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Developing a tool for the detection of the relative amount of water in shale cores using Positron Annihilation Lifetime Spectroscopy

C. A. Quarles^b, Helge Alsleben^a, James Bufkin^c, Joah Chun^d *

^aTexas Christian University, School of Geology, Energy, and the Environment, Fort Worth TX 76129 USA

^bTexas Christian University, Department of Physics and Astronomy, Fort Worth TX 76129 USA

^cAngelo State University, San Angelo TX 76909 USA

^dColorado College, Colorado Springs CO 80903 USA

Abstract

Recent investigation of positron lifetime in Barnett Shale samples has shown a small intensity of positronium (Ps) formation. The samples studied have XRF information on 35 elements and chemical information on total organic carbon (TOC). Previous research has shown that Ps is not formed in dry quartz-rich sandstone, calcite-rich limestone or dolomite-rich rocks, which contain minerals that also constitute a significant part of most shale samples. Recent study of twenty-five different common rock-forming minerals has helped to clarify the Ps contribution of different minerals commonly found in shale and the effect of hydration of some minerals on Ps formation. As a result, a better understanding of how Ps is formed in the shale samples is now available. It is suggested that the observed variation in Ps intensity in shale is due to variation in water content in the samples. While there is still no information about the possible Ps contribution of organic carbon in the sample, it is expected to be small. Development of a novel laboratory tool for the characterization of the amount of water in shale core using Positron Annihilation Lifetime Spectroscopy is discussed.

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* Corresponding author. Tel.: 817-257-7375; fax: 817-257-7742.
E-mail address: c.quarles@tcu.edu

1. Introduction

Positron Annihilation spectroscopy (PAS) is widely applied as a powerful tool to characterize diverse properties of materials such as vacancies in metals and semiconductors and free volume in polymers. (Jean et al. 2003; Prochazka, 2001; Shantarovich, 2006). But the PAS study of natural materials has been more limited due perhaps to the difficulty of interpreting PAS results in the case of heterogeneous samples. Recently investigation has begun into how PAS could help in the characterization of shale. (Ameena et al. 2014). A set of samples from a Barnett Shale core was available consisting of 196 samples spanning a range of depth from 6107 ft to 6402 ft (Bunting 2007). The core samples have been studied by XRF (Kiesel 2013) and also had total organic carbon (TOC) measured. The core was found to consist of five identifiable facies, based on visual assessment. In the initial work (Ameena et al. 2014) 14 samples were selected for PAS study. This subset of core samples were mainly from one facies and in addition to XRF and TOC had XRD composition measurements of clay and mineral content. The results of the initial study were interesting. While some correlations of PAS parameters with elemental and mineral composition were found, for the most part, the correlations observed were weak. It was shown that some PAS parameters could be modeled based on composition by assuming additivity and estimating the corresponding PAS parameters for the mineral constituents. But the more interesting reverse case of using the PAS parameters to predict composition or TOC did not prove to be possible. However, in the initial study, one correlation was found that was both unexpected and the strongest observed: Positronium (Ps) intensity with depth of the core sample. Initially no explanation was offered for this strong correlation. With the addition of 27 samples studied and presented here, this correlation is still observed. PAS studies of a variety of minerals that are important shale constituents have also been done and the results are reported at this meeting in another paper. (Alsleben et al. 2017). This study of mineral constituents of shales has helped to clarify the formation of Ps in shale. As a result, in the present work, Ps formation is interpreted primarily as a measure of water content in the samples. A novel PAS technique to characterize the water content of shale is also discussed.

Nomenclature

LT	Lifetime
PAS	Positron Annihilation Spectroscopy
Ps	Positronium
S	S parameter
TOC	Total Organic Carbon
XRF	X ray Fluorescence
XRD	X ray Diffraction

2. Caveat

In the discussion that follows, it should be remembered that PAS is a microscopic technique and that the lifetime or Doppler broadening parameters result from many positron interactions with the sample on an atomic scale. The trapping sites that influence the lifetime and S parameters are of atomic or molecular scale, atomic vacancies or defects, which may be a few atoms or molecules in size. Larger micron-size pores, which are of interest to geologists, are simply not noticed by positrons or Ps atoms, which diffuse to the nearest surface or may interact with molecules trapped in the pores or adsorbed on the surfaces. PAS is similar to XRF in sampling atomic scales.

Geological samples are very heterogeneous. Any PAS results are going to be an average over a small part of the sample, but generally enough of the sample (100s of microns or a few mm) to be considered a measure of the bulk material. Since PAS like XRF is an atomic scale techniques, sampling of the bulk assumes the principle of additivity. That is, the PAS results are the average of the many various experiences of the positrons in the bulk in proportion to the amount of a particular constituent or feature sampled.

It is generally recognized that taking XRF measurement on various parts of a sample and averaging the results is not useful (Kiesel 2013). It is sufficient to just measure one spot and assume it to be representative. It is the same for

PAS. Of course, occasional outliers in the data are then to be expected. For example, in XRF one may just accidentally hit a crystal of some sort that is not representative of the bulk sample. This will also be expected with PAS results. In this situation, the experimental or statistical error in the PAS or XRF data is typically much smaller than the variation in the sample that would come from measuring at different spots.

So, what can we hope to learn using these atomic techniques on real heterogeneous materials? Hopefully, we can obtain some average information about the bulk material. This is the same as familiar geological measurements such as density, porosity, resistivity, etc. So in this experiment we measure several bulk feature that we hope may prove to be useful in characterizing the material. The positron and Ps lifetime and intensities as well as the S and W parameters are such bulk properties.

3. Results and Discussion

A correlation of positronium (Ps) intensity with depth is shown in Figure 1. There is a correlation of Ps Intensity with depth with $r^2 = 0.69$ for region below 6200 ft and essentially no correlation for samples above 6200 ft. While not initially understood, this correlation is now thought to be due to variation of hydration of the core with depth. Studies of common shale constituents show that rocks and minerals that are dry or not hydrated do not form Ps (Urban-Klaehn et al. 1999; Alsleben et al. 2017). Typically, hydration of the minerals or water in pore spaces is needed for Ps to form. In many minerals the permeability and porosity do not allow for much if any variation in hydration in the lab. But in some clay minerals, Ca-Montmorillonite

for example, significant variation in hydration is possible and correlates with increase in Ps intensity as expected. The decrease in Ps intensity with depth below 6200 ft is thought to be due to a decrease in water content, either water in pores or hydration of the clays in the shale. Such a decrease may just be a feature of this particular core and might not happen in other cores. Samples at depth above 6200 just show a large fluctuation in Ps intensity with no correlation.

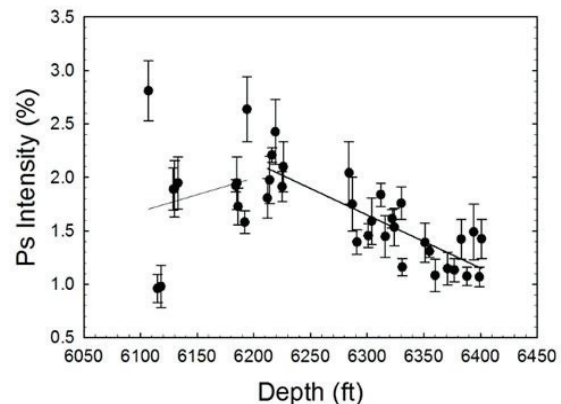


Fig. 1. Ps intensity versus depth of core

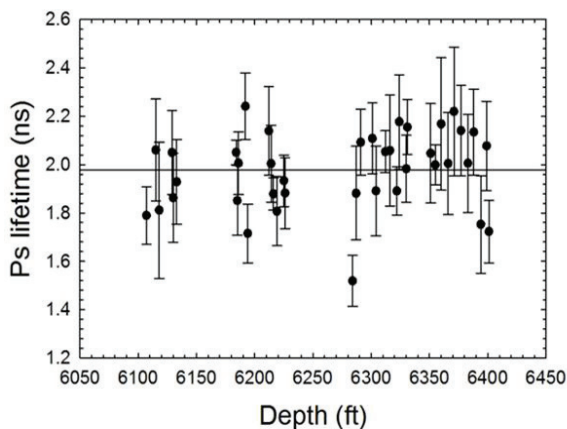


Fig. 2. Ps lifetime versus depth of core

the average observed here. While hydrocarbon liquids have lifetimes of 3 to 4 ns. This suggests that most of what we observe comes from water (Nakanishi et al. 1988).

This might be the common situation. Still, the observed correlation has helped focus attention on the role of water in the formation of Ps. Since there is not a generally accepted technique, like TOC or XRF, used by Geologists for measuring water content in shale, such a change in water content with depth as suggested here has not been discussed before.

Fig. 2 shows a plot of Ps lifetime versus depth. Essentially there is no correlation of Ps lifetime with depth: $r^2 = 0.05$. Ps lifetime is uncorrelated with any of the other XRF parameters or TOC as well. The line shown is the mean lifetime. The Ps lifetimes in the shale samples are very consistent with the range of lifetimes (1.5 – 2.3 ns) observed for various clay minerals (Alsleben et al. 2017). The iron-bearing minerals, which form Ps, have lifetimes at the extremes of this range. Ca-Montmorillonite, Kaolinite and several Illite mineral samples fall within the shale range in Fig. 2.

Water (free water) has a Ps lifetime of 1.85 ns, close to

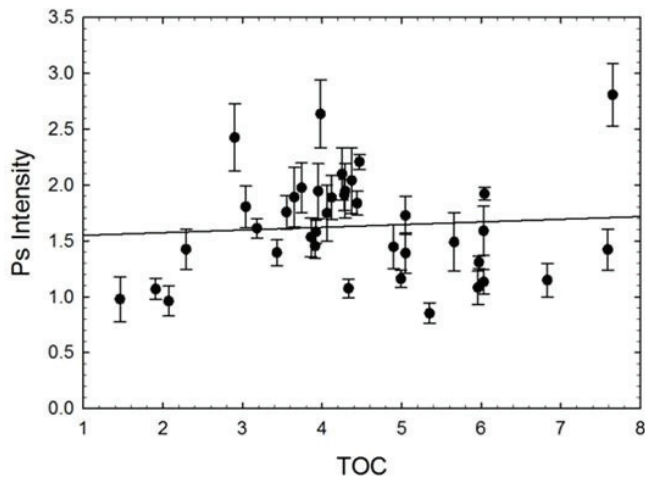


Fig. 3. Ps intensity versus Total Organic Carbon (TOC).

Figure 4. The Si/Al ratio is rather difficult to interpret since the variety of clays that could be in a sample can have a broad range of this ratio. Another parameter is the Ca concentration (not shown) with $r^2 = 0.51$. All other correlations with XRF elements are at levels from 0 to 0.4; and while certain trends may be of interest, the correlations are too weak to be significant.

4. Identification of Ps intensity with amount of water in the shale

It has been suggested in the discussion of results above that water is the main contribution to Ps formation in shale. The evidence for this conclusion is indirect, of course. First, sandstone and carbonate rock do not form Ps when dry (Urban-Klaehn et al. 1999). This means that the typical pore size is too large to trap Ps, which simply diffuses to the bulk wall. If the rock is permeable, unlike shale, then water can be adsorbed into the rock and Ps will form. Second, the situation for clays is similar. There is much more variation with clays since the degree of hydration can vary so much from one type of clay to another and from one sample of a particular clay to another. Nevertheless, there is no Ps formation in the dry or dehydrated clays and Ps formation intensity can be observed to vary when hydration is varied in a clay such as Ca-Montmorillonite. However, the hydration of most clays that have been studied cannot be varied easily because of low permeability. Third, there does not seem to be any Ps formation in the pore spaces between the clay and other mineral constituents of the shale. The pores are too large to trap Ps and the only Ps formation would arise from water adsorbed on surfaces of the various components in contact with each other. For shale, grain size is not small enough to trap Ps directly in the pores between grains. This would require nanoscale

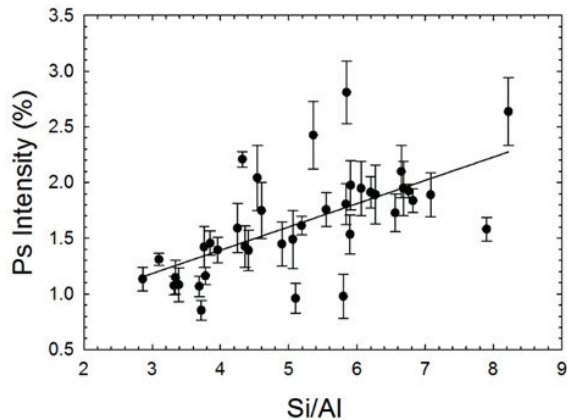


Fig. 4. Ps intensity versus Silicon to Aluminum ratio.

Fig. 3 shows Ps intensity versus TOC. Of course, it was hoped that a significant correlation of TOC with one of the PAS parameters would be found. This did not turn out to be the case. The slight increase of Ps intensity with TOC shown by the line has $r^2 = 0.01$ and thus represents no correlation at all. TOC itself shows a weak trend to increase with depth with an $r^2 = 0.18$. If Ps intensity depended on TOC one would expect it to follow the trend of TOC with depth and increase. So if there is any Ps formation in TOC it seems to be completely outweighed by the Ps formation in water and hydrated minerals.

Several shale XRF parameters are found to be more weakly correlated with Ps intensity than depth. One of these is the Silicon to Aluminum ratio. The correlation with the Ps intensity ($r^2 = 0.39$) is shown in

pores and grains. Fourth, the average Ps lifetime is consistent with the Ps lifetime in water and significantly lower than what would be expected for hydrocarbons or voids in minerals.

Finally, Ps formation might be expected in some of the organic material in the shale. However, there is no evidence for this and, as shown in Fig. 3, no significant correlation observed between TOC and Ps intensity. TOC is made up of a wide variety of hydrocarbon components that are not usually differentiated in a TOC analysis. We would not expect any Ps formation in the solid hydrocarbons. But there could be Ps formation in the liquid and gaseous components.

In summary, the evidence is compelling that Ps formation in shale is the result of Ps formation and trapping in water. Thus we propose using the intensity of Ps formation as a measure of hydration in the shale. Up to now there appears to be no other way to measure shale hydration. So the technique proposed here may provide a unique way to characterize the hydration of a shale sample.

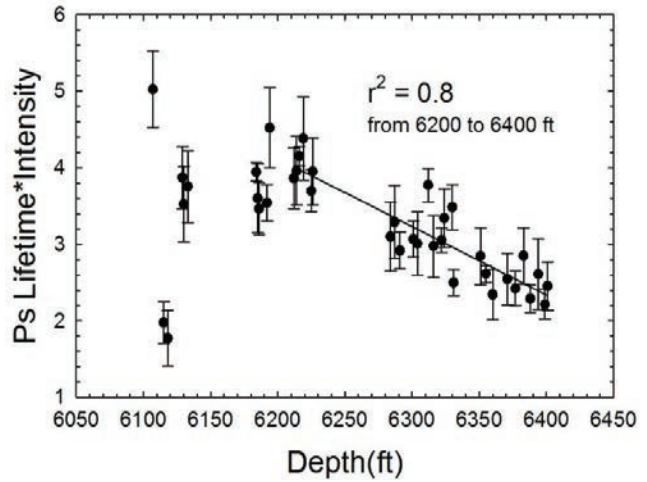


Fig. 5. Product of Ps lifetime and intensity versus

5. Proposed technique for the laboratory characterization of water in shale using PAS

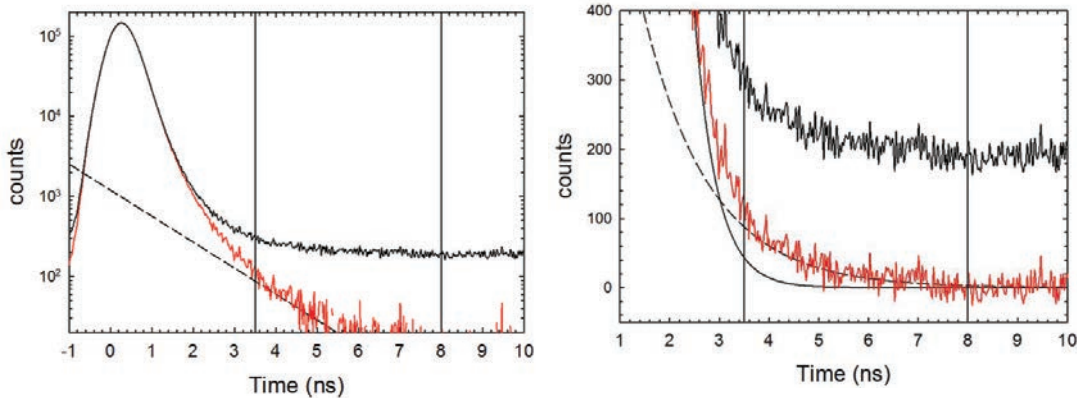


Fig. 6a. Semi-log plot of counts versus time. Times below zero just correspond to the stop signal arriving before the start signal and provide information on the timing resolution of the system.

Fig. 6b. Expanded scale to show the Positronium region of the lifetime spectrum.

The correlation of Ps intensity with depth above 6200 ft. shown in Fig. 1 is significantly improved from 0.69 to 0.80 if we consider the product of Ps lifetime and Ps intensity: Ps Lifetime*Intensity. This is shown in Fig. 5. This product is interesting since it is directly related to the total number of counts in the lifetime spectrum in the region of the spectrum dominated by Ps decay. Thus it can be directly determined from the positronium lifetime data without any

lifetime fitting procedure. The product is often related to the total free volume for the Ps formation (Jacobson et al. 2015).

Fig. 6a shows a semi log plot of the number of counts vs time for a typical positron lifetime spectrum for a shale sample. The raw data is in black; the data with constant background subtracted is in red. The dash line shows the fit to the Ps contribution to the spectrum. The two vertical lines at 3.5 and 9 ns delimit the range of Ps. In Fig. 6b, in the Ps region of the spectrum has been expanded. Here the vertical counts scale is linear. The fit to the longer component of the positron lifetime is shown as the solid black line. It can be seen that the positron and Ps fits intersect at about 3 ns. So if the lower range of the Ps region is set to 3 instead of 3.5 there would be more inclusion of positron counts into the total Ps count. So, a number, Ps counts, proportional to the product of the Ps lifetime and the Ps intensity can be obtained by simply taking the total net number of counts in the lifetime spectrum over the range where Ps contribution dominates, say in this case from 3 or 3.5 ns to 8 ns. At times longer than 8 ns the spectrum is just the constant background.

The main advantages of this Ps counts parameter are:

- (1) it is simple to calculate without a detailed fit to the lifetime spectrum,
- (2) the error is simply the statistical error in the net number of counts and is easy to calculate, and
- (3) the run can be made as long as needed to get adequate statistical error without having to run much longer to acquire the data needed to adequately carry out the multi-parameter fit to the lifetime spectrum.

This technique could facilitate scanning a core with a Na-22 source and a conventional PAS fast timing lifetime setup consisting of two photomultiplier/scintillator detectors, two constant fraction differential discriminators, a time-to amplitude (TAC) converter and an MCA. If it was desired to only measure the Ps counts, the MCA could be replaced by two discriminator/counters to select the Ps range and the background from the output of the TAC.

Since no lifetime fit is necessary, no correction needs to be made for the source as long as the Ps formation in the source is negligible. No correction needs to be made for Ti (or other foil) cover on source. The results for the product parameter can be normalized as desired and do not have to be on an absolute scale. However, the parameter could be calibrated to an absolute (ns)(%) scale by calibrating to a single lifetime run if desired.

Fig. 7 illustrates the errors in the Ps counts for two different choices of range in determining the number of counts compared with the results from the conventional fit to the lifetime spectrum. The three sets of data are arbitrarily displaced so the errors can be compared.

The individual lifetime runs had about 4×10^6 events. The mean error in Ps counts calculated from 3.5 to 8 ns from data is 2.1% and for 3 to 8 ns the error is 1.5%. The mean error for the product Ps Intensity*Ps lifetime calculated from the LT analysis is 15.8 %. So there is a significant improvement in error by determining the Ps counts directly from the data rather than doing the LT analysis. The Ps intensity and lifetime from the LT analysis are significantly affected by the need to determine the other parameters and their values and errors are influenced by the other parameters in the fit. These parameters (except background, of course) are not important in determining the number of counts in the Ps region. So the Ps counts can be measured with less error than a full lifetime analysis. An error in Ps counts of 3% would be a reasonable goal for most samples and this would only require 1000 Ps counts or about 10^5 counts in the whole

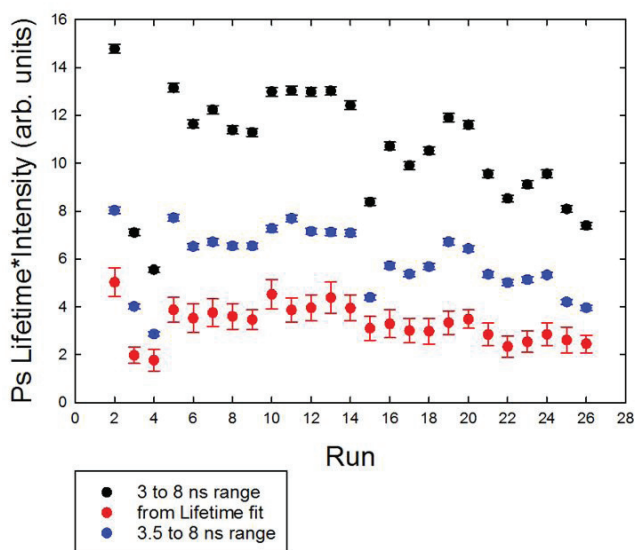


Fig. 7. Illustration of variation in errors for different choice of Ps region.

lifetime spectrum or one fourth the run time. This short run time would not yield enough LT data to do an adequate statistical analysis of the lifetimes and intensities in the conventional way, but would be adequate for determination of Ps counts. Thus, using this approach would significantly cut down on the run time needed to make a sample run and permit one to scan a larger part of a core.

Can an absolute hydration scale be established? Perhaps a standard could be developed using clays that are commonly used in ceramics. Ps counts for samples of clay such as kaolinite could be measured at different levels of hydration. The clay samples could be fired to a low temperature to drive off the pore or free water. Then the clay samples could be fired to the higher temperature (600 C) necessary to drive off the bound water. Comparison of Ps counts with sample weight could provide a standard for normalization of Ps counts to the weight percent of water.

6. Conclusions

In Barnett shale samples that have been studied, Ps is formed at the 1 to 3% level. Previous PAS studies of rocks and minerals (Urban-Klaehn et al. 1999; Alsleben et al. 2017) strongly suggest that the source of Ps formation is primarily bound water in the minerals and trapped water in the pores of the materials that constitute the shale. The relation of Ps formation with water has been proposed as an explanation of the interesting correlation of Ps intensity with depth of the core that had been observed (Ameena et al. 2014). Finally, it is proposed to use Ps formation as a measure of water in shale. Up to now, there has been no accepted way to measure the water in shale. A new method has been proposed that measures the number of counts in the lifetime spectrum in the region dominated by Ps formation rather than the conventional approach of doing a multi-parameter fit to the lifetime spectrum. The proposed technique would be simpler and faster, requiring less data collection time to obtain data of the desired precision.

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