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Chemical Geology 206 (2004) 249–258

CHEMICAL GEOLOGY
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Borehole petrophysical chemostratigraphy of Pennsylvanian black shales in the Kansas subsurface

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Accepted 23 December 2003

Abstract

Pennsylvanian black shales in Kansas have been studied on outcrop for decades as the core unit of the classic Midcontinent cyclothem. These shales appear to be highstand condensed sections in the sequence stratigraphic paradigm. Nuclear log suites provide several petrophysical measurements of rock chemistry that are a useful data source for chemostratigraphic studies of Pennsylvanian black shales in the subsurface. Spectral gamma-ray logs partition natural radioactivity between contributions by U, Th, and K sources. Elevated U contents in black shales can be related to reducing depositional environments, whereas the K and Th contents are indicators of clay-mineral abundance and composition. The photoelectric factor log measurement is a direct function of aggregate atomic number and so is affected by clay-mineral volume, clay-mineral iron content, and other black shale compositional elements. Neutron porosity curves are primarily a response to hydrogen content. Although good quality logs are available for many black shales, borehole washout features invalidate readings from the nuclear contact devices, whereas black shales thinner than tool resolution will be averaged with adjacent beds. Statistical analysis of nuclear log data between black shales in successive cyclothems allows systematic patterns of their chemical and petrophysical properties to be discriminated in both space and time.

Keywords: Borehole geophysics; Uranium; Thorium; Potassium; Atomic number; Clay minerals

1. Introduction

Black shales of Pennsylvanian age are widespread throughout the US Midcontinent. In Kansas, they outcrop as distinctive lithologies which are typically thin but widespread, and so make excellent marker beds for stratigraphic correlation. Kansas Pennsylvanian black shales occur in successions with abundant limestones that were deposited in open marine conditions. The Kansas shales can be contrasted with their stratigraphic equivalents in the Illinois Basin which are often associated with coals and may have accumulated in shallow water closer inshore. Coveney et al. (1991) suggested that these two depositional settings could be differentiated by Mo concentrations, where relative enrichment was retained by organic matter in acid pore fluids associated with nearshore sediment. Most Kansas Pennsylvanian black shales were deposited offshore under quiet, stagnant conditions in deeper water (Heckel, 1977, 1994) over a stable continental platform, although some were

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doi:10.1016/j.chemgeo.2003.12.027

formed nearshore, with a lower organic content (Schultz, 1991; Schultz and Coveney, 1992).

Black shales occur in a pivotal part of the classic Kansas cyclothem originally described by Moore (1936) and designated the core shale by Heckel (1977). The terminology differentiates this shale from other shales in the cyclothem, particularly the thicker nonmarine shales that separate the marine bundles of units that compose the majority of the cyclothems. The transgressive and regressive components of the cyclothem are readily recast as units of sequence stratigraphy (Fig. 1), where the core shale represents the highstand condensed section. Black shales exhibit lateral facies transitions into gray shales. The Pennsylvanian black shale units discussed in this paper are identified by their homologous position within cyclothems rather than by facies character alone. Consequently, they represent the condensed section of the highstand and their facies variation may be related to the eustatic signal in time and space.

Kansas Pennsylvanian black shale facies are fissile, carbonaceous shales that contain phosphatic nodules. Their clay mineralogy consists of chlorite, illite, kaolinite, and mixed-layer species (Schultz, 1987). In outcrop, the base of the black shale usually is sharp and the upper contact grades into a marine gray shale. Total organic carbon (TOC) values range between 10% and 15% (Coveney et al., 1991). Their relatively high radioactivity is caused by enhanced U content, partly as a component of organic uranyl complexes, but dominated by concentrations within phosphate nodules (Runnels et al., 1953; Hoffman et al., 1998). The black shales are usually enriched in metals (particularly zinc), but it is debatable as to which aspects of black shale geochemistry reflect depositional environment and sediment source, as distinct from overprinted patterns from diagenetic processes. However, redox-sensitive trace elements of V, Zn, Mo, and U seem to be robust measures of redox facies that allow environmental discrimination between euxinic, anoxic, and dysoxic conditions of deposition (Algeo and Maynard, 2004).

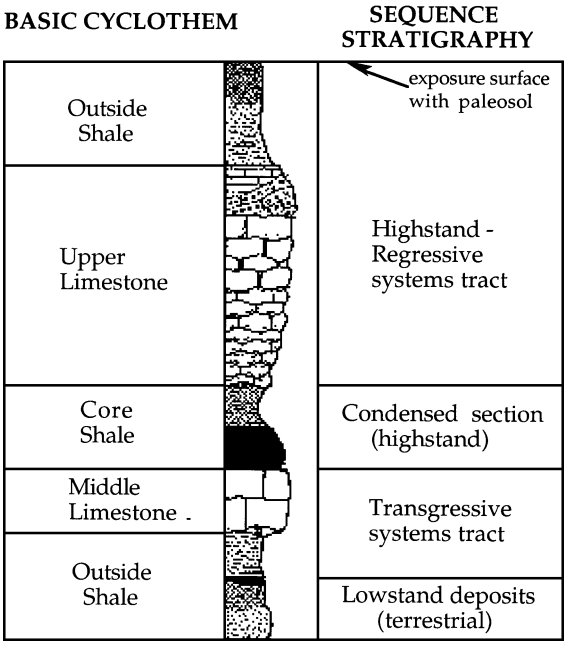

Fig. 1. Idealized Kansas Pennsylvanian cyclothem with matched sequence stratigraphic classification (modified from Heckel, 1994; Boardman et al., 1995).

2. General petrophysical logging measurements of black shales

The distinctive character of black shales on outcrop makes them readily identifiable in both core and drill-cutting samples from the subsurface. They are less obvious on resistivity logs, because their resistivity values are too similar to other mud rocks, although slightly elevated by their high carbon contents. Because of their increased U contents, however, Pennsylvanian black shales are easily recognizable as "hot shales" on gamma-ray logs, and they can be correlated for long distances in the subsurface. A typical gamma-ray log from eastern Kansas (Fig. 2) shows the position of thirteen Pennsylvanian black shales used in this study referenced to their stratigraphic groups. The measurement scale is in American Petroleum Institute (API) units, the international reference standard for gamma-ray logs that allows consistent comparisons to be made between a wide variety of gamma-ray counting devices. The API standard is set by the primary calibration test pit at the University of Houston where a radioactive cement calibrator is assigned a value of 200 API units and conceived originally so that a typical Midcontinent shale would register at about 100 API units (Ellis, 1987). The structure of the gamma-ray log (Fig. 2) shows a basic

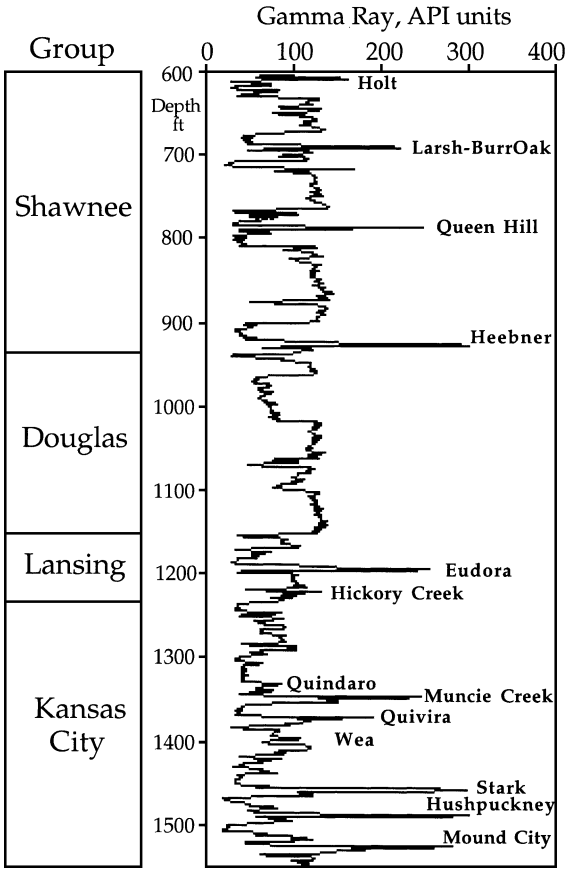

Fig. 2. Typical gamma-ray log of Pennsylvanian section from Wabaunsee County indexed with black shale units used in this study.

alternation between intervals of low-radioactivity, which are mostly limestones, and moderately radioactive shales that conform approximately with the expected value for a typical Midcontinent shale. The black shales, however, are prominent as thin anomalously radioactive zones. Their markedly different character is produced by high U content that supplement radioactive sources in gray shales of ^{40}K contained in illite and other K-bearing minerals, and Th contained in monazite in the silt and clay fraction and adsorbed at clay-mineral surfaces (Luthi, 2001).

The counts recorded on a conventional gamma-ray log are the sum of all gamma rays, most of which are emitted by ^{40}K and isotopes in the U and Th series. The energy levels of the gamma rays are characteristic of their source isotope and form distinctive spikes on a gamma-ray emission spectrum, although in practice, these spikes are smeared into a diffuse train of peaks by scattering events. However, by subdividing the total energy range into restricted windows, estimates can be made of the separate contributions of ^{40}K, U, and Th through computer processing. By contrast with the conventional gamma-ray log, which is generally scaled to the arbitrary standard of API units, the spectral gamma-ray log is displayed as three curves of Th and U, measured as ppm, and K in percent, together with the SGR (standard gamma-ray) log and the CGR (computed gamma-ray) log, which differs from the SGR by the subtraction of the U contribution (Fig. 3). The summation of the Th and K contributions as the computed gamma-ray log provides a better match with shale volume, because the disruptive influence of U has been removed.

A conventional gamma-ray log in API units can be approximately reconstructed from the elemental abundances by applying the multipliers of 8 to the U (ppm), 4 to the Th (ppm), and 16 to the K (%) estimates and summing their contributions (Luthi, 2001). This relationship provides a useful method to predict subsurface gamma-ray logging values of shale samples from outcrop and core, based on laboratory geochemical measurements. Analyses of the North American Shale Composite (NASC) reference standard (Gromet et al., 1984) reported values of Th 12.3 ppm, U 2.66 ppm, K 3.2%, which converts to an equivalent SGR log reading of 121.7 API units. Although higher than the vague assertion that a typical Midcontinent shale should read about 100 API units, the hypothetical log value of the NASC standard is a good match with the gray shales of the Pennsylvanian succession shown on Fig. 2. By way of comparison, the Marine Sciences Group Black Shale Composite (BSC) described by Quinby-Hunt et al. (1989) is characterized by values of Th 11.6 ppm, U 15.2 ppm, K 2.99%, which is equivalent to an SGR log reading of 215.84 API units. As might be expected, the K and Th contents of this composite are not markedly dissimilar from the NASC standard. However, the high variability of U contents among black shales results in a broader range about this standard, so that a maximum equivalent of about 3700 API units would be expected for the black shale with the most elevated U content reported by Quinby-Hunt et al. (1989).

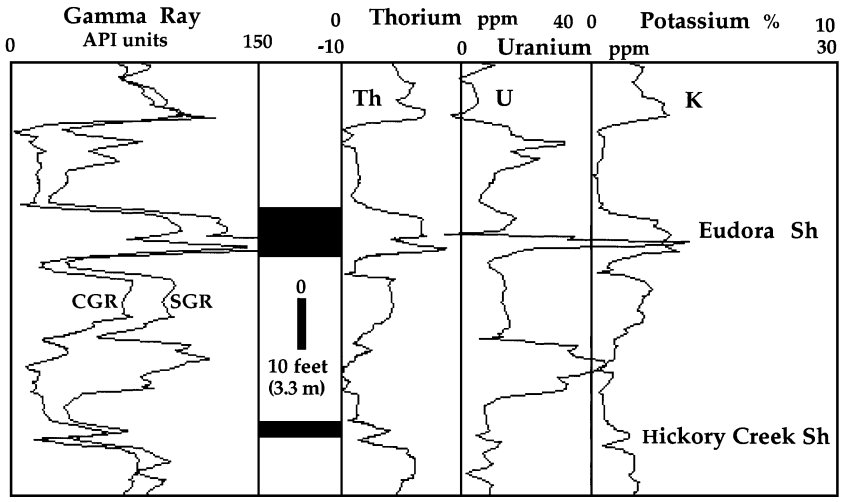

Fig. 3. Example of spectral gamma-ray log of a Lansing Group subdivision from a Wabaunsee County well (see Fig. 2) indexed with two black shale units used in this study. SGR is the standard gamma-ray log and is the summation of counts from all radioactive sources; CGR is the computed gamma-ray log that results from the subtraction of uranium sources from the SGR log.

The Th/K ratio can be applied to the recognition of clay minerals and distinction of micas and K-feldspars because the ratio is a relative measure of K richness as related to Th. The Th/U ratio also has proved to be useful as an indicator of redox potential, as suggested by Adams and Weaver (1958). More recent authors such as Jones and Manning (1994) and Dypvik and Harris (2001) have verified that this ratio is a useful practical measure of redox conditions. U has an insoluble tetravalent state that is fixed under reducing conditions, but is transformed to the soluble hexavalent state which may be mobilized into solution. In contrast, Th has a single insoluble tetravalent state which is associated geochemically with U and therefore is a useful standard for comparison purposes. Jones and Manning (1994) concluded that the Th/U ratio generally is a better indicator of redox conditions than either the Cr/V or Ni/Co ratios. Other authors such as Hoffman et al. (1998) conclude that geochemical indicators other than Th/U serve as better proxies for degree-of-anoxia, either singly or used in combinations. However, it is generally agreed that the Th/U ratio is a serviceable indicator of redox conditions and this measure is provided by the spectral gamma-ray log.

In recent years, a few spectral gamma-ray logs have been run in the Pennsylvanian succession in Kansas oil-exploration boreholes. Although they are limited in number, these logs provide important new insights on areal and temporal variations in K, Th, and U contents to extend outcrop interpretations of sedimentary environment dynamics and paleogeography. An example of this application is described by Newell et al. (2001) in which spectral gamma-ray log measurements from the Chattanooga Shale were used to map and interpret regional variability in central Kansas.

The gamma-ray log was the first downhole nuclear measurement to be introduced and made a break with older logs which were mostly records of electrical properties. This passive measurement of natural radiation was supplemented later by nuclear tools with radioactive sources of gamma rays and neutrons, whose attenuation by the formation in the borehole wall was measured by receivers. The reduction in high-energy gamma-ray flux from scattering by electrons is used as a measure of electron density and converted into an apparent bulk density in units of grams per cubic centimeter by assuming a Z/A ratio of 0.5. Density variations within black shales reflect changes in clay mineralogy and silt content, but also are affected by volumetric changes in carbonaceous material.

More recent density logs also record the photoelectric factor caused by the absorption of low-energy gamma rays, which is measured in units of barns per electron as set by the capture cross-section of formation elements, and so is a direct function of aggregate

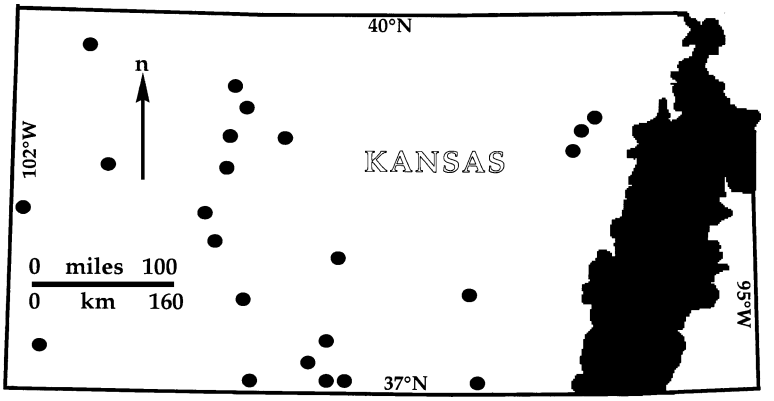

Fig. 4. Location map of Kansas marked with upper Pennsylvanian outcrop (black area) and spectral gamma-ray log locations (black circles).

atomic number. The photoelectric factor can be related to clay-mineral volume, clay-mineral iron content, and other black shale compositional elements.

Depending on tool design, the neutron porosity log records epithermal neutrons, thermal neutrons, or capture gamma ray that are generated in the progressive reduction of energy of fast neutrons from the tool source. The major loss of energy occurs as neutrons collide with hydrogen nuclei so that the neutron log is primarily a response to hydrogen concentration within the formation. Neutron log responses within black shales are compounded from hydrogen in the bound

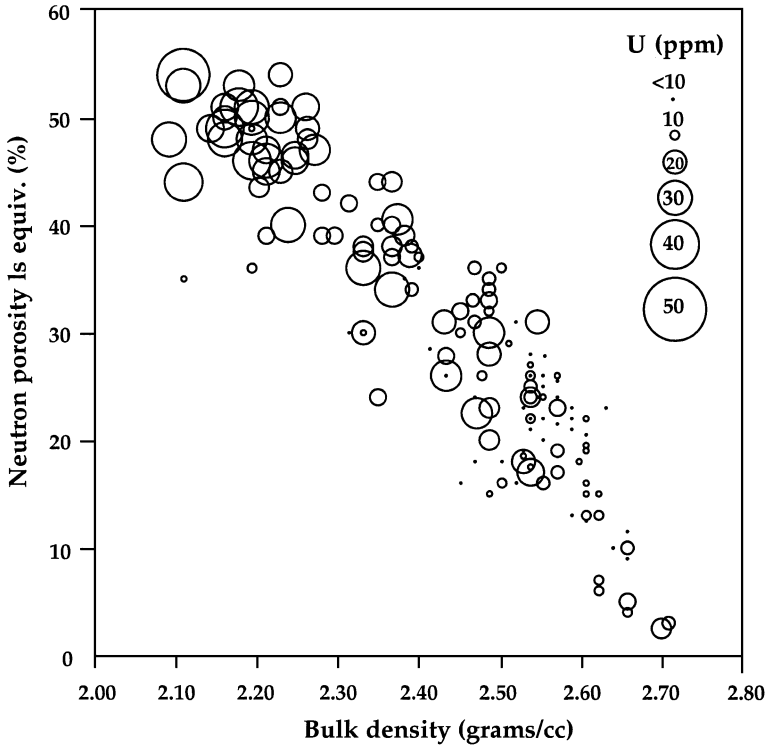

Fig. 5. Bubble plot of bulk density and neutron porosity in Kansas Pennsylvanian black shales. The bubble size is proportional to uranium content.

water of the shale, hydrogen in the lattice of the clay minerals, and neutron absorption by carbonaceous matter.

Gamma ray, neutron, density, and photoelectric logs are recorded routinely now in oil and gas exploration boreholes. In the majority of applications, the analysis of these logs is restricted to the evaluation of reservoir formations. However, the log properties of black shales have been studied in some detail where their thickness, maturity, and location identify them to be potential source rocks. The development of methods to predict total organic carbon content based on log responses has been the primary focus of these studies. The most direct method is through the use of the carbon/oxygen (C/O) log (Herron, 1987), which employs inelastic gamma-ray spectroscopy, but is not usually made outside specialized production logging evaluations. However, useable empirical relationships have been developed for TOC predictions based on the gamma ray (Schmoker, 1981), density (Schmoker, 1979), and porosity and resistivity logs (Passey et al., 1990). The predictive equations are moderately successful for shales with organic contents that exceed 3%, but are improved by calibration using cores from specific source rocks (Myers and Jenkyns, 1992). Although the thinness and shallow depth of burial of the Pennsylvanian black shales in Kansas do not make them candidates as prolific petroleum source rocks, their petrophysical properties are distinctive and can be related to composition and chemistry as discussed in the following case study.

3. Kansas Pennsylvanian black shales: a case study

Spectral gamma ray, neutron porosity, bulk density, and photoelectric factor log responses were recorded from 13 Pennsylvanian black shales in 23 wells distributed across Kansas (Fig. 4). The stratigraphy of these units is shown in Fig. 2 from a reference gamma-ray log in eastern Kansas, which was used as a type section in correlating the units across the state.

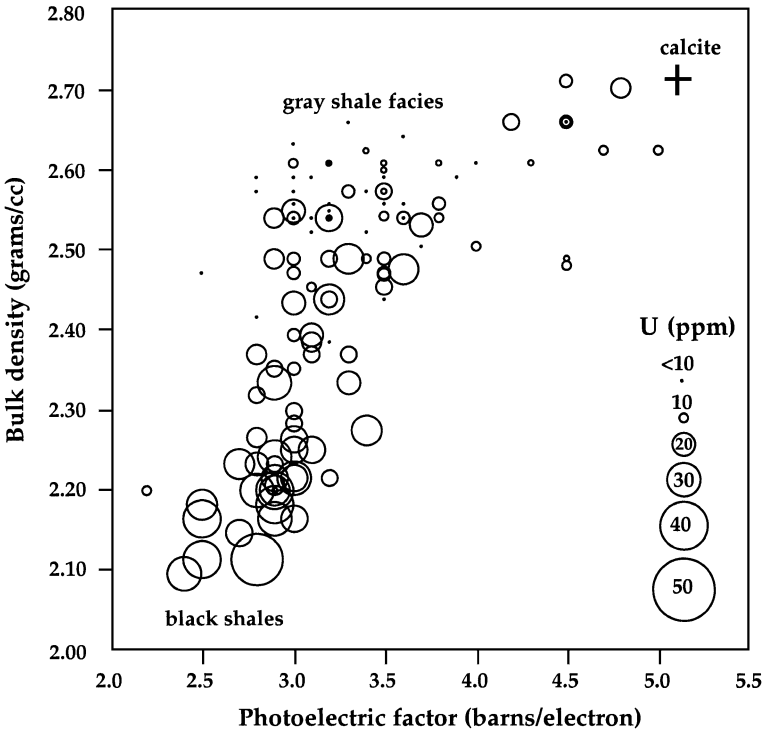

Fig. 6. Bubble plot of photoelectric factor and bulk density in Kansas Pennsylvanian black shales. The bubble size is proportional to uranium content.

Most correlations could be made with confidence, primarily because of the anomalously high gamma-ray signature. In some areas, facies changed from black to gray shale, and therefore unit recognition was based more on stratigraphic position. Excluded from consideration were black shale beds that were thinner than the resolution of the tools (about 2 ft or 0.6 m). Also eliminated were zones marked by borehole washout features that invalidate readings from the nuclear contact devices, and reduce count rates of gamma-ray measurements.

The bubble plot in Fig. 5 graphs neutron porosity and bulk density properties of the black shale sample, where the size of each bubble is proportional to the U content. Shales with high neutron porosities (about 45%), low densities (2.1–2.2 gm/cc), and high U contents contain the highest proportion of kerogen. Gray shale equivalents, with little U, have a neutron porosity of about 20% and density in the range of 2.5–2.6 g/cc. Although there are a variety of kerogen types, representative densities are of the order of 1.1–1.2 g/cc (Myers and Jenkyns, 1992) and the neutron hydrogen index somewhere between 0.67 and 0.92 (Mendelson and Toksöz, 1986). So the shale trend is a reflection of kerogen content within the black shale and matches similar patterns of log and TOC enrichment reported in many source rock studies. The U bubble plot of photoelectric factor versus bulk density in Fig. 6 shows a relationship with similar genetic implications. However, the distinctive "dog-leg" in the trend brings out the dominant three components of calcite, shale, and kerogen. The comparatively few zones with high densities and high photoelectric factors represent either highly calcareous shales or shaly limestones, as distinct from the more populous trend of the gray shale–black shale continuum. Although there is a generalized tendency for higher U in the more kerogen-rich shales, the match is not as systematic as one might expect if all the U content is linked with kerogen content and probably reflects the

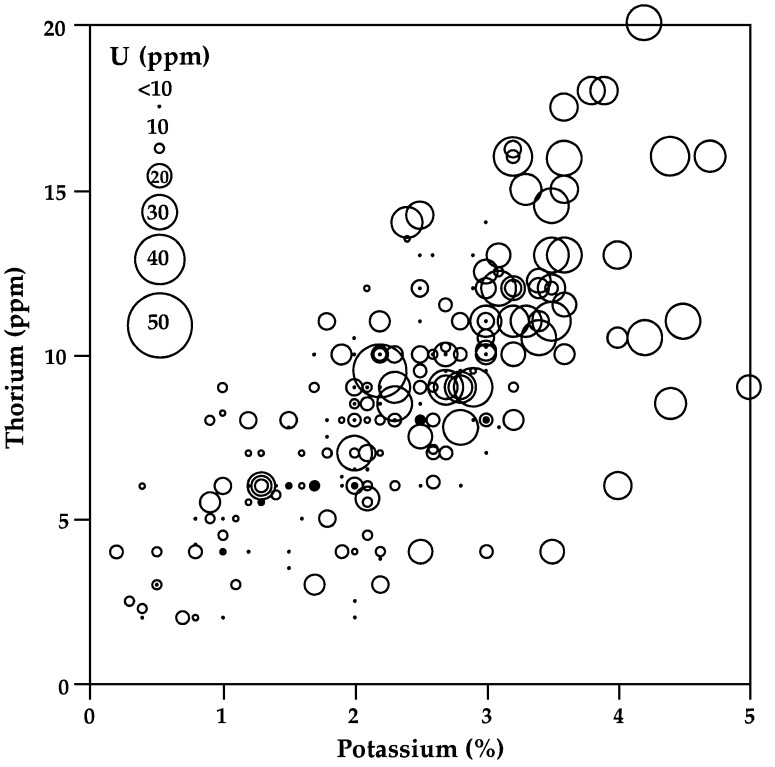

Fig. 7. Bubble plot of potassium and thorium contents estimated from spectral gamma-ray logs in Kansas Pennsylvanian black shales. The bubble size is proportional to uranium content.

fact that phosphatic nodules in the black shales also are significant hosts to U.

The crossplot of K and Th (Fig. 7) has been used widely in shale studies as a pattern recognition device to characterize clay-mineral aspects of shale successions logged by spectral gamma-ray tools. Higher Th and K contents are related to greater volumes of clay minerals. Higher U contents (indicated by the larger bubbles) seem to be associated with shales with greater clay-mineral contents rather than shales with appreciable contents of nonradioactive silt components such as quartz and calcite. The distribution of the points across the crossplot is an indication of relative K enrichment or depletion as gauged by Th content. Illitic clays are richer in K than smectites, in contrast with clay minerals such as kaolinite and chlorite that have minimal K contents. The general disposition of the data cloud is indicative of shale compositions that are dominated by illitic material, but also contain appreciable amounts of other clay minerals.

The spectral gamma-ray characteristics are particularly useful in discriminating black shale variability in time and space, and so statistical log signatures of the 13 individual black shales were extracted for comparison. In summarizing the statistics of spectral gamma-ray data by medians and quartiles, the effect of outliers caused by rogue correlations can be minimized or even eliminated. The temporal and spatial statistical variation of the black shale spectral data is summarized on Fig. 8 by median, 25th percentile, and the 75th percentile statistics for each black shale arranged as a stratigraphic succession where the depth separation of each shale is the average for the entire Kansas data set. The method is an expansion of the box-plot method introduced by Tukey (1977).

The left-hand track in Fig. 8 is an estimate of the proportional shale content (V_{sh}) as given by the summation of K and Th sources. Changes in median shale proportion reflect clay-mineral content or thickness variation. Because many of these black shales are calcareous, decreases in V_{sh} values may be caused by increases in calcite content at the volumetric expense of the clay-mineral fraction. Spectral gamma-ray tools are considered to have a resolution of about 1 ft (0.3 m), probably even better than the conventional gamma-ray tool because logging speeds are slower to improve count statistics. A decrease in shale proportion can reflect either a decrease in clay-mineral content or shales thinner than 1 ft (0.3 m), with inclusion of adjacent beds in the averaging of the log response. With these qualifiers in mind, the traces

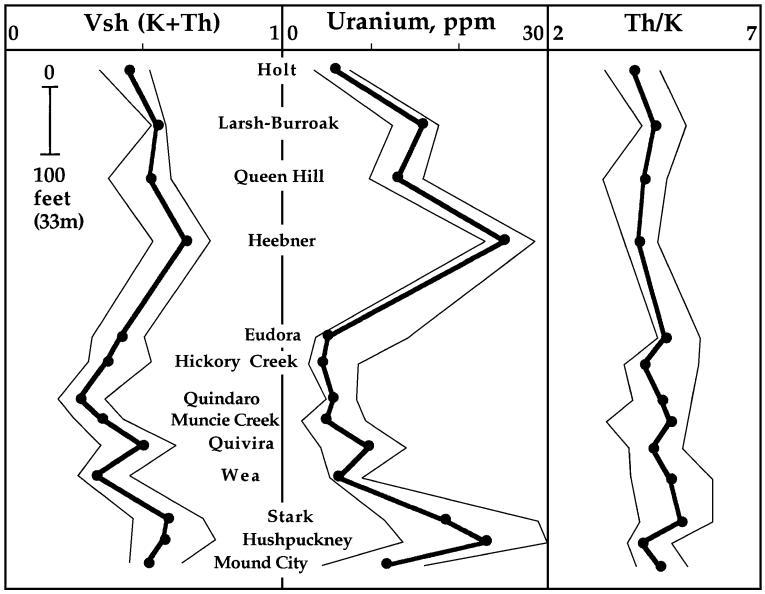

Fig. 8. Summary profile of gamma-ray spectral characters of black shales in Kansas wells. Heavy curve is median, light curves are 25% and 75% quartiles.

show both the shale content and the variability for the boreholes, taken as a representation of the Kansas platform.

A similar statistical and spatial interpretation can be applied to the central track, where the median and quartiles summarize the U content of the shales. The curves are readily interpretable in terms of a history of successive highstand condensed-section events that show comparable features with the eustatic sea-level fluctuation curve for the Upper Pennsylvanian proposed by Boardman and Heckel (1989) from outcrop studies. There are distinctive differences between the statistical patterns of individual black shales. The more radioactive units (e.g., Heebner, Hushpuckney) have generally been interpreted as deposited in deeper water and tend to have a symmetrical dispersion about their median values. By contrast, the less radioactive shales (e.g., Hickory Creek, Quindaro) may have been formed closer inshore which have pronounced asymmetry with a bias towards lower values. These patterns probably reflect secular and regional differences in the redox conditions at maximum transgression as suggested by Hoffman et al. (1998) from their study of geochemical proxies of anoxia in the Muncie Creek, Stark, and Hushpuckney shales.

Finally, the Th/K ratio shown in the right-hand track of Fig. 8 shows a relative depletion in K with increasing age. This relationship seems to be contrary to a generalized expectation of increasing illite content with depth of burial. However, the trend is significant at the 5% significance level and must reflect either diagenetic changes linked with depth of burial or changes in source material through time.

4. Conclusions

Nuclear petrophysical logs of black shales can be related directly to rock chemistry and provide a useful data source for chemostratigraphic studies in the Kansas subsurface. These remotely sensed observations extend traditional chemical analyses from the spatially restricted outcrop and occasional core into a wider areal coverage in the subsurface. The variation in neutron porosity, bulk density, and photoelectric factor logs in black shales is controlled mostly by kerogen content. Although there seems to be a generalized correlation between U and these kerogen indicators, the muted character probably is caused by U enrichment within phosphate nodules as well as kerogen uranyl complexes. The K and Th contents of the Pennsylvanian black shales is consistent with a dominant clay mineral of illite, probably with subsidiary chlorite and kaolinite. There is a systematic depletion of K relative to Th with increasing age of black shale caused either by burial diagenesis mechanisms or by a gradual change in depositional source material. Each black shale represents a highstand event so that their uranium content provides an indication of the prevailing redox conditions and the combined K and Th contents a measure of relative clay-mineral volume. The statistical log of the spectral gamma-ray elemental measures shows good concordance with eustatic sea-level fluctuations in the Pennsylvanian that have been proposed from outcrop studies.

Acknowledgements

Thoughtful reviews by R.M. Joeckel and J.B. Maynard contributed to a significant improvement to the manuscript. **[LW]**

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