325|164
9.5

2/1
34 | 640
715|225
10.0

OKLAHOMA

7/2
16 | 261
467 + 271
11.6

13/3
20 | 265
148 + 173
7.2

MISSOURI

ARKANSAS

TEXAS

36°

12/7
16 | 210
300 + 190
6.9

Figure B3. Average concentrations of molybdenum, vanadium, chromium, nickel, and organic carbon for 83 samples of Middle Pennsylvanian (Desmoinesian) marine black shales from 10 areas in southern Iowa, Missouri, northern Oklahoma, and western Kansas. Samples are from same set plotted on figure B1; ppm, parts per million.

DISTRIBUTION OF SELECTED MINOR ELEMENTS AND ORGANIC CARBON IN MIDDLE AND UPPER PENNSYLVANIAN BLACK SHALES IN THE WESTERN MIDCONTINENT REGION

Concentrations of major, minor, and trace elements in about 160 samples of Middle and Upper Pennsylvanian black shales are given in tables B5–B8. Figure B3 shows the average concentrations of molybdenum, vanadium, chromium, nickel, and organic carbon for 83 samples of Middle Pennsylvanian (Desmoinesian) "offshore" shales (Heckel, 1977) for 29 localities in 10 areas of Iowa, Missouri, Kansas, and Oklahoma. These are the same areas for which mineral proportions of these samples are given on figure B1.

Figure B3 shows that the average value for molybdenum in samples from Iowa (170 ppm, or parts per million) is four to eight times greater than in samples from areas in Missouri, Kansas, and Oklahoma. The high concentrations of molybdenum in samples of the Middle Pennsylvanian

Mecca Quarry Shale Member in Indiana and Illinois were attributed by Coveney and others (1987) to near-shore proximity of the depositional setting. Our interpretation of the relative depositional settings, based on mineral ratios and relative abundances of gypsum and apatite in our suite of samples, is in agreement with Coveney and others (1987).

The average vanadium value for Middle Pennsylvanian black shales is significantly higher (1,251 ppm) in southern Iowa than in Missouri (588 ppm), Kansas (314 ppm), and Oklahoma (336 ppm). Average vanadium values for samples from the Oklahoma panhandle (640 ppm) are two to three times higher than for samples from other areas (210–307 ppm) in Oklahoma. The lower values of vanadium are generally, but not in all cases, associated with samples that have a low content of organic matter.

The average value of chromium is highest (715 ppm) in samples from the Oklahoma panhandle and lowest (148 ppm) in samples from an area of Osage County in northeastern Oklahoma. The average concentrations of chromium (fig. B3) do not appear to follow any systematic
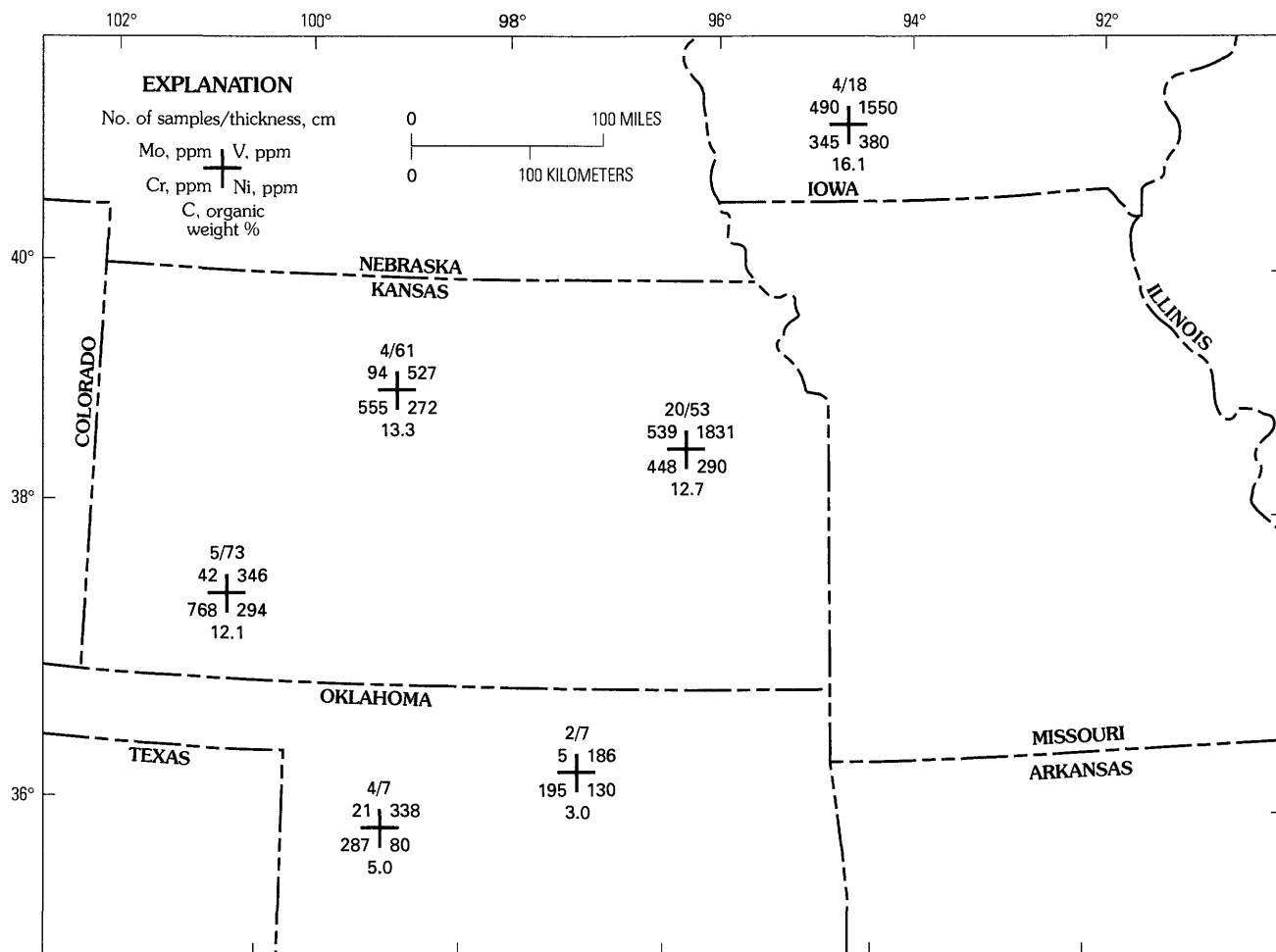
Figure B4. Thickness and average concentrations of molybdenum, vanadium, chromium, nickel, and organic carbon for 39 samples of the Upper Pennsylvanian Stark Shale Member of the Dennis Limestone (Missourian) from six areas in southern Iowa, Kansas, and Oklahoma. Samples are from same set plotted on figure B2; ppm, parts per million.

pattern on either a local or regional basis in these Middle Pennsylvanian black shales. The range in six of the average chromium values is comparable to those reported by Coveney and others (1987) for the Mecca Quarry Shale Member in Indiana and Illinois, but the values of organic carbon are much lower for samples from our study area.

The average values for nickel (fig. B3) have an approximately twofold variation that does not appear to be related to average values of organic carbon content. The values are highest for samples from northwestern and north-central Oklahoma, but these values are not significantly higher than for samples from southern Iowa. The lowest average values are for samples from strata having an average organic carbon content of less than 10 weight percent.

The average values of organic carbon are highest for samples from southern Iowa and north-central Missouri (fig. B3). The highest values for samples from elsewhere are for north-central Oklahoma; the lowest values are for northwestern Kansas.

Tables B7 and B8 give the concentrations of selected major, minor, and trace elements in Middle and Upper Pennsylvanian black shales from southern Iowa, Kansas, and northern Oklahoma, including samples of eight black shales of Missourian and Virgilian ages (table B1). Data for thickness and average values of molybdenum, vanadium, chromium, nickel, and organic carbon for the Stark Shale Member of the Dennis Limestone at one locality in southwestern Iowa, three localities in Kansas, and two localities in northern Oklahoma are summarized on figure B4.

The average concentration of molybdenum decreases tenfold from Iowa to southwestern Kansas (fig. B4); this relationship is consistent with much lower concentrations of molybdenum in areas more distal from shoreline for Middle Pennsylvanian strata studied here and those studied by Coveney and others (1987).

Average concentrations of vanadium are highest in eastern Kansas and southern Iowa, but the total amount (concentration × thickness) of vanadium at the eastern Kansas locality is two to three times more than that at the other localities (fig. B3).

Average chromium concentrations increase twofold from southern Iowa to southwestern Kansas in the Stark Shale Member, whereas the total amount (concentration × thickness) in the interval is almost ten times higher in southwestern Kansas than it is at the Iowa locality. While the average value for chromium does not correlate with total organic carbon, it probably correlates with the amount of marine (as opposed to terrestrial) organic matter. It is noteworthy that the most chromium in the Stark Shale Member occurs in the area considered most distal from shoreline, a conclusion based on mineral ratios and apatite and gypsum occurrences (fig. B3).

The average nickel concentrations in the Stark Shale Member are greatest in Iowa, but the total amount (concentration × thickness) of nickel is three times more in southwestern Kansas due to the greater thickness of the interval. The average values for nickel correlate with the amount of organic carbon (fig. B4).

The average concentration of organic carbon is highest in Iowa, but the total amount in southwestern Kansas is three times greater than the Iowa locality due to greater thickness of the Stark Shale Member in southwestern Kansas (fig. B4).

Average values for 16 black shale samples from the seven other black shale members of the Upper Pennsylvanian (table B8) in southern Iowa are molybdenum, 463 ppm; vanadium, 1,445 ppm; chromium, 330 ppm; nickel, 418 ppm; and organic carbon, 13.7 percent. These values are very close to the average values for the Stark Shale Member in Iowa (fig. B4).

DISCUSSION AND SUMMARY

Mineral assemblages in samples of these marine strata cannot be considered in terms of conventional equilibrium relations because some minerals are detrital (for example, gypsum, potassium feldspar, kaolinite, calcite, and quartz) and others are authigenic (illite, albite, apatite, pyrite, iron-rich chlorite, and siderite). Because of the intimate mixtures of the very fine grained minerals with organic matter (kerogen), mineral-water equilibrium reactions are substantially retarded or impeded. In addition, lamination of minerals and organic matter inhibits vertical water-mineral interactions. These circumstances lead to

micro-environments having different "equilibrium" conditions on a millimeter scale that generally are not indicated by a sample a few centimeters thick.

It is not clear whether the type of organic matter (humic or algal) has any influence on the metals that become concentrated in these black shales. We believe the concentrations of metals such as vanadium, chromium, nickel, molybdenum, selenium, and uranium may depend chiefly on highly reducing conditions that may be influenced by influx of fresh water from land.

The mineralogical data presented herein are taken to indicate that detrital material originated from a northerly source during deposition of the Middle and Upper Pennsylvanian black shales. However, a significant amount of the minerals present in the black shales is of authigenic or diagenetic origin.

Table B1. Stratigraphic position and age of units studied in survey of mineralogy and geochemistry of Middle and Upper Pennsylvanian black shales in the midcontinent region

[Modified from Heckel, 1977]

UPPER PENNSYLVANIAN
Virgilian Series
Larsh Shale Member of the Deer Creek Limestone
Queen Hill Shale Member of the Lecompton Limestone
Heebner Shale Member of the Oread Limestone
Missourian Series
Eudora Shale Member of the Stanton Limestone
Quindaro Shale Member of the Wyandotte Limestone
Muncie Creek Shale Member of the Iola Limestone
Stark Shale Member of the Dennis Limestone
Hushpuckney Shale Member of the Swope Limestone
MIDDLE PENNSYLVANIAN
Desmoinesian Series
Anna Shale Member of the Pawnee Limestone
Little Osage Shale Member of the Fort Scott Limestone
Excello Shale Member of the Fort Scott Limestone
Mecca Quarry Shale Member equivalents in Missouri, Kansas, and Oklahoma

Table B2. X-ray diffraction peaks used for estimation of relative abundances of minerals other than quartz in Pennsylvanian shales

Mineral	hkl	d-value used (Å)	Approximate 2θ° (CuKα)	Lowest percentage identifiable (Carroll, 1970, table 12)
Iron-rich chlorite . .	001	14.1-14.2	6.2	10
Illite	001	10.2	8.7	5
Gypsum	020	7.56	11.7	Not reported
Kaolinite	001	7.15	12.4	5
Albite	002	3.186-3.198	27.90-28.00	5
Potassium . . . . feldspar	040, 002	3.220-3.250	27.45-27.70	5
Calcite	104	3.03	29.5	5
Dolomite	104	2.88	30.96	1
Apatite	112	2.79	32.05	Not reported
Siderite[1]	104	2.79	32.05	Not reported
[2]Pyrite-py1	002	2.71	33.16	Not reported
[3]Pyrite-py2	021	2.42	37.15	Not reported

[1]Siderite cannot be detected in minor amounts due to interference of apatite.

[2]This line of pyrite is coincident with the second strongest line (202) of apatite. This line is not reported for samples containing detectable apatite.

[3]This line was measured for all samples because there are no interferences with other minerals.

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Weller, J.M., 1958, Cyclothems and larger sedimentary cycles of the Pennsylvanian: Journal of Geology, v. 66, p. 195–207.

Table B3. Organic carbon content and x-ray diffraction intensity data for minerals, except quartz, in samples of Middle Pennsylvanian (Desmoinesian) black shales from the midcontinent

[C%, weight percent organic C; ill, illite; kao, kaolinite; a, albite; k, potassium feldspar; cal, calcite; dol, dolomite; ap, apatite; py2, line of pyrite measured for all samples because there are no interferences with other minerals; gy, gypsum; sid, siderite; chl, chlorite; py1, line of pyrite that is coincident with second strongest line (202) of apatite (line not reported for samples containing detectable apatite); M, major mineral having peak intensity greater than 100; --, not detected or not measured due to interference; n.d., not determined; data are reported relative to 100 percent peak intensity for quartz]

Sample No.	C%	ill	kao	a	k	cal	dol	ap	py2	gy	sid	chl	py1
			MIDDLE PENNSYLVANIAN SHALES FROM SOUTH-CENTRAL IOWA										
			SE1/4SW1/4 sec. 36, T. 75 N., R. 20 W., Marion County										
41-1	4.0	21	9	11	--	30	12	15	0	3	--	6	0
41-13f	7.9	33	34	24	--	0	0	0	7	0	11	7	12
41-17	24.8	22	33	11	--	27	11	26	7	8	--	5	--
41-31	5.8	29	51	11	8	0	0	14	6	3	--	0	--
41-37a	1.7	34	74	11	--	0	8	0	5	0	10	6	7
41-37b	3.8	17	52	7	--	10	0	0	10	0	15	0	16
			SW1/4SE1/4 sec. 36, T. 70 N., R. 19 W., Appanoose County										
22-6d	16.4	25	20	11	--	60	22	12	9	7	--	6	--
22-11	18.7	19	14	12	7	16	14	24	4	3	--	4	--
22-14	4.3	20	10	9	6	6	5	34	2	0	--	6	--
22-22c	4.8	37	30	23	10	0	0	0	6	0	10	7	9
22-22e	25.1	31	36	9	10	20	15	10	8	0	--	6	--
22-32a	1.1	46	56	13	9	10	6	0	4	4	--	1	6
22-32b	10.6	30	38	11	8	16	16	11	7	5	--	4	--
			Core CP78-1; NE1/4 sec. 12, T. 70 N., R. 22 W., Wayne County										
CP784A	18.7	18	21	13	7	21	20	7	0	5	--	5	--
CP784B	27.6	21	14	10	5	21	24	43	3	4	--	6	--
CP7813B	6.5	28	21	16	11	0	0	18	0	0	0	4	--
CP7813D	23.7	14	15	7	9	8	24	3	0	0	0	5	--
CP7826	7.5	27	36	18	10	0	18	8	10	0	0	9	--
CP7828A	16.4	14	22	9	0	25	7	58	4	3	0	3	--
CP7828B	21.5	21	23	13	6	0	0	10	8	7	--	6	--
CP7828C	29.1	12	7	8	6	41	6	53	5	0	0	3	--
CP7828D	19.3	23	17	8	4	32	14	19	6	6	--	6	--
			Core CP 53; NE1/4SE1/4NE1/4 sec. 1, T. 71 N., R. 18 W., Monroe County										
			Excello Shale Member										
CP534A	1.4	24	23	9	7	8	41	28	0	0	--	17	--
CP534B	3.8	18	8	7	5	0	0	35	0	0	--	5	--
			Mecca Quarry Shale Member equivalent										
CP5312A	7.1	27	24	27	5	29	5	8	11	4	--	8	--
CP5312B	6.7	21	19	12	4	13	0	0	3	0	0	7	13
CP5312C	3.6	12	14	6	--	47	0	0	45	6	0	12	M
CP5312D	17.2	19	21	9	6	15	0	17	7	5	0	7	--
CP5312E	26.0	19	15	5	6	15	22	6	5	0	0	6	34
CP5312F	27.0	19	10	7	4	50	7	52	0	3	0	6	--
			Whitebreast coal										
CP5313Z	56.1	0	9	0	--	M	0	0	7	0	0	8	13
CP5313Y	48.5	7	10	0	--	M	0	0	11	5	0	0	27
CP5313A	50.1	0	21	--	7	55	0	0	11	0	6	0	16
			MIDDLE PENNSYLVANIAN SHALES FROM MISSOURI										
			SW1/4SW1/4 sec. 23, T. 65 N., R. 18 W., Putnam County										
Anna	n.d.	21	14	8	--	20	27	48	4	3	--	4	--
			NW1/4NE1/4 sec. 19, T. 56 N., R. 16 W., Chariton County										
BM14-2	23.1	21	13	9	--	73	14	49	6	0	--	5	--
BM14-3	15.0	16	15	13	--	M	12	0	12	5	6	4	19

Sample No.	C%	ill	kao	a	k	cal	dol	ap	py2	gy	sid	chl	py1
NW1/4NW1/4 sec. 4, T. 54 N., R. 14 W., Randolph County													
BM2-3	5.2	48	36	23	—	23	6	14	7	5	—	11	—
BM2-5	21.2	19	14	6	7	24	0	21	5	0	—	4	—
NW1/4NW1/4 sec. 25, T. 46 N., R. 27 W., Johnson County													
MC105-2	9.6	22	24	13	—	13	19	36	3	0	—	8	—
MC105-6	3.8	45	13	14	10	0	0	18	0	0	—	6	—
SW1/4SW1/4 sec. 9, T. 44 N., R. 26 W., Johnson County													
MC86-2	9.2	29	10	11	10	13	12	30	6	3	—	7	—
MC86-5	2.9	50	45	17	9	6	0	0	9	10	15	12	12
SW1/4SE1/4 sec. 7, T. 45 N., R. 25 W., Johnson County													
MC204-5A	2.6	5	3	3	—	M	13	0	5	0	5	0	5
SW1/4 sec. 1, T. 40 N., R. 32 W., Bates County													
MC121-2	19.7	34	16	15	—	30	14	35	6	4	—	6	—
MC121-5	1.7	19	10	12	—	M	16	0	4	0	—	6	—
SW1/4 sec. 29, T. 39 N., R. 30 W., Bates County													
MC142-3	6.0	30	38	8	—	0	0	0	10	7	7	5	17
NE1/4SE1/4 sec. 35, T. 37 N., R. 30 W., Vernon County													
MC168-4	2.4	55	59	15	—	0	0	0	0	0	26	12	6
MC168-5	18.0	33	20	17	—	14	10	23	6	10	—	6	—
MC168-7	1.7	34	32	10	14	0	0	0	0	0	30	7	0
MIDDLE PENNSYLVANIAN SHALES FROM SOUTHEASTERN KANSAS													
SW1/4SE1/4 sec. 8, T. 32 S., R. 22 E., Cherokee County													
6-1	9.4	27	17	14	—	75	19	11	9	0	—	7	—
6-12	8.5	29	37	15	—	38	14	15	10	0	—	9	—
6-27	3.0	40	64	12	—	0	0	0	5	0	23	9	—
MIDDLE PENNSYLVANIAN SHALES FROM WESTERN KANSAS													
Crist B-1; sec. 32, T. 20 S., R. 34 W., Scott County, southwestern Kansas													
CR4613.5	11.2	18	9	9	9	17	40	24	11	0	0	5	—
CR5614.5	8.7	20	6	7	11	32	45	12	6	0	0	7	—
CR4620.5	0.8	12	6	13	7	M	16	4	10	0	0	12	—
Knudson A core; sec. 16, T. 7 S., R. 32 W., Thomas County, northwestern Kansas													
KNUD4477	2.6	13	7	5	4	M	60	3	7	0	0	6	—
KNUD4480	7.6	17	9	5	7	70	50	10	9	0	0	9	—
MIDDLE PENNSYLVANIAN SHALES FROM NORTHEASTERN OKLAHOMA													
NE1/4SE1/4 sec. 30, T. 29 N., R. 18 E., Craig County													
1535u-5	9.5	27	18	18	—	26	14	16	9	0	—	6	—
1535u-23a	7.6	11	6	7	—	M	M	0	6	—	0	3	10
1535u-25	11.0	30	12	20	—	15	12	9	9	0	—	5	—
1535-7	14.8	15	8	12	—	0	10	16	12	0	—	0	—
1535-12	4.7	44	33	15	—	68	14	8	12	0	—	10	—
1535-23	7.2	32	31	14	—	36	27	9	7	0	—	5	—
1535-25	14.6	35	24	13	—	18	14	27	16	0	—	7	—
1535-66	7.9	25	31	12	—	0	0	77	6	0	—	6	—
1535-78	10.3	25	29	9	—	0	0	0	33	0	8	6	58
1535-144	1.7	38	56	11	12	0	0	0	6	0	39	7	8
1535-159	2.7	69	98	21	—	0	0	0	0	0	22	14	6
NE1/4NW1/4 sec. 4, T. 23 N., R. 10 E., Osage County													
1051-49	3.0	21	12	13	—	M	29	6	9	0	—	4	—
1051-50	11.9	25	15	15	—	0	23	11	20	0	—	5	—

Table B3. Organic carbon content and x-ray diffraction intensity data for minerals, except quartz, in samples of Middle Pennsylvanian (Desmoinesian) black shales from the midcontinent--Continued

Sample No.	C%	ill	kao	a	k	cal	dol	ap	py2	gy	sid	chl	py1
NW1/4NW1/4 sec. 12, T. 27 N., R. 6 E., Osage County													
1044-19	3.5	33	19	29	--	64	27	6	8	0	--	7	--
1044-32	9.9	16	9	17	--	11	25	17	13	0	--	5	--
1044-38	4.1	29	20	13	--	M	15	0	12	0	--	6	--
1044-46	5.5	19	19	13	--	M	23	5	12	0	--	7	--
1044-47	15.2	26	22	13	--	23	23	35	12	0	--	6	--
1044-97	4.7	27	51	11	--	0	0	0	11	0	17	3	18
1044-111	2.0	27	48	12	--	0	0	0	5	0	17	4	7
MIDDLE PENNSYLVANIAN SHALES FROM NORTHEASTERN OKLAHOMA													
NW1/4NW1/4 sec. 34, T. 25 N., R. 3 E., Osage County													
1065-2a	2.4	30	11	32	--	57	29	0	8	0	7	5	13
1065-2b	7.3	32	15	25	--	40	25	7	7	0	--	6	--
1065-6a	8.1	26	14	20	--	0	17	9	6	0	--	6	--
1065-6b	11.6	17	9	12	--	2	22	23	11	0	--	4	--
1065-15	10.0	28	22	22	--	31	19	12	10	0	--	5	--
1065-20	1.3	43	32	26	10	47	13	0	7	0	19	6	13
1065-22	1.5	42	48	25	--	0	0	0	3	0	13	8	6
1065-23	3.5	27	35	12	--	55	14	0	12	0	5	7	14
1065-39	1.1	47	49	13	9	13	12	13	0	0	--	7	--
1065-48	1.2	31	64	21	--	0	0	0	0	0	9	10	--
MIDDLE PENNSYLVANIAN SHALE SAMPLES FROM WESTERN OKLAHOMA													
Core 1580; sec. 2, T. 23 N., R. 12 W., Alfalfa County													
5991	16.8	17	9	21	5	0	14	4	10	0	0	5	--
6039.5	3.4	19	14	15	--	M	18	4	0	0	0	8	--
6040.3	8.1	35	26	23	7	0	18	8	6	0	0	10	--
6041.2	15.2	23	15	18	--	20	41	18	5	0	0	6	--
Core 1683; sec. 4, T. 25 N., R. 8 W., Grant County													
5166.7	7.4	20	17	15	7	40	22	12	7	0	0	4	--
5206.8	12.5	25	14	15	6	48	34	19	8	0	0	7	--
5222.7	17.9	34	20	18	--	0	27	6	7	0	0	8	--
Core 600; sec. 31, T. 17 N., R. 5 W., Kingfisher County													
6471	11.5	52	24	21	10	0	0	9	0	5	0	9	--
6487.5	1.6	43	43	54	7	0	0	13	0	0	0	9	--
Core 330; sec. 28, T. 13 N., R. 23 W., Roger Mills County													
12,165	1.9	25	16	25	6	34	35	5	8	0	0	6	--
12,174	3.7	23	14	27	8	44	26	5	4	0	0	5	--
Core 698; sec. 11, T. 17 N., R. 20 W., Dewey County													
9503	5.8	19	11	31	--	6	16	7	2	0	0	3	--
9504	10.7	16	12	40	--	0	6	0	17	0	0	5	28
Core 707; sec. 18, T. 17 N., R. 20 W., Dewey County													
9807	2.3	18	14	15	7	M	22	3	5	0	0	5	--
9813	3.4	21	17	24	8	36	35	7	8	0	0	6	--
Core 1609; sec. 13, T. 13 N., R. 6 W., Canadian County													
7331	12.3	9	6	8		33	13	68	20	0	0	4	--
Core 1567; sec. 11, T. 13 N., R. 6 W., Canadian County													
7402.2	8.4	13	7	8	4	47	27	67	14	0	0	4	--
7402.4	14.9	22	12	28	5	0	17	0	14	0	0	4	20
Core 497; sec. 18, T. 14 N., R. 12 W., Blaine County													
9704	5.7	13	5	15	3	0	26	57	10	0	0	4	--
Core 333A; sec. 25, T. 2 N., R. 27 E., EMC, Beaver County													
6893	10.7	18	6	14	--	8	20	60	11	0	0	4	--
6894	9.4	26	9	24	7	22	24	0	18	0	0	7	31

Table B4. Organic carbon content and x-ray diffraction intensity data for minerals, except quartz, in samples of Upper Pennsylvanian black shales from the midcontinent

[C%, weight percent organic C; ill, illite; kao, kaolinite; a, albite; k, potassium feldspar; cal, calcite; dol, dolomite; ap, apatite; py2, line of pyrite measured for all samples because there are no interferences with other minerals; gy, gypsum; sid, siderite; chl, chlorite; py1, line of pyrite that is coincident with second strongest line (202) of apatite (line not reported for samples containing detectable apatite); M, major mineral having peak intensity greater than 100; --, not detected or not measured due to interference; data are reported relative to 100 percent peak intensity for quartz]

Sample No.	C%	ill	kao	a	k	cal	dol	ap	py2	gy	sid	chl	py1
UPPER PENNSYLVANIAN BLACK SHALES FROM IOWA													
Core IBCD (Bedford core); sec. 4., T. 67 N., R. 34 W., Taylor County													
Larsh Shale Member of the Deer Creek Limestone (4.5-4.9 ft)													
A	19.5	29	15	15	—	20	13	0	10	6	6	8	14
B	9.8	24	23	24	9	21	17	0	11	4	6	6	18
C	20.7	21	12	18	—	9	10	17	6	5	—	6	—
Queen Hill Shale Member of the Lecompton Limestone (102.1-102.5 ft)													
A	10.1	37	21	23	—	35	10	0	11	7	7	9	18
B	21.0	32	17	18	7	27	17	0	8	7	8	7	13
C	5.2	34	24	26	8	26	7	0	8	4	6	9	14
Core IHC (Hillsdale/Buffington); sec. 22, T. 72 N., R. 42 W., Mills County													
Heebner Shale Member of the Oread Limestone (6.2-6.6 ft)													
D249924	16.9	20	13	16	8	60	38	0	12	0	0	5	15
Eudora Shale Member of the Stanton Limestone (100.2-100.5 ft)													
D249925	15.2	23	14	13	10	0	24	48	7	6	—	4	—
Quindaro Shale Member of the Wyandotte Limestone (166.1-166.4 ft)													
A1	5.7	36	23	31	13	5	14	0	10	7	7	7	15
B1	16.8	31	12	14	11	8	10	0	6	7	8	6	12
C1	7.5	33	19	28	12	8	12	0	10	4	7	6	15
Stark Shale Member of the Dennis Limestone (218.2-218.5 ft)													
I	4.4	35	17	20	13	50	25	0	0	0	6	8	6
Core ISC (Stanzel Qy); sec. 5, T. 75 N., R. 29 W., Madison County													
Quindaro Shale Member of the Wyandotte Limestone (36.9-37.3 ft)													
A2	5.2	28	20	30	—	36	8	0	9	0	7	9	19
B2	16.4	25	9	18	—	11	10	0	0	12	6	9	7
Muncie Creek Shale Member of the Iola Limestone (56.9-57.3 ft)													
D249928	1.2	14	22	33	10	0	0	15	3	0	—	11	—
Core IJCL (Jefferson Qy, lower); sec. 17, T. 77 N., R. 31 W., Adair County													
Stark Shale Member of the Dennis Limestone (51.6-52.2 ft)													
2A	18.4	22	18	13	8	17	52	0	11	8	0	6	17
2B	11.8	22	15	15	8	20	80	8	9	7	—	8	—
2C	23.3	22	16	15	9	12	64	0	11	6	0	4	17
2D	11.0	24	18	23	7	14	44	0	8	6	6	7	13
Hushpuckney Shale Member of the Swope Limestone (85.3-85.5 ft)													
A	27.3	24	16	14	7	31	27	0	14	11	7	8	—
B	21.4	28	20	17	—	33	26	0	12	10	5	6	—
UPPER PENNSYLVANIAN BLACK SHALES FROM KANSAS													
SE1/4SE1/4SW1/4 sec. 2, T. 6 N., R. 27 W., Sheridan County													
Muncie Creek Shale Member of the Iola Limestone (3,708-3,708.5 ft)													
406A	3.0	31	22	30	12	42	30	0	0	0	7	9	0
SW1/4SE1/4SW1/4 sec. 16, T. 9 S., R. 16 W., Rooks County													
Muncie Creek Shale Member of the Iola Limestone (3,293.7-3,294.1 ft)													
506MC	10.6	29	22	23	—	30	15	0	11	0	7	8	13

Table B4. Organic carbon content and x-ray diffraction intensity data for minerals, except quartz,in samples of Upper Pennsylvanian black shales from the midcontinent--Continued

Sample No.	C%	ill	kao	a	k	cal	dol	ap	py2	gy	sid	chl	py1
Stark Shale Member of the Dennis Limestone (3,362-3,364 ft)													
506SA	16.0	29	15	24	10	19	28	20	3	0	--	7	--
506SD	16.4	21	13	11	8	26	17	10	11	0	--	4	--
506SF	4.0	17	8	8	6	M	43	0	8	5	5	6	--
506SG	16.7	25	14	19	9	34	31	12	7	0	--	7	--
Hushpuckney Shale Member of the Swope Limestone (3,389.5-3,392 ft)													
506HA	1.1	33	16	16	11	80	43	11	6	0	--	8	--
506HB	2.5	32	15	20	15	19	43	24	5	3	--	8	--
506HC	2.5	15	7	11	--	25	25	11	3	0	--	5	--
Cen., NW1/4NW1/4 sec. 30, T. 30 S., R. 33 W., Haskell County													
Stark Shale Member of the Dennis Limestone (4,533-4,535.4 ft)													
2A,1-5	9.6	24	9	22	11	14	12	0	10	5	7	6	18
8-9	10.2	19	10	16	9	27	16	19	9	0	--	5	--
10-12	12.8	23	9	18	10	23	16	9	9	0	--	5	--
13-15	13.6	23	11	18	8	28	18	12	9	0	--	7	--
16-19	14.4	29	11	17	10	33	13	0	11	0	8	5	14
A-1 Holmdan 1, Rawlins County													
Stark Shale Member of the Dennis Limestone (interval unknown)													
D249932	0.2	26	14	22	9	72	33	10	0	0	--	8	--
UPPER PENNSYLVANIAN BLACK SHALES FROM OKLAHOMA													
Core 1389; sec. 5, T. 28 N., R. 1 W., Kay County (interval unknown)													
1389C	4.2	22	19	16	5	15	0	0	14	0	0	6	22
1389E	1.8	34	29	13	6	4	6	0	6	8	0	10	8
Core 508; sec. 1, T. 17 N., R. 51 W., Dewey County (interval unknown)													
508B	1.4	17	13	17	--	51	11	4	5	0	0	4	--
508C	2.9	17	12	18	--	36	15	0	4	0	0	3	6
508D	2.9	13	8	12	--	M	8	0	4	0	0	9	6
508E	12.9	17	12	14	--	38	18	5	14	0	0	7	--

Table B5. Selected major and minor elements in Middle Pennsylvanian (Desmoinesian) black shales from the midcontinent

[Organic carbon and sulfur analyzed with Leco WR-12 and Leco IR-32 determinators, respectively; other elements determined by inductively coupled plasma method; all in weight percent]

Sample No.	Org. C	Al	Fe	Mg	Ca	Na	K	Ti	P	S
MIDDLE PENNSYLVANIAN BLACK SHALES FROM SOUTH-CENTRAL IOWA										
Core CP78-1; NE1/4 sec. 12, T. 70 N., R. 22 W., Wayne County										
CP784A	18.7	6.4	3.2	1.4	2.2	0.30	2.2	0.31	0.18	1.4
CP7813B	6.5	7.9	3.1	1.3	2.0	.48	3.0	.32	.83	0.5
CP7813D	23.7	5.5	4.9	1.4	1.5	.25	2.0	.27	.02	3.3
CP7826	7.5	7.7	5.3	1.5	1.8	.68	2.7	.37	.21	1.6
CP7828A	16.4	5.7	2.6	1.1	9.7	.48	1.9	.21	3.60	1.0
CP7828C	29.1	2.8	2.5	0.6	8.7	.26	1.0	.11	3.10	2.0
MIDDLE PENNSYLVANIAN BLACK SHALES FROM WESTERN KANSAS										
Crist B-1; sec. 32, T. 20 S., R. 34 W., Scott County										
CR4613	11.2	4.9	3.2	2.7	6.9	.61	2.5	.21	2.20	3.2
CR4614	8.7	5.2	2.4	2.6	4.7	.59	2.6	.21	.70	1.4
CR4620	.8	5.9	3.3	4.3	6.6	1.0	2.2	.30	.12	1.5
Knudson A core; sec. 16, T. 7 S., R. 32 W., Thomas County										
KNUD4477	2.6	4.9	2.6	3.5	9.3	.49	2.1	.21	.16	1.1
KNUD4480	7.6	5.1	3.0	3.3	7.3	.46	2.4	.22	.71	1.6
MIDDLE PENNSYLVANIAN BLACK SHALES FROM WESTERN OKLAHOMA										
Core 1580; sec. 2, T. 23 N., R. 12 W., Alfalfa County										
5991	16.8	6.8	3.6	1.8	.8	.89	2.0	.30	.13	1.4
6039	3.4	6.5	2.8	2.3	9.3	.85	2.0	.25	.07	1.0
6040	8.1	7.5	3.6	2.3	1.5	.91	2.3	.31	.32	1.0
6041	15.2	5.2	3.4	2.3	6.9	.58	1.6	.21	2.00	1.3
Core 1683; sec. 4, T. 25 N., R. 8 W., Grant County										
5166.7	7.4	6.9	4.0	2.3	5.6	.87	1.8	.25	.99	1.6
5206.8	12.5	5.7	3.5	2.3	8.0	.63	1.9	.19	1.90	1.2
5222.7	17.9	6.2	3.6	2.0	1.0	.70	2.1	.28	.10	1.5
Core 600; sec. 31, T. 17 N., R. 5 W., Kingfisher County										
6471	11.5	9.6	3.1	1.1	.1	.66	3.0	.40	.02	1.0
6487.5	1.6	7.6	4.3	1.0	.3	.95	1.9	.39	.07	.4
Core 330; sec. 28, T. 13 N., R. 23 W., Roger Mills County										
12,165	1.9	8.0	4.5	1.7	4.7	.80	2.9	.38	.07	1.5
12,174	3.7	8.0	3.7	1.7	4.0	.83	2.9	.37	.07	1.1
Core 698; sec. 11, T. 17 N., R. 20 W., Dewey County										
9503	5.8	8.9	3.9	1.7	1.7	1.10	2.7	.39	.23	1.4
9504	10.7	7.9	5.1	1.4	.6	1.10	2.2	.39	.12	3.0
Core 707; sec. 18, T. 17 N., R. 20 W., Dewey County										
9807	2.3	7.7	3.5	1.8	7.9	.83	2.4	.34	.06	1.0
9813	3.4	7.9	3.9	1.9	4.2	.95	2.6	.34	.25	1.4
Core 1609; sec. 13, T. 13 N., R. 6 W., Canadian County										
7331	12.3	4.5	4.7	1.4	13	.63	1.4	.14	4.70	4.0
Core 1567; sec. 11, T. 13 N., R. 6 W., Canadian County										
7402.2	8.4	4.4	3.5	1.4	13	.56	1.4	.15	4.5	2.6
7402.7	14.9	7.5	4.0	1.6	1.0	.95	2.4	.35	.09	2.3
Core 497; sec. 18, T. 14 N., R. 12 W., Blaine County										
9704	5.7	6.4	3.3	1.3	9.9	.75	2.1	.18	4.40	2.3
Core 333A; sec. 25, T. 2 N., R. 27 E., EMC, Beaver County										
6893	10.7	5.8	2.9	1.7	11	.82	2.2	.24	4.70	2.2
6894	9.4	7.3	4.6	2.2	3.2	.95	2.9	.35	.31	3.6

Table B6. Selected minor and trace elements in Middle Pennsylvanian (Desmoinesian) black shales from the midcontinent

[Selenium was determined by energy dispersive analysis; other elements were determined by optical-emission spectroscopy. N, "nearshore" facies of Heckel (1977); others are "offshore" of Heckel (1977). Ag, As, Ba, Cd, and Sr were not determined for some samples; --, not determined. All in parts per million except P, which is in weight percent; <, less than]

Sample No.	Ag	As	Ba	Cd	Cr	Mo	Ni	Se	Sr	V	Zn	P
MIDDLE PENNSYLVANIAN BLACK SHALES FROM SOUTH-CENTRAL IOWA												
SE1/4SW1/4 sec. 36, T. 75 N., R. 20 W., Marion County												
41-1	--	--	--	--	541	70	180	25	--	1,690	1,140	0.86
41-13f	--	--	--	--	185	<10	130	10	--	439	320	.24
41-17	--	--	--	--	570	420	100	170	--	1,790	4,510	1.33
41-31	--	--	--	--	241	50	110	10	--	231	130	1.10
41-37a	--	--	--	--	136	<10	70	<10	--	147	60	.13
41-37b	--	--	--	--	143	10	90	10	--	145	50	.13
SW1/4SE1/4 sec. 36, T. 70 N., R. 19 W., Appanoose County												
22-6d	--	--	--	--	590	80	60	70	--	465	50	.94
22-11	--	--	--	--	486	170	80	70	--	1,180	1,770	1.75
22-14	--	--	--	--	914	60	170	30	--	1,390	410	2.58
22-22c	--	--	--	--	206	<10	130	<10	--	458	330	.13
22-22e	--	--	--	--	637	450	120	190	--	2,330	15,400	.44
22-32a	--	--	--	--	143	<10	80	<10	--	188	140	.10
22-32b	--	--	--	--	480	20	250	50	--	304	250	.60
Core CP78-1; NE1/4 sec. 12, T. 70 N., R. 22 W., Wayne County												
CP784A	2	30	220	26	500	260	400	135	120	670	510	--
CP784B	4	20	150	235	1160	105	390	145	180	1,020	7,120	--
CP7813B	14	30	260	<2	960	800	280	80	150	620	430	--
CP7813D	4	90	160	<2	360	170	150	120	110	1,600	110	--
CP7826	3	20	300	2	140	9	190	15	140	400	410	--
CP7828A	2	10	160	6	460	5	210	25	320	160	690	--
CP7828B	4	20	205	20	780	120	375	105	120	1,170	1,150	--
CP7828C	8	20	95	240	860	310	420	215	300	3,200	10,000	--
CP7828D	5	30	185	95	640	225	320	170	205	2,040	2,400	--
Core CP 53; NE1/4SE1/4NE1/4 sec. 1, T. 71 N., R. 18 W., Monroe County												
Excello Shale Member												
CP534A	<2	<10	260	<2	760	4	170	<10	145	220	280	--
CP534B	<2	<10	255	<2	1,240	10	205	<10	150	2,230	695	--
Mecca Quarry Shale Member equivalent												
CP5312A	<2	20	290	4	230	5	160	<10	180	455	485	--
CP5312B	<2	20	305	4	230	4	145	<10	175	460	575	--
CP5312C	3	120	295	2	105	20	290	<10	150	155	120	--
CP5312D	3	30	210	25	665	80	290	105	175	795	1,420	--
CP5312E	7	30	175	145	885	485	465	240	115	2,800	5,530	--
CP5312F	8	30	110	85	1,000	325	415	205	285	3,450	3,940	--
Whitebreast coal												
CP5313Z	<2	10	20	4	80	55	55	140	65	445	220	--
CP5313Y	<2	20	15	9	10	30	30	60	35	10	885	--
CP5313A	<2	<10	5	<2	8	20	30	210	20	15	40	--
MIDDLE PENNSYLVANIAN BLACK SHALES FROM MISSOURI												
NW1/4NE1/4 sec. 19, T. 56 N., R. 16 W., Chariton County												
BM14-2	--	--	--	--	638	50	70	80	--	805	2,280	3.26
BM14-3	--	--	--	--	158	20	80	<10	--	142	190	.23
NW1/4NW1/4 sec. 4, T. 54 N., R. 14 W., Randolph County												
BM2-3	--	--	--	--	187	<10	90	<10	--	205	670	.35
BM2-5	--	--	--	--	542	90	140	80	--	694	1,460	1.60

Table B6. Selected minor and trace elements in Middle Pennsylvanian (Desmoinesian) black shales from the midcontinent--Continued

Sample No.	Ag	As	Ba	Cd	Cr	Mo	Ni	Se	Sr	V	Zn	P
NW1/4NW1/4 sec. 25, T. 46 N., R. 27 W., Johnson County												
MC105-2	--	--	--	--	894	10	270	75	--	1,710	200	2.83
MC105-6	--	--	--	--	695	20	210	25	--	503	350	1.17
SW1/4SW1/4 sec. 9, T. 44 N., R. 26 W., Johnson County												
MC86-2	--	--	--	--	622	50	300	140	--	642	1,960	1.68
MC86-5	--	--	--	--	123	<10	70	<10	--	226	80	.12
SW1/4SE1/4 sec. 7, T. 45 N., R. 25 W., Johnson County												
MC204-5A	--	--	--	--	60	<10	110	<10	--	69	1,010	.13
SW1/4 sec. 1, T. 40 N., R. 32 W., Bates County												
MC121-2	--	--	--	--	784	40	110	140	--	522	1,190	1.92
MC121-5	--	--	--	--	65	<10	40	<10	--	63	30	.07
SW1/4 sec. 29, T. 39 N., R. 30 W., Bates County												
MC142-3	--	--	--	--	132	<10	150	<10	--	127	40	.11
NE1/4SE1/4 sec. 35, T. 37 N., R. 30 W., Vernon County												
MC168-4	--	--	--	--	119	<10	50	<10	--	184	120	.11
MC168-5	--	--	--	--	427	30	200	60	--	205	160	1.10
MC168-7	--	--	--	--	127	<10	80	<10	--	143	60	.13
MIDDLE PENNSYLVANIAN BLACK SHALES FROM SOUTHEASTERN KANSAS												
SW1/4SE1/4 sec. 8, T. 32 S., R. 22 E., Cherokee County												
6-1	--	--	--	--	323	20	170	55	--	255	1,030	.84
6-12	--	--	--	--	245	30	140	10	--	200	120	.99
6-27	--	--	--	--	156	<10	110	<10	--	165	140	.13
MIDDLE PENNSYLVANIAN BLACK SHALES FROM WESTERN KANSAS												
Crist B-1; sec. 32, T. 20 S., R. 34 W., Scott County, southwestern Kansas												
CR4613.5	4	20	180	20	670	39	260	70	250	260	1,500	--
CR4614.5	3	20	180	<2	410	20	220	70	160	140	29	--
CR4620.5	<2	<10	220	<2	76	<2	57	10	290	90	45	--
Knudson A core; sec. 16, T. 7 S., R. 32 W., Thomas County, northwestern Kansas												
KNUD4477	<2	20	170	8	220	22	82	15	250	210	350	--
KNUD4480	3	10	180	4	390	58	180	45	190	720	170	--
MIDDLE PENNSYLVANIAN BLACK SHALES FROM NORTHEASTERN OKLAHOMA												
NE1/4SE1/4 sec. 30, T. 29 N., R. 18 E., Craig County												
1535u-5	--	--	--	--	421	20	140	45	--	266	430	.83
1535u-23a	--	--	--	--	170	<10	80	<10	--	67	40	.09
1535u-25	--	--	--	--	370	40	160	50	--	508	600	.48
1535-7	--	--	--	--	537	110	200	90	--	865	1,280	.30
1535-12	--	--	--	--	133	<10	120	<10	--	167	80	.26
1535-23	--	--	--	--	241	20	160	10	--	202	410	.48
1535-25	--	--	--	--	582	30	240	70	--	344	910	1.65
1535-66	--	--	--	--	223	20	230	<10	--	200	680	4.76
1535-78	--	--	--	--	109	<10	110	<10	--	157	50	.08
1535-144	--	--	--	--	144	<10	80	<10	--	172	60	.15
1535-159	--	--	--	--	146	<10	80	<10	--	181	160	.14
NE1/4NW1/4 sec. 4, T. 23 N., R. 10 E., Osage County												
1051-49	--	--	--	--	139	10	100	<10	--	95	40	.48
1051-50	--	--	--	--	576	30	270	60	--	382	750	.76

Table B6. Selected minor and trace elements in Middle Pennsylvanian (Desmoinesian) black shales from the midcontinent--Continued

Sample No.	Ag	As	Ba	Cd	Cr	Mo	Ni	Se	Sr	V	Zn	P
NW1/4NW1/4 sec. 12, T. 27 N., R. 6 E., Osage County												
1044-19	—	—	—	—	131	<10	150	<10	—	132	340	.21
1044-32	—	—	—	—	472	40	210	80	—	449	1,090	.96
1044-38	—	—	—	—	116	<10	80	<10	—	123	60	.15
1044-46	—	—	—	—	198	10	140	<10	—	147	420	.35
1044-47	—	—	—	—	492	40	230	45	—	333	810	2.72
1044-97	—	—	—	—	104	<10	70	<10	—	126	50	.20
1044-111	—	—	—	—	128	<10	70	<10	—	159	130	.13
NW1/4NW1/4 sec. 34, T. 25 N., R. 3 E., Osage County												
1065-2a	—	—	—	—	133	<10	130	<10	—	133	300	.20
1065-2b	—	—	—	—	346	30	150	40	—	344	590	.43
1065-6a	—	—	—	—	255	10	190	50	—	189	770	.43
1065-6b	—	—	—	—	623	50	210	105	—	562	930	1.73
1065-15	—	—	—	—	445	40	220	65	—	324	740	.64
1065-20	—	—	—	—	91	<10	60	<10	—	117	350	.08
1065-22	—	—	—	—	115	<10	60	<10	—	169	160	.10
1065-23	—	—	—	—	165	<10	110	<10	—	148	150	.19
1065-39	—	—	—	—	261	<10	170	<10	—	237	160	.52
1065-48	—	—	—	—	105	<10	60	<10	—	139	90	.12
MIDDLE PENNSYLVANIAN BLACK SHALES FROM WESTERN OKLAHOMA												
Core 1580; sec. 2, T. 23 N., R. 12 W., Alfalfa County												
5991	4	20	160	3	550	15	380	110	250	230	1,000	—
6039.5	<2	<10	180	<2	170	5	160	10	760	110	290	—
6040.3	<2	10	250	3	290	11	210	35	250	200	540	—
6041.2	4	20	150	11	800	30	260	105	570	490	840	—
Core 1683; sec. 4, T. 25 N., R. 8 W., Grant County												
5166.7	<2	10	130	<2	410	5	230	35	400	130	360	—
5206.8	3	20	180	8	630	22	220	50	530	440	850	—
5222.7	4	20	180	4	420	21	440	80	160	230	950	—
Core 600; sec. 31, T. 17 N., R. 5 W., Kingfisher County												
6471	<2	10	400	<2	81	12	54	10	220	140	120	—
6487.5	<2	10	340	<2	83	<2	44	<10	200	92	100	—
Core 330; sec. 28, T. 13 N., R. 23 W., Roger Mills County												
12,165	<2	10	390	<2	72	4	130	<10	360	130	270	—
12,174	<2	10	500	<2	180	9	170	10	310	280	470	—
Core 698; sec. 11, T. 17 N., R. 20 W., Dewey County												
9503	<2	10	290	<2	240	16	220	<10	540	230	670	—
9504	4	30	200	2	430	18	320	75	430	400	840	—
Core 707; sec. 18, T. 17 N., R. 20 W., Dewey County												
9807	<2	<10	280	<2	140	<2	150	<10	930	110	230	—
9813	<2	<10	310	<2	180	3	200	<10	640	150	450	—
Core 1609; sec. 13, T. 13 N., R. 6 W., Canadian County												
7331	3	60	100	3	550	54	250	20	1,200	150	610	—
Core 1567; sec. 11, T. 13 N., R. 6 W., Canadian County												
7402.2	2	30	110	<2	590	25	200	15	1,000	140	480	—
7402.7	8	30	200	11	800	41	320	125	190	560	840	—
Core 497; sec. 18, T. 14 N., R. 12 W., Blaine County												
9704	<2	30	180	<2	270	14	230	<10	1,500	150	670	—
Core 333A; sec. 25, T. 2 N., R. 27 E., EMC, Beaver County												
6893	5	20	150	13	840	27	200	15	660	540	680	—
6894	5	30	180	9	590	41	250	65	200	740	320	—

Table B7. Selected major and minor elements in Upper Pennsylvanian black shales from the midcontinent

[Organic carbon was measured with a Leco WR-12 carbon determinator; other elements were determined by inductively coupled plasma method; all in weight percent; --, not determined]

Sample No.	Org. C	Al	Fe	Mg	Ca	Na	K	Ti	P	S
UPPER PENNSYLVANIAN BLACK SHALES FROM SOUTH-CENTRAL IOWA										
Core IBCD (Bedford core); sec. 4., T. 67 N., R. 34 W., Taylor County										
Larsh Shale Member of the Deer Creek Limestone (4.5-4.9 ft)										
A	19.5	5.9	3.8	1.5	1.9	0.35	2.0	0.23	0.03	--
B	9.8	6.6	3.8	1.4	2.3	.55	2.0	.27	.03	--
C	20.7	6.1	3.4	1.4	3.0	.45	2.1	.23	.93	--
Queen Hill Shale Member of the Lecompton Limestone (102.1-102.5 ft)										
A	10.1	6.2	3.6	1.3	2.7	.64	2.0	.26	.02	--
B	21.0	4.9	3.2	1.2	2.4	.44	1.6	.20	.02	--
C	5.2	6.3	3.6	1.2	2.3	.74	1.9	.26	.02	--
Core IHC (Hillsdale/Buffington); sec. 22, T. 72 N., R. 42 W., Mills County										
Heebner Shale Member of the Oread Limestone (6.2-6.6 ft)										
D249924	16.9	4.8	3.6	1.9	4.8	.44	2.0	.20	.02	--
Eudora Shale Member of the Stanton Limestone (100.2-100.5 ft)										
D249925	15.2	4.8	2.8	1.4	6.4	.42	2.1	.10	2.6	--
Quindaro Shale Member of the Wyandotte Limestone (166.1-166.4 ft)										
A1	5.7	7.1	3.7	1.6	1.2	.81	2.7	.31	.16	--
B1	16.8	5.0	3.3	1.3	1.0	.45	2.2	.22	.05	--
C1	7.5	6.7	3.6	1.7	1.2	.60	2.7	.28	.03	--
Stark Shale Member of the Dennis Limestone (218.2-218.5 ft)										
I	4.4	6.9	2.9	1.9	3.6	.68	2.9	.28	.03	--
Core ISC (Stanzl Qy); sec. 5, T. 75 N., R. 29 W., Madison County										
Quindaro Shale Member of the Wyandotte Limestone (36.9-37.3 ft)										
A2	5.2	6.4	4.1	1.5	3.0	.73	2.1	.26	.02	--
B2	16.4	5.8	3.8	1.3	1.2	.48	2.0	.23	.02	--
Muncie Creek Shale Member of the Iola Limestone (56.9-57.3 ft)										
D249928	1.2	7.5	2.9	1.5	1.9	.74	2.6	.27	.75	--
Core IJCL (Jefferson Qy, lower); sec. 17, T. 77 N., R. 31 W., Adair County										
Stark Shale Member of the Dennis Limestone (51.6-52.2 ft)										
2A	18.4	4.9	3.7	2.1	3.3	.34	1.7	.21	.02	--
2B	11.8	4.8	3.7	2.5	4.9	.34	1.7	.20	.18	--
2C	23.3	4.4	3.5	2.1	3.1	.30	1.6	.20	.03	--
2D	11.0	6.3	3.9	2.1	3.1	.57	2.1	.26	.03	--
Hushpuckney Shale Member of the Swope Limestone (85.3-85.5 ft)										
A	27.3	4.0	3.9	1.4	3.0	.28	1.4	.17	.03	--
B	21.4	4.8	3.8	1.5	2.8	.36	1.7	.20	.03	--
UPPER PENNSYLVANIAN BLACK SHALES FROM KANSAS										
SE1/4SE1/4SW1/4 sec. 2, T. 6 N., R. 27 W., Sheridan County										
Muncie Creek Shale Member of the Iola Limestone (3,708-3,708.5 ft)										
406A	3.0	7.0	2.6	2.5	4.5	.97	2.5	.29	.09	--
SW1/4SE1/4SW1/4 sec. 16, T. 9 S., R. 16 W., Rooks County										
Muncie Creek Shale Member of the Iola Limestone (3,293.7-3,294.1 ft)										
506MC	10.6	5.7	3.6	1.9	3.2	.75	2.1	.24	.03	--
Stark Shale Member of the Dennis Limestone (3,362-3,364 ft)										
506SA	16.0	5.6	2.3	1.9	4.5	.69	2.2	.22	1.1	--
506SD	16.4	5.2	3.6	1.8	4.4	.61	2.0	.21	.61	--
506SF	4.0	4.7	2.9	2.2	13	.61	1.9	.17	.11	--
506SG	16.7	5.1	2.7	1.9	5.2	.56	2.1	.19	.81	--

Table B7. Selected major and minor elements in Upper Pennsylvanian black shales from the midcontinent--Continued

Sample No.	Org. C	Al	Fe	Mg	Ca	Na	K	Ti	P	S
			Hushpuckney Shale Member of the Swope Limestone (3,389.5-3,392 ft)							
506HA	1.1	6.3	2.7	2.4	6.8	.71	2.6	.24	.42	--
506HB	2.5	6.5	2.6	2.4	4.9	.71	2.7	.23	.61	--
506HC	2.5	6.0	2.5	2.2	7.2	.73	2.5	.10	2.4	--
			Cen. NW1/4NW1/4 sec. 30, T. 30 S., R. 33 W., Haskell County							
			Stark Shale Member of the Dennis Limestone (4,533-4,535.4 ft)							
2A,1-5	9.6	6.1	3.8	1.7	1.9	.79	2.4	.25	.17	--
8-9	10.2	5.0	2.7	1.7	6.2	.63	2.0	.14	1.5	--
10-12	12.8	5.4	3.1	1.7	4.0	.67	2.2	.21	.80	--
13-15	13.6	5.3	2.8	1.6	4.1	.67	2.0	.22	.80	--
16-19	14.4	5.9	2.7	1.7	3.3	.68	2.3	.23	.23	--
			A-1 Holmdan 1, Rawlins County							
			Stark Shale Member of the Dennis Limestone (interval unknown)							
D249932	0.2	6.7	2.4	2.5	6.6	.85	2.6	.29	.39	--
			UPPER PENNSYLVANIAN BLACK SHALES FROM OKLAHOMA							
			Core 1389; sec. 5, T. 28 N., R. 1 W., Kay County (interval unknown)							
1389C	4.2	7.9	7.6	1.3	1.6	.73	2.7	.26	.05	5.5
1389E	1.8	9.6	4.7	1.4	1.1	.77	3.1	.29	.06	1.2
			Core 508; sec. 1, T. 17 N., R. 51 W., Dewey County (interval unknown)							
508B	1.4	7.2	3.7	1.4	6.2	.86	2.3	.25	.07	1.0
508C	2.9	7.7	4.0	1.6	3.6	.83	2.6	.29	.05	1.1
508D	2.9	5.9	3.0	1.2	9.9	.61	2.0	.21	.22	1.0
508E	12.9	6.1	4.9	1.5	4.2	.58	2.0	.20	.24	3.0

Table B8. Selected minor and trace elements in Upper Pennsylvanian black shales from the midcontinent

[Selenium was determined by energy dispersive analysis. Other elements were determined by inductively coupled plasma method. --, not determined; <, less than; all in parts per million]

Sample No.	Ag	As	Ba	Cd	Cr	Mo	Ni	Se	Sr	U	V	Zn
UPPER PENNSYLVANIAN BLACK SHALES FROM IOWA												
Core IBCD (Bedford core); sec. 4, T. 67 N., R. 34 W., Taylor County												
Larsh Shale Member of the Deer Creek Limestone (4.5-4.9 ft)												
A	<4	20	140	11	310	520	420	85	72	74	1,900	340
B	<4	30	220	20	220	460	330	60	110	55	1,100	720
C	<4	20	150	19	470	120	440	80	140	--	990	480
Queen Hill Shale Member of the Lecompton Limestone (102.1-102.5 ft)												
A	<4	<20	190	32	180	610	260	45	120	58	930	1,100
B	<4	<20	140	180	280	1,000	400	55	110	60	1,800	9,700
C	<4	<20	270	92	180	280	210	20	120	--	1,000	5,000
Core IHC (Hillsdale/Buffington); sec. 22, T. 72 N., R. 42 W., Mills County												
Heebner Shale Member of the Oread Limestone (6.2-6.6 ft)												
D249924	<4	50	160	85	320	430	330	85	140	48	1,800	2,400
Eudora Shale Member of the Stanton Limestone (100.2-100.5 ft)												
D249925	<4	20	150	<4	570	130	680	90	150	81	1,100	40
Quindaro Shale Member of the Wyandotte Limestone (166.1-166.4 ft)												
A1	<4	30	310	<4	190	840	340	110	110	--	1,300	50
B1	<4	30	150	<4	480	630	890	175	61	--	2,300	50
C1	<4	30	290	<4	310	140	430	100	67	--	690	1,600
Stark Shale Member of the Dennis Limestone (218.2-218.5 ft)												
I	<4	<20	300	<4	370	51	140	95	130	64	1,600	40
Core ISC (Stanzel Qy); sec. 5, T. 75 N., R. 29 W., Madison County												
Quindaro Shale Member of the Wyandotte Limestone (36.9-37.3 ft)												
A2	<4	30	270	31	160	270	250	75	130	36	810	480
B2	<4	30	160	130	270	750	410	140	110	49	1,500	2,100
Muncie Creek Shale Member of the Iola Limestone (56.9-57.3 ft)												
D249928	<4	<20	290	<4	400	<4	240	<10	120	--	1,100	770
Core IJCL (Jefferson Qy, lower); sec. 17, T. 77 N., R. 31 W., Adair County												
Stark Shale Member of the Dennis Limestone (51.6-52.2 ft)												
2A	<4	50	170	130	460	330	410	100	60	--	1,700	3,700
2B	<4	60	160	54	290	170	300	80	70	--	1,300	1,600
2C	<4	40	150	82	390	870	510	115	50	--	1,900	2,300
2D	<4	50	280	35	240	590	300	75	66	--	1,300	950
Hushpuckney Shale Member of the Swope Limestone (85.3-85.5 ft)												
A	<4	70	140	170	490	2,000	570	175	80	153	2,500	6,200
B	<4	90	150	140	430	640	480	130	100	202	2,300	4,900
UPPER PENNSYLVANIAN BLACK SHALES FROM KANSAS												
SE1/4SE1/4SW1/4 sec. 2, T. 6 N., R. 27 W., Sheridan County												
Muncie Creek Shale Member of the Iola Limestone (3,708-3,708.5 ft)												
406A	<4	30	260	6	370	130	150	45	130	48	330	340
SW1/4SE1/4SW1/4 sec. 16, T. 9 S., R. 16 W., Rooks County												
Muncie Creek Shale Member of the Iola Limestone (3,293.7-3,294.1 ft)												
506MC	<4	30	180	23	380	130	320	80	130	34	910	490
Stark Shale Member of the Dennis Limestone (3,362-3,364 ft)												
506SA	<4	20	160	32	770	76	310	55	140	54	300	1,200
506SD	5	50	150	63	830	150	300	100	150	62	620	1,100
506SF	<4	70	130	210	150	30	160	45	420	--	88	8,500
506SG	5	30	150	88	470	120	320	90	170	53	1,100	1,900

Table B8. Selected minor and trace elements in Upper Pennsylvanian black shales from the midcontinent--Continued

Sample No.	Ag	As	Ba	Cd	Cr	Mo	Ni	Se	Sr	U	V	Zn
			Hushpuckney Shale Member of the Swope Limestone (3,389.5-3,392 ft)									
506HA	<4	<20	230	<4	480	5	140	<10	200	31	160	180
506HB	<4	<20	170	<4	870	14	180	35	140	47	190	270
506HC	<4	<20	160	<4	990	19	160	20	200	74	310	250
			Cen. NW1/4NW1/4 sec. 30. T. 30 S., R. 33 W., Haskell County									
			Stark Shale Member of the Dennis Limestone (4,533-4,535.4 ft)									
2A,1-5	<4	<20	150	<4	540	13	290	45	130	22	150	760
8-9	<4	<20	140	6	820	36	270	55	260	31	200	1,300
10-12	<4	<20	130	7	910	28	310	80	200	30	230	960
13-15	6	<20	150	35	870	79	280	85	160	54	580	970
16-19	5	<20	150	17	700	53	320	95	150	41	570	590
			A-1 Holmdan 1, Rawlins County									
			Stark Shale Member of the Dennis Limestone (interval unknown)									
D249932	<4	<20	170	<4	380	<4	110	<10	200	15	88	140
			UPPER PENNSYLVANIAN BLACK SHALES FROM OKLAHOMA									
			Core 1389; sec. 5, T. 28 N., R. 1 W., Kay County (interval unknown)									
1389C	--	3	130	275	<2	240	10	145	45	155	215	290
1389E	--	5	20	150	<2	150	<2	115	<10	165	155	240
			Core 508; sec. 1, T. 17 N., R. 51 W., Dewey County (interval unknown)									
508B	--	<2	<10	325	<2	115	<2	85	<10	455	105	245
508C	--	<2	10	375	<2	245	2	130	15	255	145	300
508D	--	<2	10	215	<2	135	<2	100	<10	590	95	260
508E	--	9	70	210	60	655	80	310	130	230	1,010	1,180

Chapter C

Mineralogical and Geochemical Analysis of the Metal- and Organic-Rich Grassy Creek Shale of the New Albany Group (Upper Devonian and Lower Mississippian) in Hardin County, Southern Illinois

By GEORGE A. DESBOROUGH

CONTENTS

Mineralogical and Geochemical Analysis of the Metal- and Organic-rich Grassy Creek Shale of the New Albany Group (Upper Devonian and Lower Mississippian) in Hardin County, Southern Illinois

By George A. Desborough

Abstract

The mineralogy and geochemistry of continuous core samples of the uppermost part of the Upper Devonian and Lower Mississippian New Albany Group on the east flank of Hicks dome in southeastern Illinois were studied in order to place constraints on its mineral content. Fifty-four samples from 61 ft of a single core were studied, including the Henryville Bed, the Falling Run Bed, and the underlying additional parts of the Grassy Creek Shale. Shales in the study area have high metal and organic contents because they occur in the depocenter of the basin and are thus least diluted by detrital material. Thermal alteration of the shale has been high, and, therefore, it is past the oil-generation window. Therefore, the shale would not yield significant oil by retorting (pyrolysis).

Geochemical data for bulk samples indicate that the metal content is low. Therefore, these shales will be of minimal economic interest during the next several decades in the absence of technological advances in metal recovery from metalliferous black shales.

Mineralogical studies show that the shale consists predominantly of illite, quartz, feldspar, and minor pyrite. Dolomite is abundant in the lower part, whereas the upper part is essentially free of carbonates.

The observed sodium content in the shales correlates strongly (r=0.90, where r is correlation coefficient) with the albite peak as measured by x-ray powder diffraction (XRD). The potassium content also correlates well with the intensity of the potassium feldspar peak (r=0.76). For pyrite, the intensity of the py2 (XRD) peak correlates well with both the sulfur content (r=0.93) and the iron content (r=0.82). In addition,

arsenic content correlates with the pyrite (XRD) peak intensity (r=0.71).

Cobalt, copper, chromium, nickel, vanadium, strontium, zinc, thorium, and lead are highest in concentration in the upper 10 ft of the interval studied, whereas arsenic and pyrite are highest in the lowest 10 ft of the interval studied. The Henryville Bed has the highest concentrations of copper, molybdenum, and nickel.

INTRODUCTION

This study was conducted as part of the U.S. Geological Survey Midcontinent Strategic and Critical Minerals Project. This report presents the results of mineralogical and chemical investigations of the Rose core from the upper 66 ft of the Grassy Creek Shale of the New Albany Shale Group (Upper Devonian and Lower Mississippian) on the east side of Hicks dome, in Hardin County, Ill. (fig. C1). Stratigraphic nomenclature is that of Cluff and others (1981), with the exception that their term "New Albany Shale Group" is here changed to "New Albany Group." These strata consist of laminated to massive Grassy Creek Shale (table C1) that includes the Henryville Bed at the top (1.9 ft thick), the Falling Run Bed (1.7 ft thick), and undivided Grassy Creek Shale at the bottom of the core. The Henryville Bed is very dark brown to black and massive to only weakly laminated. The Falling Run Bed is massive, dark-gray-green to green shale that contains carbonate fluorapatite. The rest of the Grassy Creek Shale is massive to strongly laminated, containing thin (< 2 mm) gray layers

of detrital quartz. Pyrite nodules as much as 3 cm in diameter are present at 93 ft.

The purpose of this study was to determine the mineralogy and metal content in the most organic-rich part of the New Albany Group in an area considered to be near the basin depocenter of the Grassy Creek Shale (Cluff and others, 1981). Frost and others (1985) reported that, compared to other stratigraphic units in the New Albany Group, the Grassy Creek Shale has the greatest enrichment in organic material and pyrite, and higher than usual enrichment in selenium, antimony, vanadium, zinc, and silver. Beier and Hayes (1989) studied core from the upper part of age-equivalent strata (New Albany Shale) in southern Indiana and found that the most metal-rich and organic-rich parts were near the top of the black shale

interval. For these reasons it was thought that the Devonian black shale that would have the greatest potential for metals would be the uppermost part of the New Albany Group in southern Illinois, where it is thickest and richest in organic material. However, the core was drilled for exploration purposes to study mineral occurrences unrelated to black shales.

Organic petrographic studies show that the New Albany Group in the study area has a mean random vitrinite reflectance of $R = 1.2$ (Barrows and others, 1980, p. 68) and, thus, indicates organic maturation at the upper limit of oil generation due to heating on a regional scale that was probably related to the emplacement of the Hicks dome intrusive body.

METHODS OF STUDY

The core studied extends from a depth of 88.9 to 150.2 ft; a carbonatite dike (or sill) of the Hicks dome breccia complex occurs at the base of the black shale interval that was sampled. Segments of core (broken for boxing) were sawed into quarters, and one quarter was crushed and pulverized for geochemical and mineralogical studies.

The mineralogy of the samples (table C1) was determined by means of nickel-filtered Cu-K$_\alpha$ radiation at a diffractometer scan rate of 2°/min. The same operating conditions and x-ray tube were used for all analyses. Powdered samples were packed into 2-mm-thick mounts. X-ray peak intensities reported were corrected for background. For each mineral, except quartz, the x-ray diffraction maximum was used (table C1).

Selenium was determined by x-ray fluorescence using a cadmium radio-isotope source and an energy-dispersive analyzer. The geochemical abundances, except for selenium, were determined by the inductively coupled plasma atomic-emission spectroscopy method as described by Lichte and others (1987), for which the precision is 1–2 percent of the relative standard deviation.

MINERALOGY

The very fine grained nature of the Grassy Creek Shale (Cluff and others, 1981), in which individual mineral grains are mostly less than 10 μm, and laminae of mineral grains are commonly only 20 μm to 1 cm thick, precludes using polished thin sections for accurate mineral identification. Near the contact with the carbonatite dike there is no obvious recrystallization of the black shale, nor is there any introduction or mobilization of elements in the black shale.

Illite is present in all samples, and it has been shown by Cluff and others (1981) to be the most abundant clay mineral in the Grassy Creek Shale (table C1). Kaolinite is a
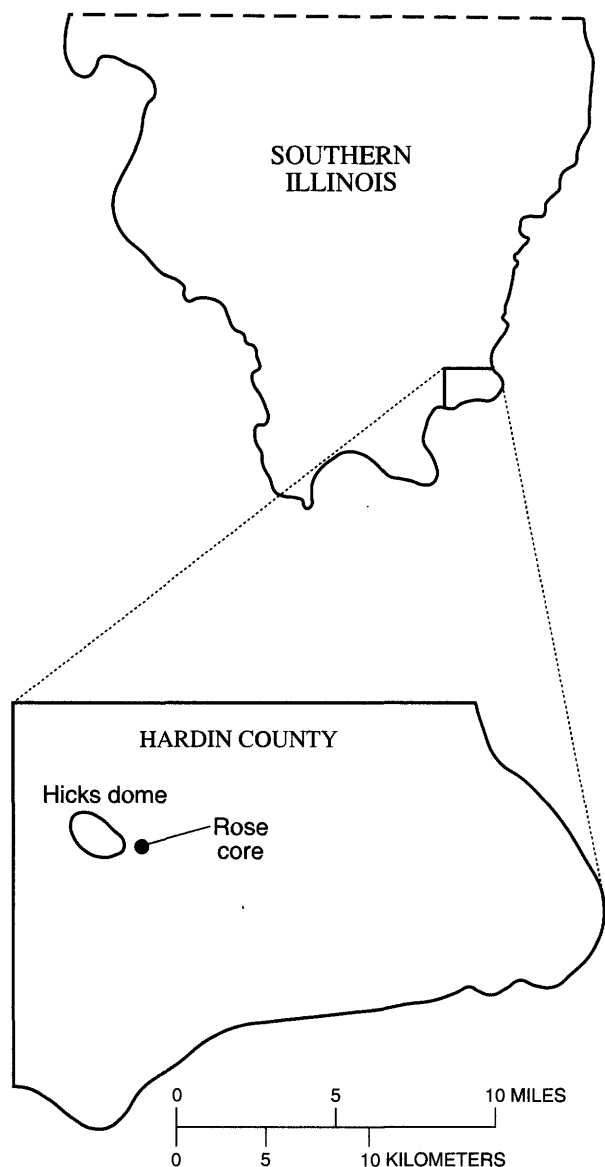
Figure C1. Approximate locality for Rose core near Hicks dome, Hardin County, Ill. Hicks dome outline is outcrop of New Albany Group.

minor or trace mineral that was detectable in 63 percent of the samples. Only 30 percent of the samples have detectable chlorite. Albite is present in 89 percent of the samples, but is apparently absent in the Henryville Bed (table C1, fig. C2). Potassium feldspar is relatively abundant in all samples (table C1, fig. C3). Calcite was detected in only four samples. Dolomite is present in 44 percent of the samples and is most abundant in the lower part of the interval studied (table C1). Dolomite is absent in both the Henryville Bed and the Falling Run Bed. Apatite was detected only in the Falling Run Bed, which is defined as a bed containing phosphatic nodules (Cluff and others, 1981); the apatite occurs as nodules as much as 3 cm in diameter in the core studied. Pyrite is present in all samples, occurring as framboids, subhedral to euhedral grains, and nodules several centimeters in diameter.

GEOCHEMISTRY

Geochemical data for certain major, minor, and trace elements are given in tables C2 and C3. Correlations of these data with mineral abundances determined by x-ray diffraction techniques were used to determine the most likely mineralogical residence of various elements whether or not metals occur in concentrations sufficient to be of economic interest.

Correlations between element concentrations and mineral abundances determined by x-ray diffraction (table C1, figs. C2 and C3) help constrain the occurrence of elements of interest. For instance, the absence of correlation between vanadium concentrations and illite abundance in midcontinent Pennsylvanian black shales demonstrates that the vanadium residence is not in illite (Desborough and others, this volume). The sodium concentration correlates well with the intensity of the albite peak (r=0.90, see
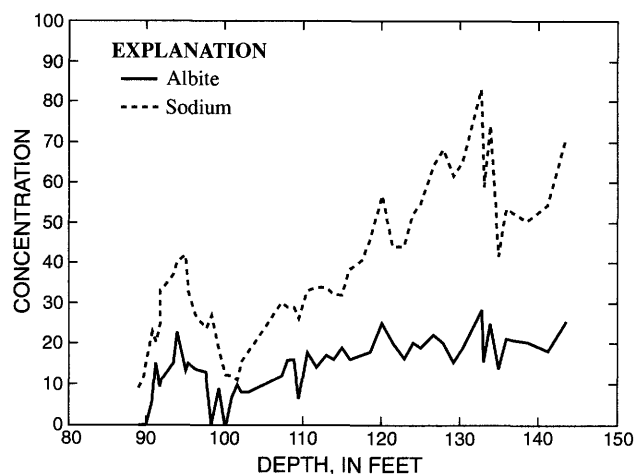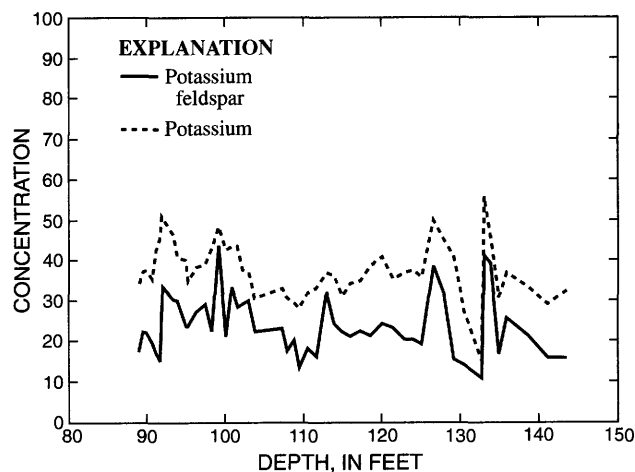
Figure C3. Relation of potassium concentration (weight percent ×10) to abundance of potassium feldspar (x-ray diffraction peak) in Grassy Creek Shale, Hardin County, Ill.

fig. C2), and the potassium content correlates fairly well with the intensity of the potassium feldspar peak (r=0.76, fig. C3). This suggests that most of the sodium is in albite and that most of the potassium is in potassium feldspar. For pyrite, correlation of the py2 peak intensity (table C1) with sulfur is very good (r=0.93). Correlation of iron content with the py2 peak intensity is good (r=0.82). The data suggest that some of the arsenic (table C3) is in pyrite: there is a positive correlation (r=0.71) between the intensity of the pyrite peak (py2) and the arsenic concentration (fig. C4). Frost and others (1985) found that arsenic concentrations correlated with both pyritic sulfur content (r=0.84) and organic content (r=0.73). They also found that uranium, nickel, copper, molybdenum, lead, and pyritic sulfur correlated with organic carbon. I observe no correlation of these elements with any mineral.

The vanadium concentrations are higher in the upper part of the core studied than in the lower (fig. C5). Also, the highest chromium, copper, and nickel concentrations are near the top of the interval studied (fig. C6)

Statistical data for selected major, minor, and trace elements are given in table C4 for the purpose of comparison with the summary statistics of Frost and others (1985, table 9) for the Grassy Creek Shale and undivided Grassy Creek and Sweetland Creek Shales in Illinois. The average values for cobalt, chromium, copper, and molybdenum in the present study are essentially the same (within 15 percent) as those of Frost and others (1985, table 9). The average value for lead obtained in the present study is about one-half as much as the average found by Frost and others (1985). Average values for nickel, selenium, thorium, vanadium, and zinc are about two times those of Frost and others (1985). This is explained by the fact that the samples of the present study were taken from the deepest part of the basin, whereas those of Frost and others (1985) were taken from many localities basinwide.

Figure C2. Relation of sodium concentration (weight percent ×100) to abundance of albite (x-ray diffraction peak) in Grassy Creek Shale, Hardin County, Ill.

Figure C4. Relation of arsenic concentration (parts per million ×10) to abundance of pyrite (py2 x-ray diffraction peak) in Grassy Creek Shale, Hardin County, Ill.

Figure C6. Variations in concentrations (parts per million) of chromium, copper, and nickel in Grassy Creek Shale, Hardin County, Ill.

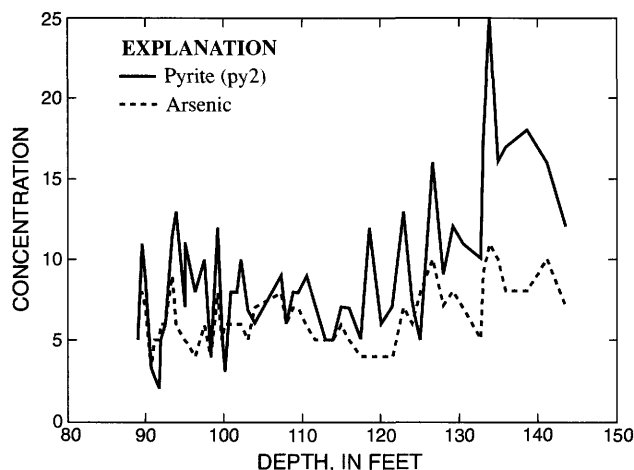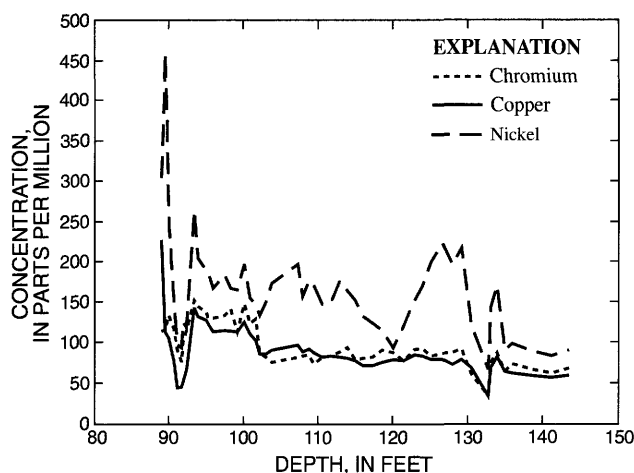Frost and others (1985, p. 77) noted that the Grassy Creek Shale was the unit of the New Albany Group that had the ". . . greatest enrichment of trace metals and black shale indicators: pyritic S, Co, Zn, As, Se, Mo, Sb, Pb, and U . . ." and ". . . samples with an unusually high enrichment of Se, V, and Zn were from the top 30 feet of the Grassy Creek Shale." The present study shows general agreement with Frost and others (1985).

ECONOMIC ASPECTS

The average amounts of metals such as Cr (94 ppm, or parts per million), Mo (67 ppm), Ni (160 ppm), Se (19 ppm), V (533), and Zn (392 ppm) in the upper part of the

Figure C5. Variation in vanadium concentration (parts per million) in Grassy Creek Shale, Hardin County, Ill.

Grassy Creek Shale in the study area are too low to be considered of economic interest at the present. The most metal-rich zones are too thin (<3 ft), and, furthermore, there is no known extraction technology for metals such as chromium, molybdenum, nickel, selenium, vanadium, and zinc in black shales that are thermally altered beyond the oil generation window.

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Table C1. X-ray diffraction intensity data for minerals in drill-core samples from the upper 61 ft of the Upper Devonian and Lower Mississippian New Albany Group in Hardin County, Ill.

[ill, illite; kao, kaolinite; a, albite; k, potassium feldspar; cal, calcite; dol, dolomite; ap, apatite; py2, line of pyrite measured for all samples because there are no interferences with other minerals; f, fluorite; gy, gypsum; q2, quartz; chl, chlorite; py1, line of pyrite that is coincident with second strongest line (202) of apatite (line not reported for samples containing detectable apatite); M, major mineral having peak intensity greater than 100; –, interference with apatite. USGS black shale standard SDO-1 is given for comparison. Query (?) indicates detection is questionable; data are reported relative to 100 percent peak intensity for quartz]

Sample interval, in feet	ill	kao	a	k	cal	dol	ap	py2	f	gy	q2	chl	py1
USGS STANDARD SDO-1													
	30	20	12	?	0	11	0	15	0	4?	M	5	32
GRASSY CREEK SHALE													
Henryville Bed													
88.9-89.4	33	7	0	17	0	0	0	5	0	2?	M	0	9
89.4-89.9	35	5	0	22	0	0	0	11	0	0	81	0	16
89.9-90.8	29	5	0	22	0	0	0	9	0	3	M	3	16
Falling Run Bed													
90.8-91.1	27	3	6	20	0	0	36	5	0	0	M	3	–
91.1-91.7	31	3	15	18	0	0	15	3	0	5	78	4	–
Grassy Creek Shale, undivided													
91.7-91.8	39	3	9	15	0	0	0	2	7	3	78	0	9
91.8-92.4	35	4	11	21	0	32	0	5	4	0	87	0	7
92.4-93.5	33	4	13	33	0	46	0	6	10	0	88	3	13
93.5-93.9	38	0	15	30	0	0	0	12	7	0	M	0	20
93.9-95.0	32	2	23	30	0	0	0	13	0	0	M	0	18
95.0-95.2	25	0	13	25	0	0	0	7	0	0	M	3	12
95.2-96.1	25	3	15	23	0	0	0	11	0	0	M	3	15
96.1-97.0	22	3	14	26	0	0	0	8	0	0	M	0	14
97.5-98.2	28	5	13	29	0	0	0	10	0	0	M	0	20
98.2-99.2	26	0	0	22	0	0	0	4	0	0	67	5	9
99.2-99.8	20	2	9	30	0	0	0	12	6	0	84	0	26
99.8-100.1	18	3	0	44	0	0	0	6	5	0	M	0	14
100.1-101.1	19	0	0	21	0	0	0	3	0	0	65	4	8
101.1-101.7	28	6	8	33	0	0	0	8	0	0	M	2	20
101.7-102.2	42	5	10	30	0	0	0	8	0	4	M	3	16
102.2-102.9	24	3	8	28	0	0	0	10	5	3	M	0	26
102.9-103.6	19	4	8	30	0	0	0	7	10	0	M	0	14
104.0-105.2	23	2	9	22	0	0	0	6	11	0	M	0	15
107.2-108.0	29	2	12	23	0	6	0	9	0	0	M	0	16
108.0-108.8	25	0	16	17	0	0	0	6	0	0	M	0	11
108.8-109.2	35	0	16	20	0	10	0	8	0	0	M	0	13
109.5-110.5	21	0	6	13	0	8	0	8	0	0	81	3	12
110.5-111.7	31	0	18	18	0	18	0	9	0	0	M	0	13
111.7-113.0	26	0	14	16	0	9	0	7	0	0	M	3	9
113.0-113.5	25	0	17	32	0	0	0	5	0	0	M	0	9
114.0-115.0	22	5	16	24	0	0	0	5	0	0	M	3	10
115.0-116.0	31	4	19	22	0	0	0	7	0	0	M	3	13
116.0-117.4	23	0	16	21	0	0	0	7	0	0	M	3	12
117.5-118.7	25	2	17	22	0	15	0	5	0	0	M	0	11
118.7-120.1	31	0	18	21	0	0	0	12	0	0	M	0	13

Table C1. X-ray diffraction intensity data for minerals in drill-core samples from the upper 61 ft of the Upper Devonian and Lower Mississippian New Albany Group in Hardin County, Ill.--Continued

Sample interval, in feet	ill	kao	a	k	cal	dol	ap	py2	f	gy	q2	chl	py1
120.1-121.4	28	5	25	24	0	28	0	6	0	0	M	0	12
121.4-122.9	34	4	20	23	0	25	0	7	0	0	M	3	14
122.9-123.8	30	0	16	20	8	0	0	13	0	0	M	0	20
124.0-125.2	33	0	20	20	7	9	0	7	0	0	M	0	18
125.2-126.6	26	0	19	19	0	19	0	5	0	0	61	0	15
126.6-127.8	19	0	22	38	0	8	0	16	5	0	73	0	20
127.8-129.2	23	0	20	33	0	7	0	9	0	0	82	0	17
129.2-130.5	26	3	15	15	0	5	0	12	3	3	73	0	19
130.5-132.1	17	0	19	14	37	M	0	11	0	0	34	0	17
132.9-133.0	7	3	28	10	19	M	0	10	0	0	20	0	13
133.0-134.0	13	0	15	41	0	51	0	17	6	0	58	0	28
134.0-134.9	15	3	25	30	0	34	0	25	5	0	53	0	42
134.9-135.8	21	0	13	16	0	10	0	16	0	0	77	0	27
136.0-138.7	37	5	21	25	0	26	0	17	0	0	83	0	31
138.7-141.2	33	0	20	21	0	40	0	18	0	0	87	0	37
141.2-143.5	26	4	18	15	0	34	0	16	0	0	M	0	27
143.5-144.8	23	3	25	15	0	29	0	12	0	0	M	0	29
145.3-147.2	26	3	37	19	0	42	0	12	0	0	80	0	26
147.2-150.2	17	3	48	16	0	60	0	9	5	0	87	0	21

Table C2. X-ray diffraction peaks used for estimation of relative abundances of minerals in the New Albany Group, Hardin County, Ill.

Mineral	hkl	d-value used (Å)	Approximate 2θ° (CuKα)	Lowest percentage identifiable (Carroll, 1970, table 12)
Iron-rich chlorite . .	001	14.1-14.2	6.2	10
Illite	001	10.2	8.7	5
Gypsum	020	7.56	11.7	Not reported
Kaolinite	001	7.15	12.4	5
Albite	002	3.186-3.198	27.90-28.00	5
Potassium . . . . feldspar	040, 002	3.220-3.250	27.45-27.70	5
Calcite	104	3.03	29.5	5
Dolomite	104	2.88	30.96	1
Apatite	112	2.79	32.05	Not reported
[1]Pyrite-py1	002	2.71	33.16	Not reported
[2]Pyrite-py2	021	2.42	37.15	Not reported
Quartz[3]	100	4.26	20.85	Not reported
Fluorite	220	1.93	47.06	Not reported

[1]This line of pyrite is coincident with the second strongest line (202) of apatite. This line is not reported for samples containing detectable apatite.

[2]This line was measured for all samples because there are no interferences with other minerals.

[3]Second strongest peak of quartz.

Table C3. Selected major and minor elements in the uppermost interval of the New Albany Group east of Hicks dome, Hardin County, Ill.

[Sulfur was analyzed with a Leco IR-32 determinator; other elements determined by the inductively coupled plasma method; N/A, not analyzed; all values in weight percent]

Sample No.	Al	Ca	Fe	K	Mg	Na	P	Ti	S	F
USGS STANDARD SDO-1										
	6.49	1.1	6.53	2.78	0.93	0.28	0.05	0.02	5.35	N/A
GRASSY CREEK SHALE										
Henryville Bed										
R89.0	6.3	0.36	3.76	3.39	.48	.09	.06	.31	N/A	N/A
R89.4	6.24	.13	.41	3.64	.47	.10	.06	.28	N/A	N/A
R89.9	6.07	.33	2.99	3.71	.42	.15	.17	.29	N/A	N/A
Falling Run Bed										
R90.8	5.33	6.83	1.58	3.51	.30	.23	3.46	.21	N/A	N/A
R91.1	7.21	2.41	2.07	4.00	.53	.20	1.12	.25	N/A	N/A
Grassy Creek Shale, undivided										
R91.7	7.70	.84	1.60	4.46	.54	.25	.27	.37	N/A	N/A
R91.8	7.40	1.50	2.86	4.41	.88	.33	.11	.32	N/A	N/A
R92.4	7.02	2.08	2.83	5.06	.81	.34	.10	.31	N/A	N/A
R93.5	6.74	.45	3.09	4.69	.47	.37	.08	.31	N/A	N/A
R93.9	6.05	.73	2.44	4.07	.40	.40	.31	.27	N/A	N/A
R95.0	5.90	.31	2.07	3.96	.39	.42	.11	.27	N/A	N/A
R95.2	5.46	.39	2.64	3.41	.48	.33	.09	.23	N/A	N/A
R96.1	5.62	.19	1.95	3.76	.37	.27	.08	.25	N/A	N/A
R97.5	5.39	.25	3.01	3.82	.38	.24	.04	.24	N/A	N/A
R98.2	5.88	.33	1.97	4.14	.38	.27	.09	.26	N/A	N/A
R99.2	5.46	.36	4.26	4.48	.22	.18	.07	.23	N/A	N/A
R99.8	5.51	.14	1.89	4.83	.21	.13	.06	.24	N/A	N/A
R100.1	5.98	.12	2.12	4.21	.34	.12	.05	.28	N/A	N/A
R101.1	5.91	.13	2.67	4.29	.31	.12	.06	.27	N/A	N/A
R101.7	6.44	.10	2.42	4.35	.38	.11	.05	.30	N/A	N/A
R102.2	5.19	.21	2.92	3.73	.24	.15	.05	.23	N/A	N/A
R102.9	4.93	.46	2.03	3.69	.20	.19	.04	.22	N/A	N/A
R104.0	4.73	.36	2.80	3.02	.33	.22	.03	.22	N/A	N/A
R107.5	5.14	.41	2.63	3.27	.47	.30	.03	.23	N/A	N/A
R108.0	4.94	.33	2.12	3.02	.44	.29	.03	.22	N/A	N/A
R108.8	5.03	.68	2.16	2.97	.57	.29	.04	.22	N/A	N/A
R109.5	4.63	.67	3.60	2.74	.54	.26	.03	.21	N/A	N/A
R110.5	5.24	.64	2.32	3.13	.52	.33	.03	.24	N/A	N/A
R111.7	5.30	.46	1.98	3.24	.49	.34	.03	.24	N/A	N/A
R113.0	5.25	.19	1.94	3.64	.31	.34	.04	.27	N/A	N/A
R114.0	5.42	.21	1.78	3.60	.33	.32	.03	.27	N/A	N/A
R115.0	5.05	.32	2.20	3.03	.45	.32	.03	.21	N/A	N/A
R116.0	5.40	.52	2.03	3.34	.52	.38	.03	.22	N/A	N/A
R117.5	5.60	.41	2.14	3.45	.49	.40	.03	.22	N/A	N/A
R118.7	6.09	.28	2.36	3.79	.45	.46	.03	.22	N/A	N/A

Table C3. Selected major and minor elements in the uppermost interval of the New Albany Group east of Hicks dome, Hardin County, Ill.--Continued

Sample No.	Al	Ca	Fe	K	Mg	Na	P	Ti	S	F
R120.1	6.46	1.28	2.77	4.04	.88	.57	.03	.22	N/A	N/A
R121.4	5.70	1.10	2.67	3.44	.79	.44	.03	.20	N/A	N/A
R122.9	6.16	.47	4.22	3.61	.53	.44	.06	.23	N/A	N/A
R124.0	6.26	.83	2.85	3.71	.62	.52	.08	.27	N/A	N/A
R125.2	5.79	.89	3.45	3.49	.69	.55	.05	.32	N/A	N/A
R126.6	6.06	.40	4.67	4.93	.33	.63	.04	.28	4.5	.03
R127.8	6.25	.74	3.67	4.51	.75	.68	.03	.28	2.7	.05
R129.2	6.65	.42	4.29	4.11	.71	.61	.04	.30	3.5	.08
R130.5	4.85	8.34	4.36	2.77	4.45	.65	.07	.20	3.3	.08
R132.1	2.5	14.7	3.34	1.43	7.84	.83	.04	.10	2.2	.03
R133.0	6.20	2.16	4.74	5.53	1.11	.58	.04	.26	4.4	.05
R134.0	6.50	1.47	6.37	4.67	.84	.74	.04	.26	6.5	.11
R134.9	5.07	.75	4.51	2.99	.58	.41	.03	.20	4.5	.06
R136.0	6.02	1.30	4.39	3.62	.87	.53	.04	.23	4.2	.07
R138.7	5.53	1.52	4.51	3.27	.97	.50	.03	.22	4.1	.05
R141.2	5.03	1.67	4.92	2.82	.91	.54	.03	.20	4.9	.12
R143.5	5.61	1.28	3.42	3.15	.81	.70	.03	.22	3.1	.06
R145.3	5.49	2.00	3.99	2.78	1.10	1.18	.03	.21	3.5	.05
R147.2	5.01	2.24	3.83	2.12	1.09	1.61	.05	.20	3.3	.04

Table C4. Selected minor and trace elements in the uppermost interval of the New Albany Group east of Hicks dome, Hardin County, Ill.

[Selenium was determined with an energy-dispersive analyzer; other elements were determined by the inductively coupled plasma method; <, less than; all data are in parts per million]

Sample No.	As	Ba	Cd	Co	Cr	Cu	Mo	Ni	Pb	Se	Sr	Th	V	Zn
USGS STANDARD SDO-1														
	69	397	79	47	66	60	134	100	28	3-7	75	10	160	64
GRASSY CREEK SHALE														
Henryville Bed														
R89.0	80	447	51	13	114	228	184	304	31	10	97	14	959	744
R89.4	80	518	25	20	116	115	242	458	35	<10	137	10	1,220	1,570
R89.9	70	558	9	15	134	109	110	279	30	<10	176	14	1,170	642
Falling Run Bed														
R90.8	30	396	3	14	118	78	31	169	19	<10	715	59	404	261
R91.1	50	413	<2	21	92	45	13	97	24	<10	275	36	306	306
Grassy Creek Shale, undivided														
R91.7	50	409	<2	30	78	45	8	95	21	<10	158	40	330	269
R91.8	60	635	<2	67	96	51	2	127	21	<10	126	22	275	106
R92.4	60	420	<2	48	110	65	9	117	22	<10	202	41	465	182
R93.5	90	371	17	20	151	144	73	267	36	20	123	25	1,310	894
R93.9	60	424	13	13	144	132	52	205	26	30	159	21	1,010	723
R95.0	50	372	8	12	139	128	46	189	22	35	105	18	873	481
R95.2	50	429	14	11	129	123	55	188	25	40	96	12	1,070	663
R96.1	40	324	7	11	130	113	28	166	22	35	78	16	681	445
R97.5	60	311	9	10	132	115	38	184	36	45	80	27	897	438
R98.2	40	329	11	10	141	115	25	168	24	35	119	23	705	743
R99.2	80	317	14	10	112	113	32	163	40	<10	244	42	605	901
R99.8	50	310	38	11	120	126	51	198	29	70	147	58	665	2,320
R100.1	60	328	11	12	149	118	36	178	24	55	118	22	852	614
R101.1	60	315	6	11	122	110	34	151	28	40	103	22	584	448
R101.7	60	339	2	12	129	105	32	146	27	25	97	20	583	236
R102.2	60	295	3	11	88	88	42	133	34	10	121	23	438	250
R102.9	50	278	3	12	83	85	54	145	30	35	169	38	478	27
R104.0	70	296	12	13	76	91	88	175	31	35	210	15	743	823
R107.5	80	321	4	15	82	96	102	196	29	25	164	19	866	234
R108.0	60	350	8	12	83	89	83	156	19	30	125	12	881	420
R108.8	70	308	6	13	85	92	92	177	25	75	95	7	890	410
R109.5	70	269	9	13	74	88	98	172	32	25	82	9	802	702
R110.5	60	311	<2	12	82	81	59	146	26	30	90	9	642	92
R111.7	50	314	3	12	84	83	64	147	24	50	81	13	657	233
R113.0	50	293	<2	14	82	88	95	177	22	55	78	37	570	170
R114.0	50	311	11	14	81	95	94	163	16	50	181	17	664	1,100
R115.0	60	309	5	14	77	81	83	152	18	50	116	9	586	449
R116.0	50	322	3	12	81	72	59	132	17	35	137	10	441	287
R117.5	40	343	<2	13	82	71	51	122	14	20	151	11	335	138
R118.7	40	333	<2	12	91	76	32	115	13	15	137	11	291	262

Table C4. Selected minor and trace elements in the uppermost interval of the New Albany Group east of Hicks dome, Hardin County, Ill.–Continued

Sample No.	As	Ba	Cd	Co	Cr	Cu	Mo	Ni	Pb	Se	Sr	Th	V	Zn
R120.1	40	335	<2	14	88	79	28	93	15	<10	151	10	202	120
R121.4	40	319	2	15	78	77	54	120	16	<10	128	9	271	307
R122.9	70	352	<2	16	91	85	55	152	23	<10	139	7	632	115
R124.0	60	349	<2	19	92	84	61	167	18	<10	165	10	582	198
R125.2	80	335	<2	31	82	80	80	197	20	10	164	9	382	204
R126.6	100	291	3	37	86	79	80	222	24	<10	266	18	259	298
R127.8	70	309	3	31	86	71	75	193	18	10	218	14	284	172
R129.2	80	366	3	37	91	79	83	217	17	<10	151	9	319	254
R130.5	70	265	<2	37	62	69	74	121	14	<10	440	10	172	49
R132.1	50	115	<2	23	33	36	39	67	10	<10	580	11	86	10
R133.0	90	249	<2	42	75	70	71	141	23	<10	299	18	158	82
R134.0	110	303	2	55	86	82	98	169	17	<10	193	19	195	95
R134.9	100	280	<2	31	65	65	78	89	29	<10	172	10	139	42
R136.0	80	376	<2	31	73	61	93	97	15	<10	114	12	163	64
R138.7	80	353	<2	29	66	58	94	88	22	<10	179	12	154	39
R141.2	100	376	<2	29	61	56	98	82	32	<10	114	12	138	48
R143.5	70	479	3	31	67	59	84	90	24	<10	121	18	146	169
R145.3	80	299	<2	30	65	56	86	83	31	<10	117	15	136	49
R147.2	70	189	<2	30	65	58	79	98	47	15	159	26	138	23

Table C5. Statistical data for selected major, minor, and trace elements in 54 samples from the upper part of the Grassy Creek Shale of the New Albany Group in Hardin County, Ill.

[Selenium was determined with an energy-dispersive analyzer; other elements were determined by the inductively coupled plasma method; min., lowest value or lowest limit of detectability; max., highest value reported; <, less than; all data are in parts per million]

Element	USGS standard SDO-1	Average	Sample standard deviation	Min.	Max.
Weight percent					
Al	6.49	5.7	0.8	2.6	7.7
Ca	1.1	1.25	2.4	0.1	14.7
Fe	6.53	3.0	1.0	1.6	6.4
K	3.39	3.7	0.7	1.4	5.5
Mg	0.93	0.76	1.1	0.2	7.8
Na	.28	.41	.27	.09	1.61
P	.05	.14	.48	.03	3.46
Ti	.31	.25	.04	.10	.37
Parts per million					
As	69	64	18	30	110
Ba	397	344	82	115	635
Cd	79	6	9	<2	51
Co	47	21	13	10	67
Cr	66	94	26	33	151
Cu	60	88	31	36	228
Mo	134	67	40	2	242
Ni	100	160	65	67	458
Pb	28	24	7	10	47
Se	3-7	19	21	<10	75
Sr	75	170	115	78	715
Th	10	19	12	7	59
V	160	533	321	86	1,310
Zn	64	392	412	10	2,320