Internal Radiation Levels in Natural Quartz Crystals Collected from Southwestern Nigeria; Implications on Thermoluminescence Studies

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Abstract: The relationship between natural thermoluminescence (TL) signal, activity concentrations and the TL sensitivities of twelve (12) quartz samples from different origins were investigated in this study. Gamma spectrometry measurements on the samples were carried out with coaxial-type Germanium detectors (Canberra Industries Inc., Meriden, CT, USA). The TL measurements on the samples were measured using a RISØ TL/OSL reader (model TL/OSL–DA–15). Concentrations of radionuclide activities were only detected in three samples with very low values as compared with world’s average. The highest dose rate in one of the samples was observed to be a factor of 15 lesser than a case of self-dose reported in the literature. The three samples with detectable activity concentrations are the one that possess highest TL signals. All the samples with an exception of one exhibit dependence of sensitization factor of 110 °C TL glow-peak on the equivalent dose (ED). This observation suggested a correlation between the ED of quartz and the sensitization factor of its 110 °C TL peak, an indication of the importance of ED in quartz TL and Optically Stimulated Luminescence (OSL) characteristics. There was no possibility of self-dose effect in all the samples and their radiation safety in exploration and applications in electronics and gemology are validated.

Keywords: quartz; gamma spectrometry; natural thermoluminescence; activity concentration; dose rates; dating

1. Introduction
Quartz and feldspar exhibit Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) signals with intensity levels corresponding to the amount of prior irradiations they received. Such luminescence signals have been used over the last 50 years in dating geological and archaeological materials [1–10]. The natural luminescence signal from a material to be dated is the basic tool that is employed in luminescence dating [7]. This is the basic principle for determination of the radiation dose that the materials received since they were either heated or exposed to sunlight [10–12].

Low luminescence sensitivity is a malign feature that makes the reliable luminescence ages to be dated difficult to determine. Possible presence of substantial quantity of feldspar as inclusion inside quartz crystal is always undesirable when it is to be used for luminescence dating or study. This is because feldspar is relatively more sensitive than quartz [3]. Therefore, its considerable inclusion in quartz usually undermines the overall result of luminescent measurements. Usually, this is checked by exposing aliquots to infrared (IR) stimulation at ambient temperatures, in order to check whether there is an infrared stimulated luminescence (IRSL) signal; in addition a light microscope is normally used to estimate the level of contaminations [13,14].
One interesting feature of the majority types of feldspar is that they show a significant content of $^{40}$K which can constitute a large percentage of the total ionizing irradiation dose to the sample. This “internal” component is unaffected neither by variation in interstitial water nor by the thickness of the overburden, and hence the overall uncertainty in the dose rate is reduced [3]. Some authors have laid emphasis on the importance of inclusions of radioisotopes in phosphors to be employed for luminescence dating [15–20]. In particular, the natural TL signal observed in ZrSiO$_4$ was ascribed to self-irradiation arising from the presence of U and Th content in the material by Siyanbola et al. [21]. Nevertheless, there is a need of striking a balance on this; for the reason that a considerable presence of radioisotopes in a phosphor can lead to self-dosing [22,23]. Application of KMgF$_3$ in environmental dosimetry was reported to be affected by a high self-dose owing to the presence of the natural isotope $^{40}$K which induces a TL signal superimposed on the TL signal arising from external irradiation [24,25]. This shows the importance of investigating of radiation levels in materials that are considered to be employed for luminescence dating and retrospective dosimetry.

Generally, the gamma ray spectrometric technique has been a conventional method for determination of radiation levels in any material of interest [26–30]. This technique has been widely employed in determination of radiation levels or radionuclide concentrations in various minerals and rock samples [28,29,31–37]. As part of the efforts of Balogun et al. [38] to characterize TL response of naturally occurring fluorite (CaF$_2$), they have investigated self-dose effect on the sample. They have reported a low-level radioactivity measurement, using gamma ray spectrometry, and the results showed no evidence of self-irradiation in the sample.

A major concern in quartz-based luminescence research and applications is the issue of its sensitivity which is very complex in nature [39,40]. Factors like geological origins as well as complex sedimentary history of various quartz samples, along with the effects of different laboratory procedures each sample is subjected to, have been reported to influence their luminescent sensitivities [41]. Much attention has not been paid to possible impacts of internal radiation levels of a quartz sample on its luminescence sensitivity. Therefore, three major approaches have been developed in the present work to assess the possible impacts of internal radiation levels of quartz sample on its luminescence sensitivity. The first was to evaluate internal radiation levels in some natural quartz samples collected from south-western Nigeria using gamma ray spectrometry. The second approach was to study the sensitivity of the TL signal in each sample and possibly correlate them with internal radiation levels and lastly, to check the possibility of the presence of $^{40}$K leading to potassium feldspar inclusions inside clean quartz samples.

2. Materials and Methods

2.1. Sampling

Twelve different quartz samples collected from south western Nigeria were given laboratory code names S1, S2, S3, S4, S5, S6, S7, S8, S9, S10, S11 and S12 respectively as shown in Figure 1. Fortunately, some of the quartz samples were recovered as bulk materials, without being of sedimentary (wind transported) origin. The modus operandi behind sample selections in this study was to have quartz grains that possessed the same radiation, optical and thermal histories for each sample used. That was devised to rule out the possibility of grain to grain different sensitizations. Thus, instead of using sedimentary quartz samples, the original quartz samples were crystals of hydrothermal and metamorphic type which occurred in veins associated with metamorphic rocks. S1, S2, S3, S4 (clear rock crystal type) and S6 (rose-pink type) are hydrothermal while S5, S7, S9, S8, S10, S11 and S12 (milky quartz species), are of metamorphic origin associated with granites. Cylindrical boreholes with samples were collected using sledge hammering. After collection, the samples were kept inside light proof containers while all handling and pre-treatment was performed in dim red light conditions. These samples, which could be considered as poorly bleached quartz species, were then crushed using an agate mortar, pulverized, sieved and finally
cleaned in acetone. Thereafter the pulverized samples were packaged into labeled airtight plastic dispensing sachets for analysis. No other chemical treatment procedure was applied. Grains with dimensions between 90 and 140 μm after the acetone cleaning procedure were used in the present study, for both TL and gamma spectroscopy measurements.

Figure 1. Map showing sample locations. (* = degree).

2.2. Activity Determination and Calculation of the Absorbed Dose Rates

About 200 g of each of the dried samples was repacked into an empty radon impermeable cylindrical plastic container of uniform size, which is comparable to that of the detector. They were sealed for about 24 days to allow $^{238}$U and $^{232}$Th and their respective progenies to reach secular equilibrium [37]. The samples were later subjected to gamma spectroscopy to determine the activities of their constituent radionuclides.

Gamma spectrometry measurements on the samples were carried out with coaxial-type Germanium detectors (Canberra Industries Inc., Meriden, CT, USA) at Laboratory of Environmental Radioactivity, University of Bremen, Germany. The detectors are within 50% relative efficiency and a resolution of 2.4 keV at 1.33 MeV. The system was set up to cover about 2 MeV photon energy ranges over 4 k channels. The detectors are properly shielded in lead castles [37]. Calibration of the measuring systems were carried out using certified reference standard for various radionuclides. Spectra analyses were performed with the Genie 2K spectrometry software, version 2.1 (Canberra Industries Inc., Meriden, CT, USA). A library of radionuclides, containing the energy of the characteristic gamma peaks for each of nuclides analyzed and their corresponding emission probabilities, was built from the data stored in the software. The characteristic gamma peak energies of the various nuclides were used for their identification. Counting time was 24 h for each sample, in order to achieve minimum counting error. It should be noted here that prior to every sample measurement, the environmental gamma background at the laboratory site was determined with an empty plastic container under identical measurement conditions,
which was later subtracted from the gamma spectra of each sample. Specific activities of the radionuclides were expressed in Bq kg\(^{-1}\) of dry mass of the samples and corrected for the time elapsed since the sample collection in the sampling site.

With the aid of the detection systems used for this analysis, nineteen different nuclides were monitored in the framework of the present study. The energy corresponding to the characteristic gamma peaks for each one of the nineteen nuclides, their corresponding emission probabilities and representative of their detectable limit (DL) are presented in Table 1. This approach was employed in an attempt to detect \(^{40}\)K and at least the activity concentration of a daughter product of the three natural radioactive families \(^{238}\)U, \(^{232}\)Th and \(^{235}\)U to represent the family. This was necessary since activities in all the twelve samples were very low, rendering thus the estimation of the corresponding dose rate in all samples difficult if not impossible. This assumption is justified in as much as the universal necessary procedure for reaching secular equilibrium [37] between these radioactive families and their respective progenies was religiously observed during this analysis.

Table 1. Energy of the characteristic gamma peaks for each of the nineteen nuclides, their corresponding emission probabilities and representative of their detectable limit (DL).

| Nuclide Name | Energy of Gamma Peaks (keV) | Emission Probability (%) | Detection Limit (DL) Bq kg\(^{-1}\) |
|--------------|----------------------------|--------------------------|------------------------------------|
| Be-7         | 477.60                     | 10.44                    | 1.154                              |
| K-40         | 1460.83                    | 10.67                    | 2.783                              |
| Co-60        | 1173.23, 1332.49           | 99.85, 99.98             | 0.123                              |
| Cs-134       | 563.24, 569.33, 604.72, 795.86, 801.95 | 8.63, 15.39, 97.63, 85.40, 8.69 | 0.109                              |
| Cs-137       | 661.66                     | 85.00                    | 0.123                              |
| Ti-208       | 277.36, 583.19, 860.56     | 6.31, 84.50, 12.42       | 0.128                              |
| Pb-210       | 46.54                      | 4.24                     | 1.413                              |
| Bi-212       | 727.33, 1620.50            | 6.58, 1.49               | 1.659                              |
| Pb-212       | 238.63, 300.09             | 43.30, 3.28              | 0.228                              |
| Bi-214       | 609.31, 1120.29, 1764.49   | 46.10, 15.10, 15.40      | 0.337                              |
| Pb-214       | 53.23, 242.00, 295.22, 351.93 | 1.20, 7.43, 19.30, 37.60 | 0.3367                             |
| Ra-224       | 240.99                     | 4.10                     | 2.433                              |
| Ra-226       | 186.10                     | 3.51                     | 2.506                              |
| Th-227       | 235.97, 256.50, 329.80     | 12.10, 7.00, 2.80        | 0.776                              |
Table 1. Cont.

| Nuclide Name | Energy of Gamma Peaks (keV) | Emission Probability (%) | Detection Limit (DL) Bq kg\(^{-1}\) |
|--------------|-----------------------------|--------------------------|-------------------------------------|
| Ac-228       | 338.32, 911.20, 968.97, 1588.20 | 11.27, 25.80, 15.80, 3.22 | 0.452                               |
| Th-228       | 84.37, 215.98              | 1.22, 0.25              | 4.454                               |
| Pa-234M      | 766.37, 1001.03            | 0.32, 0.84              | 0.136                               |
| Th-234       | 63.30, 92.50               | 4.10, 4.63              | 1.242                               |
| U-235        | 143.76, 163.33, 185.72, 205.31 | 10.96, 5.08, 57.20, 5.01 | 0.154                               |
| Am-241       | 59.54                      | 35.90                   | 0.142                               |

In addition to this, it has been reported by Chiozzi et al. [42] that for rocks older than \(10^6\) years in most geological environments, particularly for those with very low salinity [43,44], there is secular equilibrium between \(^{232}\)Th and \(^{238}\)U and their decay products. By following this rationale, Hamby and Tynybekov [27] and Tzortzis et al. [28] have reported an accurate estimation of radionuclide concentration of \(^{232}\)Th that was obtained from average concentrations of \(^{212}\)Pb and \(^{228}\)Ac.

The calculated absorbed dose rate, \(DR\), due to the mean activity concentrations of \(^{238}\)U, \(^{232}\)Th and \(^{40}\)K in the quartz samples was calculated, in nGy h\(^{-1}\) using the formula [45–47]

\[
DR = (0.427A_U + 0.662A_{Th} + 0.0432A_K)
\]

where \(A_U\), \(A_{Th}\) and \(A_K\) are the mean activity concentrations of \(^{238}\)U, \(^{232}\)Th and \(^{40}\)K, respectively. However, based on the above assumption of secular equilibrium, concentrations of \(^{226}\)Ra was used as \(^{238}\)U concentration [48], while that of \(^{212}\)Pb was employed for \(^{232}\)Th concentration [27,28] and in addition, a direct measurement of \(^{40}\)K, was utilised for its dose rates (DR) estimation.

2.3. TL Measurements

All TL and IRSL measurements on the 12 quartz samples that were pulverized and cleansed in acetone were carried out using a RISØ TL/OSL reader (model TL/OSL–DA–15) equipped with a 0.075 Gy/s \(^{90}\)Sr/\(^{90}\)Y \(\beta\) ray source [49]. The reader was fitted with a 9635QA photomultiplier tube. The detection optics consisted of a combination of a Pilkington HA-3 heat absorbing and a Corning 7–59 (320–440 nm) blue filter for the case of TL measurements while a Hoya U-340 filter was used for the IRSL measurements. A heating rate of 1 °C s\(^{-1}\) was used in all TL readouts in order to avoid significant temperature lag, up to a maximum temperature of 500 °C. The test dose applied was 10 Gy in all cases. Each measurement is the average over three individual TL/IRSL measurements using multiple aliquots, each one containing roughly 800–1000 grains in the specific grain size.

3. Results and Discussion

3.1. Activity Concentrations

The activity concentrations of \(^{40}\)K, \(^{212}\)Pb, \(^{214}\)Bi, \(^{214}\)Pb, \(^{210}\)Pb, \(^{226}\)Ra, \(^{234}\)Th and \(^{235}\)U that could be detected, at least, in one of the 12 quartz samples analysed in this work are presented in Table 2. Henceforth, each one of the samples will be referred to by the
laboratory code given to, as indicated in Table 2. Activity is reported in Bq kg\(^{-1}\) on the basis of the sample’s dry weight. The absorbed dose rates calculated in the remaining four samples are as well presented in Table 2. No artificial radionuclides were detected in any of the samples.

Table 2. Activity concentration of radionuclides detected for the 12 quartz samples and calculated dose rates.

| Sample’s Lab. Name | Sample Locations | Activity Concentration (Bq kg\(^{-1}\)) | Calculated Dose Rates |
|--------------------|----------------|
| Sample’s Lab. Name | Sample Locations | Activity Concentration (Bq kg\(^{-1}\)) | Calculated Dose Rates |
| S1 Okerimi Oro     | BDL BDL BDL BDL BDL BDL BDL BDL BDL | 40K 210Pb 212Pb 214Bi 214Pb 226Ra 234Th 238U D(nGy h\(^{-1}\)) |
| S2 Ijomu Oro       | BDL 0.32 ± 0.15 0.97 ± 0.19 0.90 ± 0.15 BDL BDL BDL BDL BDL | 0.33 |
| S3 Olorunsogo Oro  | BDL BDL BDL BDL BDL BDL BDL BDL BDL | 0.33 |
| S4 Ijero Ekiti     | 29.23 ± 2.34 7.39 ± 1.61 BDL 3.33 ± 0.37 3.98 ± 0.35 8.96 ± 2.93 BDL BDL BDL BDL BDL | 7.19 |
| S5 Olorunsogo Igara| BDL BDL BDL BDL BDL BDL BDL BDL BDL | 0.33 |
| S6 Aramoko Ekiti   | BDL BDL BDL BDL BDL BDL BDL BDL BDL | 0.33 |
| S7 Ado Ekiti       | BDL BDL BDL BDL BDL BDL BDL BDL BDL | 0.33 |
| S8 Ugbe Akoko      | BDL BDL BDL BDL BDL BDL BDL BDL BDL | 0.33 |
| S9 Okeagbe Akoko   | BDL BDL BDL BDL BDL BDL BDL BDL BDL | 0.33 |
| S10 Akure          | BDL 0.47 ± 0.25 1.51 ± 0.37 BDL BDL BDL BDL BDL BDL | 0.09 |
| S11 Kabbba         | BDL BDL BDL BDL BDL BDL BDL BDL BDL | 0.09 |
| S12 Igwe Marble Deposit | BDL BDL BDL BDL BDL BDL BDL BDL BDL | 0.09 |

BDL = Below detection limit.

As can be observed from Table 2, all the activity concentrations of all the radionuclides in 8 quartz samples (S1, S3, S5, S6, S7, S8, S11 & S12) out of the total of 12 samples are below detection limit. As a matter of fact, the threshold detectable limits for these radionuclides (Table 1) being extremely low, indicate the high sensitivity of the detection systems used for this work. Sample with code name S4 was observed with the highest radioisotope concentration of 40K, 238U and 232Th respectively. These values are very low as compared with activity concentrations in rock samples in Ikogosi-Ekiti Nigeria, a town that falls within the study area. Average activity concentrations of rock samples in this town for 40K, 238U and 232Th, are 1203.1 ± 687.2, 57.9 ± 28 and 81.6 ± 23.8 Bq kg\(^{-1}\) respectively [31].

The sample observed with the highest activity concentration of radionuclide out of the remaining four quartz samples with detectable activity was S4. As reflected in Table 2, 40K in this sample was observed to have activity of 29.23 ± 2.34 Bq kg\(^{-1}\) while 4.46 ± 1.29 and 2.15 ± 1.74 Bq kg\(^{-1}\) were the corresponding values observed in S2 and S10 respectively. The 40K activity concentration detected in these 3 samples is higher compared to the activity detected in each of other radionuclides. The higher activity of 40K is expected, because findings have shown activity concentration of 40K to be always higher than those of 234Th and 238U [26,36,48]. However, the activities of 40K observed in the present study are relatively too low compared to those found in the literature of the world mean activity concentrations of 40K in granites and Earth crust that are 1055 and 400 Bq kg\(^{-1}\) respectively [46,50]. Although, Malczewski et al. [48] reported activity concentrations in quartz to be lower as compared to the activity concentrations they observed in other minerals in their work, the activity of 324 ± 7 Bq kg\(^{-1}\) for 40K that they still reported is far higher than that of sample 4 in this study by a factor of 11.

Activity concentrations of 226Ra, chosen to represent 238U since they are generally in approximate equilibrium [26], measured in this work for S4 is 8.96 Bq kg\(^{-1}\). This value is
very low also as compared to the world average $^{226}$Ra activity concentration in granites and Earth crust that are 42 and 35 Bq·kg$^{-1}$ respectively [46,50]. Noted to be as well far higher than that of the present study is the activity concentration of 46.8 ± 6.6 Bq·kg$^{-1}$ for $^{226}$Ra in quartz as reported in their study. Table 2 also depicts the activity concentrations of other three progenitors of $^{238}$U series detected in S4 to be 7.39 ± 1.61, 3.33 ± 0.37, and 3.98 ± 0.35 Bq·kg$^{-1}$ for $^{210}$Pb, $^{214}$Bi and $^{214}$Pb respectively. These three activity concentrations are lower than that of $^{226}$Ra reported above in the same sample. This observation is due to the well-known gaseous mobility of $^{222}$Rn that can be airborne before the next step of transformation to $^{218}$Po; therefore yielding reduced $^{214}$Pb, $^{214}$Bi and $^{210}$Pb activity concentrations as observed in this work [48,51].

Notwithstanding, these concentrations of $^{214}$Pb and $^{214}$Bi are informative on concentration of $^{238}$U in S2 and S10 in which higher progenitors of $^{238}$U were not detectable. As depicted in Table 2, the activity concentrations of $^{214}$Pb and $^{214}$Bi in S2 and S10 in questions are much lower than that of S4. These low values are in good agreement with the reason why $^{226}$Ra activity is below detection limit in the two samples. This establishes the fact that $^{238}$U activity concentration is far low as compared to the one present in S4. The only radionuclide detected in S9 was $^{214}$Pb with activity concentration 1.01 ± 0.37 Gy/kg. This value is as well comparatively low to that of S4 thereby establishing the level of radioactivity in this sample to be low also. Information contained in Table 2 as related to $^{232}$Th series is only $^{212}$Pb representing the series with activity concentration of 0.32 ± 15 Bq·kg$^{-1}$ that was detected in S2. Except this, none of its series was detected in any of the 12 samples analyzed in this work. Similarly, it was only in S4 that $^{235}$U was detected with a low activity concentration of 0.55 ± 0.18 Gy/kg.

The low radionuclides’ activity in the 12 samples is better portrayed by the absorbed dose rates’ evaluation of the 3 samples noted with highest activity concentrations. As illustrated in Table 2, S4, S2 and S10 are with dose rates 7.19, 0.33 and 0.09 mGy/h respectively. These dose rates are far less as compared with the ~1.5 mGy/h observed in KMgF$_3$ by [24,52]. They reported the high self-dose owing to the presence of the natural isotope $^{40}$K in their samples. This effect resulted in inducing a TL signal that superimposes on the TL signal of external irradiations, thus, posing a major drawback for the application of this material in environmental dosimetry.

### 3.2. Thermoluminescence

The TL measurements on all samples in the present study were carried out according to the sequence outlined in Table 3. It is obvious that the laboratory dose (Step 1 in the table) on each of the quartz samples was administered without prior heating which made the natural TL still intact. Equally, the TL response of the 110 °C TL recorded in Step 2 has no pre-dose contributions [53,54], consequently leaving the observed 110 °C TL sensitivity as a product of the applied artificial laboratory dose in each of the samples. The case of the TL of the thermally stable traps (i.e., in the high temperature TL region above 180–200 °C) that are traditionally used for dating is different from this. The TL measurement in Step 2 of the table will be hereafter termed as “first glow” for both cases of 110 °C and thermally stable traps. In this “first glow” TL measurements, the 110 °C TL intensity corresponds solely to the dose attributed inside the laboratory before the measurement. Different factors are, however, responsible for the TL signal measured in the repeated Step 3 that was carried out on the same aliquot. The TL readout of Step 2 that produced the “first glow” plays significant dual roles. While it serves as the thermal activation [54–56] for 110 °C TL peak, by it the thermally stable traps are also evicted; the signal corresponding to the deeper traps corresponds to the sum of natural irradiation plus the artificial dose inside the laboratory. For both cases of 110 °C and thermally stable traps, the TL recorded will be referred to as “second glow” henceforth; this corresponds to the regenerated TL signal. Importantly, the use of the same aliquots provides the opportunity to also study relative sensitization pattern among the samples.
Table 3. TL measurement protocols.

| Step | Description |
|------|-------------|
| 1    | A test dose (10 Gy) was given to a same sample |
| 2    | TL readout up to 500 °C was carried out on the same sample |
| 3    | Steps 1 to 2 were repeated for the same sample |
| 4    | Steps 1 to 3 were repeated for another sample |

A selection of representative glow curves in the cases of both first as well as second glow measurements described above are respectively presented in Figure 2. Samples with codes S2, S4 and S10 are selected for plotting because they yielded measurable activity concentration of radionuclides and at the same time having the highest signals. Included also is S8 that represents the group of samples with activities below the detection threshold. However, information about integrated luminescence signal for all the samples is contained in Figure 3. Different geological origins, complex sedimentary and diverse radiation histories of each quartz sample, are part of the known contributors to the general differences in luminescence properties of quartz [41]. These factors are responsible for different sensitivity patterns exhibited by all the samples as depicted for “first glow” in (A) of Figure 2. Recall that the sensitivity is defined as the amount of luminescence emitted per unit sample mass in response to a fixed laboratory dose [23]. The reasons behind the relative low response of 110 °C TL peak “first glow” with respect to its counterpart in the “second glow” in (A) of Figure 2 are as follows. The natural charges of shallow traps like those occupying the 110 °C TL peak, are not generally retained for long because they are consequently evicted within few hours after they are trapped for the case of “first glow”. Secondly, there are no contributions from the popular pre-dose and thermal activation as earlier pointed out equally for “first glow”. Conversely, the enormous response recorded for “second glow” for the 110 °C TL (in (B)) over its “first glow” is a function of the heat dependent pre-dose and the thermal sensitization effects.

Figure 2. A selection of TL glow curves for 4 quartz samples in a semi-log scale for better view. TL signals of (A) “first glow” (B) “second glow”.

Figure 3 gives room for featuring all the just explained illustrations for all the samples. It equally presents the corresponding TL integral recorded for all the samples for better comparative analyses. Worthy of mentioning is the observation that the three samples earlier noted with measurable activity concentrations above BDL (Table 2) are the three sets with highest “first glow” TL response in Figure 3 for both 110 °C TL ((A) in Figure 3) and thermally stable trap (C) in Figure 3). Sample S4 yields the highest TL signal, followed by S10 and S2 that are with nearly identical levels of 110 °C TL integral ((A) in Figure 3), whereas, S2 leads S10 with a clear demarcation for the thermally stable traps (C) in Figure 3). However, S2 is observed to be the one leading in “second glow” ((B) in Figure 3) with S4 and S10 following respectively. The integrated TL signal of the remaining samples with activity concentration BDL for all the just aforementioned cases do not follow a specific pattern. Similarly, “second glow” (D) in Figure 3) for thermally stable traps entirely exhibits arbitrary trend for all the samples. It is important to note that S4, S2 and S10 that possess highest “first glow” signals are the three samples with detectable activity concentrations. Two plausible inferences are possible. The presence of the activity concentrations in the three samples, no doubt, contributed to the naturally accumulated dose acquired in them that (i). enhances the pre-dose and thermal sensitization of the 110 °C TL integral ((B) in Figure 3) and (ii). also boosts the level of the filling of the thermally stable traps with naturally acquired dose ((C) in Figure 3). There is a need to consider other factors since the observed activity concentration is limited to only three out of twelve samples.
The thermally stable traps trail a different order with higher intensities of “first glow” over the “second glow” (Figure 2). The “first glow” could gain enormous output by the combined effects of the predominant natural irradiation each samples had received and the laboratory dose. The extent to which the thermally stable traps are filled is respectively reflected to the intensity and the structure of each quartz samples. Therefore, the TL readout that produces the “first glow” has out rightly left the laboratory dose of Step 3 in Table 3 as a sole dose contributor producing the “second glow” for the thermally stable traps. This elucidates why the signal of the “second glow” of the thermally stable traps is relatively dim.

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Other factors apart from the popular intrinsic nature of each sample and the geological history of each sample are; (i) the level of the external background radiations received by each sample from the environment, (ii) and the level of feldspar inclusions inside each quartz. The first factor is inferable by evaluating the equivalent dose (ED) accumulated onto each sample. Since the samples under study are neither of fluvial nor of sedimentary origins, it is believed that their sensitivities could not have been heavily susceptible to external factors like reworking and weathering differences.

Therefore, the additive dose procedure was applied in order to estimate the ED for each quartz sample [57,58]. However, all 12 quartz samples studied were semi-transparent to light, excluding bleaching of the light sensitive traps before collection. In other words, the measured ED for each case results from both light sensitive traps, such as the 325 °C TL trap [59,60] as well as the light insensitive traps, such as the 375 °C TL trap [7]. In the case of the light sensitive TL trap, the remnant ED could be used to estimate the natural TL and should be compared to the ED yielded by the insensitive trap. This is possible since TL signal is never totally zeroed due to incomplete bleaching that leads to unbleachable residual component [61,62]. The histogram with these ED values is presented in Figure 4. Error bars indicate 1σ values over the values of the light sensitive and light insensitive TL traps. This figure together with the level of the filling of the thermally stable traps with naturally acquired dose ((A) in Figure 2 and (C) in Figure 3) provide evidence that thermally stable TL traps are never totally zeroed. The plot of the integrals of the high temperature TL peaks which were monitored after the second glow are presented versus the ED values in Figure 5A. As this figure is going to further reveal, the TL integral yields a straightforward, increasing tendency with ED for five samples. Surprisingly, the three same samples that yield measurable activities due to the decay of specific radionuclides are inclusive. Out of the other seven that are independent on the accrued dose, a group of six indicate similar sensitivities with an exception of sample S7. The plot of the integrals corresponding to high temperature peaks for “first glow” versus the ED values do not seem to reveal any systematic trend of dependence. As a result, they are not presented here.

![Figure 4](image-url) Figure 4. Plot showing remnant ED estimated in each sample. Error bars indicate 1σ values.
Figure 5. Plot showing the integral of second glow of high temperature TL glow peaks versus remnant ED estimated in each sample (A). Error bars indicate 1σ values. Plot (B) presents the sensitization factor versus the remnant ED.

Figure 5B presents the sensitization factor of the 110 °C TL peak versus the equivalent dose. All the samples exhibit gross dependence of sensitization factor on the ED with an exception of only S7 again. This observation is very interesting because it establishes a viable dependence of the ED on the sensitization of the 110 °C TL peak. This is not only the main premise for the application of the pre-dose effect, but also the sensitivity of the 110 °C TL glow-peak of quartz is a basic tool routinely used for monitoring, checking and correcting variations of sensitivity of TL and OSL dating and retrospective dosimetry protocols. Therefore, the correlation of ED and the sensitization factor of the 110 °C TL peak iterating the importance of ED in TL and OSL features [53,55,63]. Finally, both plots of Figure 5 indicate that the sample with code S7 indicates both low sensitivity as well as low sensitization factor. As all radioactive elements were below detection limits, this low sensitivity and sensitization could be attributed to the a rich content in iron centers, which at the same time act as killer centers for both sensitivity and sensitization in TL signal.

Finally, there is a need to confirm that these sensitivities are not contributions from feldspar contamination. This was undertaken by conducting IRSL measurements in other aliquots of each sample following administration of 10 Gy on natural (Natural + 10 Gy) of each (Table 4). As shown in Figure 6, it is observed that S12, S11, and S5 show feldspar inclusions, with S12 indicating the highest content followed by S11 and S5. From this, it is clear that feldspar inclusion contributed to the sensitivities and TL signals of these three samples.

Figure 6. IRSL curves showing 4 samples that are affected along with S2 and S4 that are representing the remaining samples that are free of feldspar infection.
Table 4. IRSL Measurement protocols.

| Step | Description |
|------|-------------|
| 1    | A test dose was given to a same sample |
| 2    | IRSL measurement was carried out on the same sample |
| 3    | Steps 1 and 2 were repeated for another sample |

The evidence of considerable natural TL signals in all the 12 samples investigated in this work shows that they can be used for dating and generally supports the idea of using quartz from the area as a TL dating material. However, for the 3 samples that exhibited feldspar inclusion, it is recommended that the necessary treatments be applied to them before utilizing them for dating and luminescence studies.

4. Conclusions

Activity concentrations of 12 quartz samples collected from different locations over Nigeria have been investigated using gamma spectrometric technique in this work. The overall radionuclide activities detected in three of all the 12 samples are very low as compared to the world average. Only the three samples with detectable activity concentrations are those that possess highest TL signals. Nearly all the samples exhibited dependence of sensitization factor of 110 °C TL glow-peak on the ED. This observation suggested a correlation between the ED of quartz and the sensitization factor of its 110 °C TL peak. This implies, an indication of the importance of ED in quartz TL and OSL characteristics. There was no evidence of self-dose in any of the samples. Therefore, radiation safety is secured during exploration and in diverse areas of applications of these samples, mostly in electronics and gemmology.

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