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## Positron Annihilation Spectroscopy Study of Barnett Shale Core

Fnu Ameena<sup>a</sup>, Helge Alsleben<sup>b</sup>, Carroll A. Quarles<sup>a\*</sup>

<sup>a</sup>Physics and Astronomy, Texas Christian University, TCU Box 298840, Fort Worth TX 76129, United States

<sup>b</sup>Geology, Texas Christian University, TCU Box 298830, Fort Worth TX 76129, United States

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### Abstract

Measurements are reported of positron annihilation lifetime and Doppler broadening parameters on 14 samples of Barnett shale core selected from 196 samples ranging from depths of 6107 to 6402 feet. The Barnett shale core was taken from EOG well Two-O-Five 2H located in Johnson county TX. The selected samples are dark clay-rich mudstone consisting of fine-grained clay minerals. The samples are varied in shape, typically a few inches long and about 1/2 inch in width and thickness, and are representative of the predominant facies in the core. X-ray fluorescence (XRF), X-ray diffraction (XRD), petrographic analysis and geochemical analysis of total organic carbon (TOC) were already available for each of the selected samples. The lifetime data are analyzed in terms of three lifetime components with the shortest lifetime fixed at 125 ps. The second lifetime is attributed to positron annihilation in the bulk and positron trapping; and the third lifetime is due to positronium. Correlations of the lifetimes, intensities, the average lifetime and S and W parameters with TOC, XRF and XRD parameters are discussed. The observed correlations suggest that positron spectroscopy may be a useful tool in characterizing shale.

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### 1. Introduction

The Mississippian Barnett Shale is a large oil and natural gas resource in the Fort Worth Basin in north-central Texas. Originally considered only a source rock for hydrocarbons in the Fort Worth Basin, the Barnett Shale has become one of the first so-called unconventional shale gas resources, where hydrocarbons are extracted from very

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\* Corresponding author. Tel.: +1-871-257-7375; fax: +1-817-257-7742.

E-mail address: [c.quarles@tcu.edu](mailto:c.quarles@tcu.edu)

fine-grained, low porosity, low permeability rocks (e.g., Pallastro et al., 2007). Hydraulic fracture stimulation paired with advances in horizontal drilling allow the economic extraction of the resource (Steward, 2007). Since the Barnett Shale became a prolific gas producer, many other major shale deposits have been discovered and are currently being exploited. Discovery and exploitation of these shale gas resources have a significant economic impact on the US energy program (EIA, 2014). However, while exploration and exploitation of the resource is commencing, understanding the composition, textures, and overall behavior of these rocks remains challenging. Challenges arise because more traditional techniques and analyses are often insufficient because of the overall fine-grained nature of these rocks. Therefore, it is important to develop new ways to improve the characterization of shale and other fine-grained rocks.

Studies reporting positron annihilation spectroscopy (PAS) results in rocks are scarce (e.g., Urban-Klaehn and Quarles, 1999; Patterson et al., 2003). The scarcity of studies is perhaps the result of the complexity of the natural rock. Urban-Klaehn and Quarles (1999) report on the PAS study of sandstone and carbonate reservoir rocks. Their study is relevant to the present investigation since shale, just like sandstone and carbonate rocks, contain quartz and other silicate minerals, calcite and dolomite as important constituents. Patterson et al. (2003) present the only available PAS study of shale and report an interesting correlation between the S parameter and the total organic carbon (TOC) in a shale core. Based on the small number of available reports on PAS in rocks, additional studies are certainly warranted.

The long-range goal of this research is to develop PAS into a useful tool to supplement existing techniques such as X-ray fluorescence (XRF), X-ray diffraction (XRD) and rock evaluation to determine total organic carbon (TOC). Combining PAS with existing techniques may provide a more complete characterization of shale cores in the lab. The purpose of the present work is to understand how the PAS parameters, such as the S parameter and the positron and positronium (Ps) lifetimes, are influenced by the composition and structure of the various mineral components of the shale as established by other laboratory measurements such as XRF, XRD, and TOC determinations.

### Nomenclature

|     |                                    |
|-----|------------------------------------|
| PAS | Positron Annihilation Spectroscopy |
| Ps  | Positronium                        |
| XRF | X-ray fluorescence                 |
| XRD | X-ray Diffraction                  |
| TOC | Total organic carbon               |

## 2. Samples

Fourteen samples from a Barnett Shale core are selected from 196 samples ranging from depths of 6107 to 6402 feet. The Barnett Shale core was taken from EOG well Two-O-Five 2H located in Johnson county, TX. A small section of the core samples is shown in figure 1. The selected samples are all dark, clay-rich mudstone consisting of fine-grained clay-sized minerals. The samples are varied in shape, typically a few inches long and about 1/2 inch in width and thickness, and are representative of the predominant facies of five separate facies identified in the core (Bunting and Breyer, 2012).

X-ray fluorescence (XRF) measurements of 34 elements are available for each of the 196 samples (Kiesel, 2013). The 34 elements include the weight % of 10 elements Mg, Al, Si, Ca, Ti, K, P, S, Fe, Mn, which are primary constituents of the major mineral fractions in the shale, such as quartz, calcite, dolomite, pyrite, and illite. In addition, 24 other trace level elements are measured at the ppm level or as normalized K x-ray intensities.

X-ray diffraction (XRD) measurements are available for the selected samples (Bunting, 2007). The weight % of fourteen clay minerals are determined, including: quartz ( $\text{SiO}_2$ ), K-feldspar ( $\text{KAlSi}_3\text{O}_8$ ), plagioclase ( $\text{NaAlSi}_3\text{O}_8$ ,

$\text{CaAl}_2\text{Si}_2\text{O}_8$ ), calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), Fe-dolomite, siderite ( $\text{FeCO}_3$ ), pyrite ( $\text{FeS}_2$ ), Apatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}_2, \text{F}_2, \text{Cl}_2)$ ), akaganeite ( $\text{Fe}_3\text{O}(\text{OH}, \text{Cl})$ ), illite/smectite and illite ( $(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2(\text{H}_2\text{O})$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), and chlorite ( $(\text{Mg}, \text{Fe})_3(\text{Si}, \text{Al})_4\text{O}_{10}$ ). The samples vary in mineral concentration. For example for the major constituents, such as quartz, concentrations range from 24.4% to 69.5%, dolomite ranges from 1.6% to 56.9%, clay from 8.8% to 36.3%, and calcite from 0.2% to 54.3%.

Petrographic and geochemical analysis of total organic carbon (TOC) is also already available for each of the selected samples (Bunting, 2007). The TOC concentration of the samples range from 1.91% to 6.04%.



Fig. 1. Example of shale samples from Bunting (2007).

### 3. Experimental Details

The Doppler broadening measurements are made with a 2 inch Ortec high purity Germanium detector. The source was Ge-68 deposited on and sealed between two 12.7 micron Ti foils. The source is placed on a selected and marked flat side of the sample and covered with a 1.4 mm Titanium foil. The data are analyzed using a Sigma Plot transform, which first calculates and subtracts the background from the data and then calculates the S and W parameters. The data are accumulated at a high counting rate, which results in a broader spectrum. The S and W parameters are corrected for detector deadtime using the technique discussed previously (Quarles, 2009) and extrapolates the parameters to zero deadtime. We have found that deadtime correction is important unless the counting rate is kept very low and constant, which is difficult to do with variously shaped samples. No correction is made for positron annihilation in the source or the Ti foil.

The lifetime measurements are made with a conventional fast-fast setup using barium fluoride scintillation crystals coupled to Photonis XP2020/URQ photomultiplier tubes. The sample-source arrangement is the same as used for the Doppler broadening measurement except that a Na-22 source is used. In the lifetime analysis correction is made for the positron annihilation in the source and the Ti foil. The lifetime spectra are analyzed using the LT

(ver. 9) program (Kansy, 1996). The spectrum is fitted from about 1/10 the peak to well beyond the flat, random coincidence background. Two Gaussian functions are used to describe the resolution function. The spectrum is fitted to three discrete lifetimes with the shortest lifetime fixed at 125 ps to stabilize the fitting process and reduce dependence on the resolution function model. The weighted average of the 125 ps lifetime and second lifetime is calculated and interpreted as the average positron lifetime for annihilation in the bulk and trapping in the large variety of trapping sites in the sample. The third or longest lifetime is interpreted as the positronium pickoff lifetime. The weighted average lifetime is also calculated.

#### 4. Discussion of Results

The R statistical program (R project, 2014) has been used to investigate the large number of correlations between the PAS parameters and the some 40 composition and mineral components of the shale sample determined by TOC, XRF and XRD.

##### 4.1. Correlations among the PAS parameters

The six PAS parameters include the Doppler broadening parameters S and W, the positron lifetime and intensity and the positronium (Ps) lifetime and intensity. The shale is a heterogeneous mixture of many compositionally different, irregularly shaped, crystalline mineral grains of various sizes. One basic assumption of the following discussion is additivity: that the PAS parameters are the result of an average of the annihilations in the many shale components. Of course, deviations from additivity can be expected especially for very small grain size where positron annihilations with grain surface and interface sites may become more important than annihilation in the bulk grain.

Positron annihilation occurs in the bulk in the shale grains and from a wide variety of trapping sites. Ps, if formed, annihilates by pick-off from a variety of trapping sites. Positron lifetime in the bulk is the shortest. Positron lifetime increases with size of trapping site. Since many lifetimes are expected and the PAS apparatus is not able to resolve them, the data are analyzed in terms of an average positron lifetime and intensity. Since average positron lifetime and S both increase with larger trapping sites, some correlation between them is expected.

One Ps lifetime can be resolved from the average positron lifetime and represents the average of Ps formation and trapping in the various grains. It is known that Ps is not formed in many types of mineral grains such as quartz, calcite or dolomite. However, Ps does form in some clay minerals. Like positron lifetime, Ps lifetime is larger for larger trapping sites.

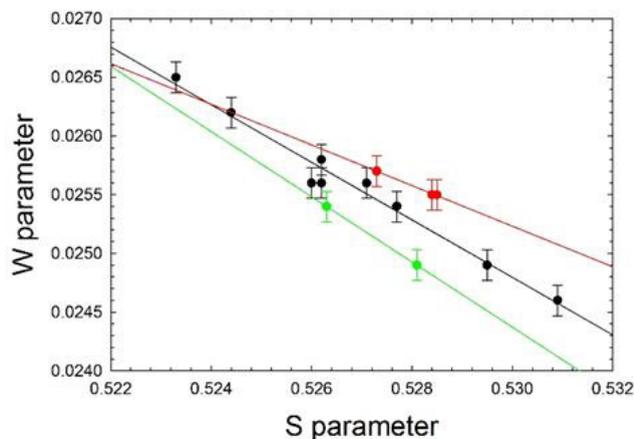


Fig.2. W parameter versus S parameter.

The S and W parameters depend on the probability of annihilation with valence and core electrons, respectively. S depends on both chemical composition and on structure and is expected to be larger when the probability of annihilation with valence electrons is higher, when positron trapping sites are larger, and when more Ps is formed. So, the weak correlation ( $r = 0.41$ ) observed between S and Ps intensity is expected. S is correlated with average lifetime ( $r = 0.63$ ). This is also expected since both S and positron lifetime increase with the size of the positron trapping sites.

S and W are negatively correlated ( $r = -0.81$ ) as shown in figure 2. Points that lie along one line have the same type of trapping site. Points that lie off the line have different types of trapping sites. In figure 2, two secondary lines are suggested as different from the main line. Of course, several points could be associated with either line.

#### 4.2 Correlations among the PAS and shale components

Previous work (Urban-Klaehn, 1999) has shown an important relationship among the average S parameters and positron lifetimes for sandstone, limestone and dolomite reservoir rocks that is useful for interpreting the present data. Sandstone is often dominated by quartz with minor amounts of other silicate minerals. These minerals also form one of the major components of Barnett Shale. Limestone (calcite) and dolomite are also major components of the shale. The two remaining components of shale are clay minerals and organic carbon. In a separate study, not yet completed, we are investigating the major shale clay minerals under various degrees of hydration. While this work is not yet complete and only four types of clay have been examined so far, some preliminary information about positron and Ps lifetime and intensity in some clays is available to help us in the present interpretation of the shale data.

Urban-Klaehn (1999) has shown that there is no Ps formation in sandstone, calcite or dolomite, that there is a correlation between the positron lifetime and S parameter and that the average S parameter and the average positron lifetime decrease from sandstone (0.5193, 0.342 ns) to calcite (0.5052, 0.284ns) to dolomite (0.4994, 0.259 ns). For the clay samples studied so far, the positron lifetime ranges from 0.3 ns for kaolin to ~0.4 ns for smectite and Na- or Ca-Montmorillonite. Ps intensity ranges from ~0 for smectite and Na-Montmorillonite to ~2% for kaolin to ~10%, depending on hydration, for Ca-Montmorillonite. We have yet to study other clays important in the shale composition.

There is a high degree of correlation between the elemental constituents of illite clay: Aluminum (Al), Potassium (K) and Titanium (Ti) as well as trace elements of Rubidium (Rb) and Niobium (Nb), which are also highly correlated with Al and K since these elements occur in the illite. On the other hand, Silicon (Si) is not well correlated with the other clay components, since it also occurs in quartz.

Some of the main correlations observed among the PAS parameters and the shale components are summarized in Table 1. The correlation coefficients ( $r$ ) are given by the R program. Some other common statistical programs report  $r^2$  instead of  $r$ , but we are interested in the sign of the correlation. So an  $r$  of 0.5 corresponds to  $r^2$  of 0.25 and would be considered a weak correlation. By common convention, most of the correlations in Table 1 are considered weak. Only a few correlations are at the level of  $r \sim 0.7$  ( $r^2 = 0.5$ ): the correlations of positron lifetime with the clay components Al, K, Ti, Nb, Rb and with Ca and carbonates ( $\text{CO}_3$ ); the correlations of the S parameter with quartz and with carbonates ( $\text{CO}_3$ ); and, finally, the correlations of Ps intensity with depth and Yttrium (Y).

S is correlated with quartz (0.73) and to lesser degree with Si (0.56). S is higher for quartz than carbonates, so increases with concentration. Similarly, S decreases with concentration of carbonates/dolomites (-0.78) and Ca or calcite (-0.54).

S increases with sulfur (and pyrite) concentration (0.68) suggesting a shorter bulk lifetime and smaller trapping site for the sulfur in the pyrite crystal structure. S decreases with Mn since Mn concentration tracks the carbonates.

Positron lifetime is correlated (~0.8) with illite clay components (Al, K, Ti, Rb, Nb) determined by XRF analyses, but correlation is only at 0.65 with clay from XRD measurements. The elemental components are highly correlated with each other. The positron lifetime is correlated with quartz, Si and pyrite at the ~0.5-0.6 level. The lifetime is higher for these materials compared to carbonates and so increases with concentration. Similarly, the

positron lifetime decreases with concentration of carbonates. On the other hand, the positron lifetime is weakly correlated with an increase in concentration of apatite. Perhaps this is due to the apatite structure.

The Ps lifetime does not show any significant correlation with any shale parameters. There is very weak negative correlation (-0.4) with concentration of apatite, yttrium and iron.

Ps intensity is perhaps most interesting and challenging to interpret. It shows one of the stronger negative correlations (-0.8) with depth. While we do not understand this at this point, it seems unlikely to be due simply to a decrease in trapping sites as pressure increases since the range over the core sample is only 200 feet. It is probably due to a combination of weaker correlations with various parameters that also decrease with depth. We know that there is no Ps formation in quartz, calcite or dolomite and that Ps does form in some clays and not in others. But the Ps intensity is positively correlated with quartz and negatively correlated with the clay elements. There is, however, a very weak positive correlation with apatite. Ps intensity is also correlated with the trace element Y and to a lesser degree with Ni and Cu, which are often associated with TOC. But, Ps intensity is not correlated with TOC. So, the interpretation is difficult. Perhaps, for example, Ps trapping sites are more prevalent in the small connective regions of clay between quartz grains rather than in bulk clay grains.

Table 1. Correlation of PAS parameters with selected compositional properties

|                 | <b>S parameter</b> | <b>Positron lifetime</b> | <b>Ps lifetime</b> | <b>Ps intensity</b> |
|-----------------|--------------------|--------------------------|--------------------|---------------------|
| Depth           | -0.50              | 0.17                     | 0.10               | -0.79               |
| TOC             | 0.39               | 0.54                     | 0.07               | 0.13                |
| Si              | 0.56               | 0.59                     | -0.30              | 0.34                |
| Quartz          | 0.73               | 0.46                     | -0.08              | 0.55                |
| Al, K...Nb      | ~0.30              | ~0.80                    | ~0.1               | ~0.52               |
| Clay            | 0.28               | 0.66                     | 0.14               | -0.47               |
| Apatite         | 0.58               | 0.41                     | -0.39              | 0.30                |
| Ca              | -0.54              | -0.79                    | 0.0                | -0.09               |
| Mn              | -0.66              | -0.62                    | -0.18              | -0.26               |
| CO <sub>3</sub> | -0.78              | -0.81                    | 0.03               | -0.12               |
| Calcite         | 0.58               | -0.57                    | 0.28               | 0.39                |
| Cu              | 0.17               | -0.26                    | -0.34              | 0.58                |
| Ni              | 0.49               | 0.33                     | -0.20              | 0.47                |
| Y               | 0.4                | -0.35                    | -0.37              | 0.69                |
| Fe              | 0.38               | 0.63                     | -0.39              | 0.01                |
| Pyrite          | 0.68               | 0.65                     | -0.27              | 0.12                |

#### 4.3 Correlations with %TOC

Of special interest to the geologist is the correlation of TOC with other shale parameters. The more significant correlations are summarized in Table 2. In geological studies of shale, Ni and Cu K x-ray intensities are often used as TOC markers. In these samples, Cu was not significantly correlated with TOC ( $r = 0.33$ ), and Ni was one of the weaker correlations. Several other elemental or mineral factors, alone or taken together, might prove to be better markers of TOC than Cu or Ni alone. While the positron lifetime was more significantly correlated with TOC than the S parameter or other PAS parameters, the correlation with positron lifetime was of the same order or weaker than many of the elemental or structural factors. The correlation of S parameter and positron lifetime with %TOC for the samples is shown in figure 3.

Table 2. Correlation of TOC with various shale and PAS parameters

| Shale Parameter   | TOC correlation |
|-------------------|-----------------|
| Si                | 0.59            |
| Mg                | -0.57           |
| Ca                | -0.70           |
| Ti                | 0.55            |
| Mn                | -0.78           |
| V                 | 0.61            |
| Cr                | 0.76            |
| Ni                | 0.59            |
| U                 | 0.53            |
| CO <sub>3</sub>   | -0.74           |
| Clay              | 0.57            |
| Feldspar          | 0.51            |
| Pyrite            | 0.57            |
| Positron Lifetime | 0.54            |
| S parameter       | 0.39            |

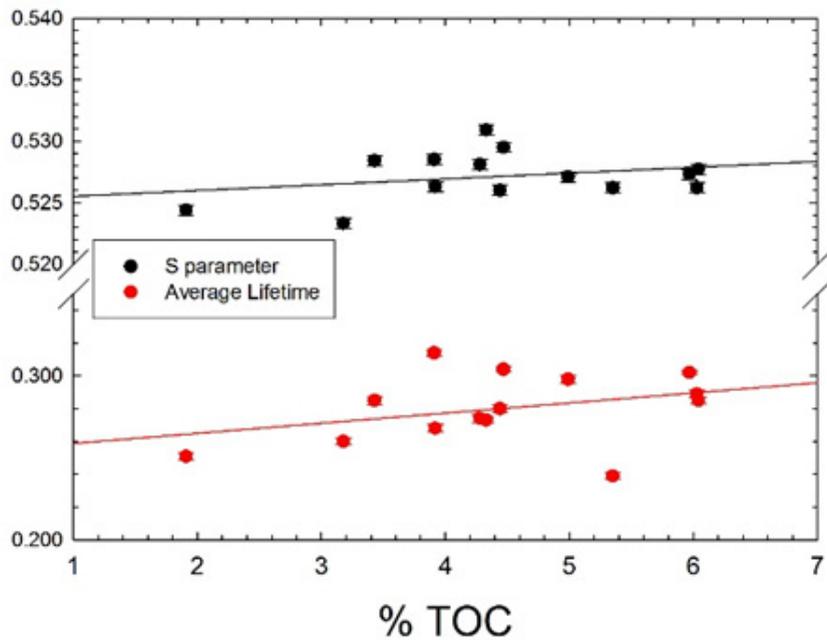


Fig. 2. Correlation of S parameter and positron lifetime with %TOC

## 5. Models

The S function and positron lifetime can be thought of as complicated functions of the composition and structure of the shale. We have tried some simple linear models to try to describe the PAS parameters.

For example:  $S = c_1 + c_2 * (\% \text{Quartz}) + c_3 * (\% \text{TOC}) + c_4 * (\% \text{Clay})$ .

Such models are certainly not unique, and we have not studied the problem long enough to claim that we have identified the best model. Examples of two models are shown in figure 4. The first model depends on weight percent of quartz, TOC and clay. The second model only depends on weight percent of quartz and TOC. The errors are the standard deviation of the data, which seems more reasonable than using the actual statistical error on the data points. The actual statistical error is much smaller, but in this modeling we expect to find much larger variation from data point to data point since samples are not expected to be uniform for any of the parameters, measurements of PAS parameters have not been done at the same place on the sample as mineral, elemental or TOC weight percent. Four (or three for the second fit) of the 12 data points were used to determine the coefficients of the model then calculate the fit to the remaining points. With the standard deviation errors shown, the reduced Chi Square for the first fit is 0.67, a good fit. The fit for the second model is not quite as good with a reduced Chi Square of 0.82.

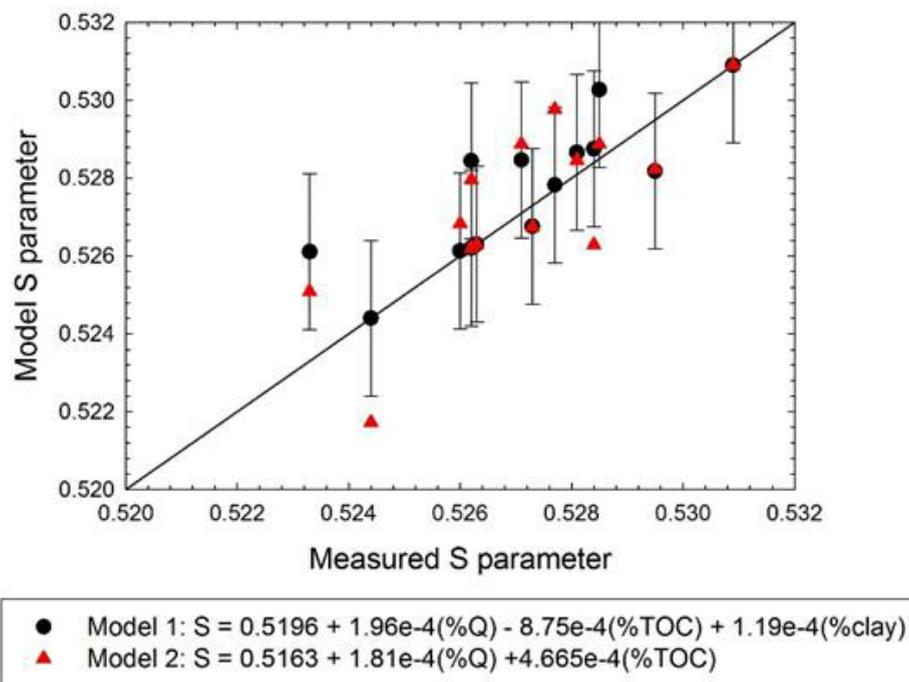


Fig. 3. S parameter from linear model vs measured S parameter.

## 6. Conclusions

The present work demonstrates that the PAS parameters are a bulk property of the shale just as TOC, resistivity, porosity or elemental composition. The region of sensitivity of PAS parameters is atomic or nano-scale, like elemental composition.

Some interesting correlations have been found between PAS parameters and various shale composition factors determined by XRF and XRD. The many, weak correlations observed support the hypothesis that the PAS parameters are determined by the shale parameters in a complex way, depending on such factors as elemental and chemical composition, structure, grain size and surface, and atomic scale vacancies that form positron and Ps

trapping sites. The average values of S parameter and positron lifetime are determined by a combination of bulk annihilation, positron trapping in a variety of sites and Ps formation, but show correlations with elemental and mineral concentrations consistent with what is observed for other reservoir rocks.

Preliminary work suggests that a linear model based on selected elemental and mineral concentration may be able to explain the PAS parameters. But such models are not unique, nor has a best model yet been determined.

Planned future work includes additional measurements of PAS parameters for the remaining samples (~100) of the dominant facies of the core as well as the study of other facies and comparison with the dominant facies. Further work with models is planned with the emphasis on determining whether certain composition factors, such as TOC, which are of interest to geologists, can be determined or predicted by the PAS parameters, perhaps in conjunction with a few selected elemental factors. If a predictive model can be developed, it would make the PAS measurements much more relevant to the characterization of the shale and ultimately be of more interest to the geologist.

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