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Positron lifetime spectroscopy applied to pure Sulphur and Selenium

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Abstract

High purity crystalline orthorhombic Sulphur and hexagonal Selenium have been investigated using Positron Lifetime Spectroscopy technique. Annealed for 3 hours at 120 ºC Selenium lifetime (308(1) ps) has been compared with previous Positron Lifetime Spectroscopy knowledge in order to validate the measurements and the analysis procedure, and also compared with theoretical calculations available in literature, including different methods and parametrizations, resulting on the best match of LMTO-ASA method with GGA parametrization. Annealed for 3 hours at 80 ºC Sulphur samples were studied by the same means providing a single lifetime component with value 300(1) ps that has been assigned to the positron annihilation in the bulk that is not present in the current literature.

Keywords: Positron Annihilation Spectroscopy; Positron Lifetime; Sulphur; Selenium, Bulk.

1 Introduction

Selenium (Se) and Sulphur (S), that belong to Group VI of semiconductors, are widely used in many compounds due to their unique properties. Se is currently used in different fields such as phase change memory devices [1], solar cells [2], or thermoelectric materials [3]; whereas S is present in compounds like ZnS that presents properties like a highly conducting Pauli paramagnetic state or a nearly temperature independent resistivity [4].

Positron Annihilation Spectroscopy (PAS) are advanced characterization techniques that have been used to characterize a wide variety of materials from elements [5, 6] (that act as basic knowledge required to understand more complex materials and to refine theoretical calculations), to simple [4, 7] or complex materials [8, 9]. In simpler cases, such as pure elements, theoretical calculations can be relatively easily performed, but experimental data can be required to refine the formalism and to determine the approach for different cases as the variety of models and parametrizations can better describe certain atomic configurations compared to others. For this reason, it is important obtaining new or more accurate data from pure elements (or same elements in different crystalline structures) to improve the results from theoretical calculations.

While PAS has been used and developed in metals during decades [5], and in semiconductors [6, 10]. The properties in the semiconductors and its compounds are strongly dependent not only on their intrinsic characteristics but also on their dopants and defects. As PAS techniques can provide information about the defects of the materials (as they act as positron traps when charged negatively) but also about their bulk (if defect density doesn't saturate the positron trapping) they are a powerful technique to study those materials.

Positron Annihilation Lifetime Spectroscopy (PALS) studies of complex materials involving S and Se are present in current literature [11-14]. Even when they present useful

information about the studied materials, the understanding of the results could greatly benefit from the existence or improvement of background knowledge, both experimental and theoretical, about their basic elemental components. The aim of this work is studying pure elemental S by PALS to determine its positron annihilation lifetime to improve the background knowledge that can lead to a better application of theoretical models in simple and complex materials that include it. In order to evidence the reliability of the measurements, Se has been also studied and obtained results have been compared to previous literature values corresponding to different preparation samples.

2 Experimental Procedures

2.1 PALS technique

PAS are advanced characterization techniques that probe the atomic structure and the local electron density at the annihilation site that is strongly affected by the interaction of the positron and the environment. The resulting radiation after the annihilation provides information about the nearby structures allowing the study not only of the bulk of the material but also of the structures present on it such as vacancies, vacancy clusters, and other.

The thermalization process of the positron in solid matter takes around 1 ps to be achieved [15, 16] so it doesn't significantly affect the positron annihilation lifetime in metals or semiconductors that are typically 100 ps to 350 ps. After thermalization, the positron whose wave-function (free state) is concentrated in the space between atoms due to the core's Coulomb repulsion, will interact with electrons and will annihilate with probability based on the overlap with the electron's wave-function. This results in a momentum distribution and lifetime determined by the electronic distribution of the annihilation site. When a defect is present in the material, the electronic local density is reduced, so the

annihilation lifetime is increased compared to the perfect lattice annihilation and the moment distribution of the resulting radiation is also affected. Defects also act as *positron sinks* due to the distribution of the Coulomb potential in the lattice symmetry breaking so positron is highly sensitive to the presence of defects. The pass of the positron from the free state to a localized state in a defect is called *trapping*. Trapping is an effect that competes with annihilation and depends on the concentration of defects and the trapping coefficient that depends on the material. Lifetime associated with trapped states in defects is longer than in a perfect lattice (annihilation in the bulk of the material) because of the reduction of the electronic density. This lifetime increases as the open volume of the defects does, and provides information about the size of the defects in the case of small ones (like single vacancy [17]) or the size order of magnitude in the case of big defects (such as vacancy-clusters or nano-pores [18]).

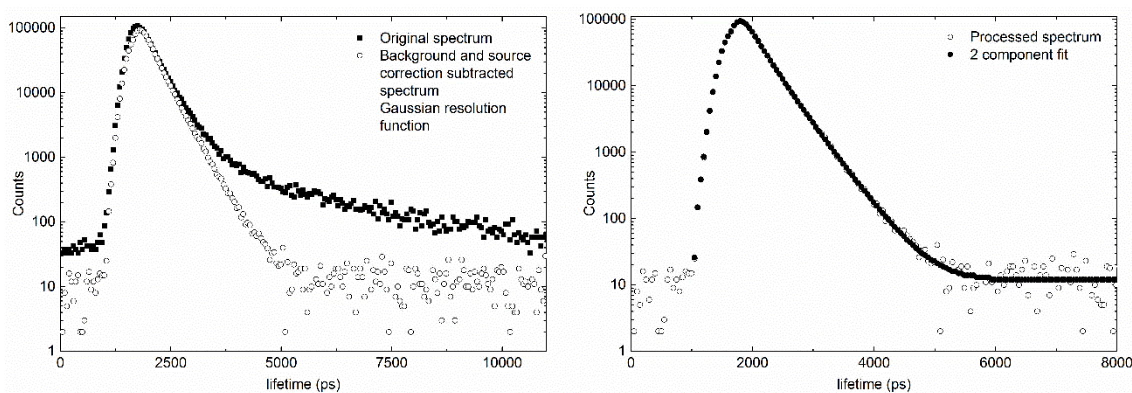

Fig 1 (a) Raw PALS spectra (solid dot) compared to processed spectra (empty dot) where the background and source contributions have been subtracted. Gaussian resolution function is shown (dash line). (b) Processed PALS spectrum (empty dot) and fit (solid dot) with the two-component fit (320 ps and 370 ps with 45% and 55% relative intensities respectively) represented as dashed straight lines

In PALS, a positron source (typically ^{22}Na) is used to continuously direct positrons to the studied samples. The spectrometer used for PALS registers the time between the start signal (1.2754 MeV γ-emission from an excited state of daughter nuclei ^{22}Ne in the case

of ^{22}Na source decay) and the stop signal (detection of the 511 keV annihilation radiation) that are detected in coincidence by each of the detectors the spectrometer is composed by. The resulting spectrum (see Fig. 1 (a)) can be fitted, after some considerations, to a sum of weighted exponentials (Eq. 1) each of them corresponding to the annihilation at each annihilation site (bulk, vacancies, clusters…).

$$N(t) = \sum I_k e^{-\lambda_k t} \quad (1)$$

The measured spectrum is affected by some effects that must be included in the data processing and analysis. These are the time resolution function of the system, the positron annihilation in the positron source, and the background (typically reduced by electronics fine tuning). The time resolution function is typically the Gaussian response of the detection system that must be determined experimentally. This function is convoluted with the exponentials in Eq. 1 (where I_k are the relative intensity of each component, and λ_k are the decay rate constants whose inverse are the associated lifetime τ_k) to reproduce the experimental spectrum, specially the inset around the origin of time where the resolution function rules over its shape. The annihilation in the source, caused because the source is not completely transparent to the positrons, produces an extra lifetime component in Eq. 1 that must be added to the analysis of the experimental spectrum from the studied material.

The lifetime associated with the source is roughly 400 ps and its intensity depends on the studied material due to the positron reflection on the surface of the samples [19, 20] as a function of the atomic number Z (typically between 4% to 17% relative intensity). This component is determined experimentally, measuring a reference sample of well-known lifetime with a single lifetime that is not associated with defects, so trapping is not observed, and it is considered during the fitting process. This component is usually called

source correction, and it is subtracted during the fitting process as it is not related with the measured sample but with the source. A second long-lifetime (above 1200 ps) low intensity (less than 1% intensity) component is usually associated also to the source and it is caused by surface effects (and even polymeric sealing materials) by the production of positronium. Positronium [21] is a non-stable bound state between the positron and an electron that is usually formed in low electronic density regions such as pores or polymeric materials. If this state is formed with total spin equal to zero (singlet state) is called para-positronium, while the state with total spin equal to one (triplet state) is called ortho-positronium. Lifetimes associated to these states are 125 ns and 142 ns respectively in void, but they can be affected by the atomic environment by the pick-off annihilation reducing these values [22].

Once all these effects can be considered, the experimental data can be fitted. The number of components associated with the sample is, in principle, unknown. Nevertheless, the expected realistic number of components in non-complex materials is usually 1 to 3 (excluding positronium or any other spurious effects) corresponding to the annihilation in the bulk of the material and in different kinds of defects that act as positron traps. Spectra after the source corrections subtraction and considering the time resolution is shown in Fig. 1 (a) and Fig. 1(b). When two or more components cannot be resolved or are not separated during the fit due to the number of considered components, the measured lifetime is an average lifetime corresponding to the weighted mean of the components based on their relative intensities (Eq. 2). This mean lifetime can be also determined using all the fitted components and considered as the general lifetime associated with the studied sample.

$$<\tau>=\sum I_k \tau_k \quad (2)$$

It is worth noting that the annihilation in the bulk of the material that is measured if the samples present defects is a reduced bulk lifetime that is shorter than the real bulk lifetime. This is caused by the effect of the positron capture rate in the defects that couples with the annihilation in the bulk. When a single type of defects exists, the shorter measured lifetime (typically corresponding to the annihilation in the bulk) is a reduced lifetime that includes the capture rate of the positron in the defects ($\tau_{rb}=(\tau_b^{-1}+\kappa_d)^{-1}$), and the second component inverse is directly the positron annihilation lifetime on them ($\tau_d=\lambda_d^{-1}$) [23, 24]. As capture rates can be hard to determine, it is desirable using defect-less samples to perform the measurement of the annihilation lifetime in the bulk of the materials, nevertheless it is also possible to determine it in samples with low concentration of defects.

2.2 Experimental details

Commercial 99.99% purity Se and S samples were prepared in as-received state (10 mm×10 mm, 5 mm thick and 7 mm×7 mm, 6 mm thick respectively) and annealed during 3 hours at 120 ºC in the case of Se and 80 ºC in the case of S, and cooled down in vacuum during 5 hours. Samples were studied by XRD to determine its crystalline structure using an XRD (Cu, Kα =1,5418Å) with a step of 0.05° (2θ).

PALS measurements were performed using a fast-fast coincidence spectrometer consisting of two plastic scintillators placed face-to-face with the measurement area between them (same setup used in many previous studies such as [7, 25]). A ^{22}Na source sealed in kapton with size 4 mm×4 mm, and 0.5 MBq activity was used to perform the measurements. Annealed (3 hours at 800 ºC) pure Fe (99.999% purity) reference sample was used to determine the time resolution of the spectrometer resulting in 240 ps.

No evidence of electronic shift was observed between individual spectra, so they were added into a cumulative final spectrum with more than 1×10^6 counts (statistics enough to

identify components with intensity as low as 2%). PALSFIT [26] software was used to analyse the obtained cumulative spectra achieving a normalized to the degree of freedom Chi-square better than $6 \cdot 10^{-3}$.

As already mentioned, the source correction depends on the studied material [19, 20] as a function of the atomic number Z, so annealed single lifetime component Aluminium (Z=13) and Copper (Z=29) samples were used to closely match the atomic numbers of S (Z=16) and Se (Z=34) respectively. The determined source corrections resulted in 384(3) (15.2% intensity) for S and 382(3) ps (16.7% intensity) for Se. These source corrections were provided to PALSFIT during the analysis, so they are subtracted from the data in the first cycle of the fitting process before the inclusion of the remaining components in the fit's second cycle [26].

Additional low intensity (~0.3%) source correction lifetime component associated with the sealing material and surface effect was determined with value around 2.4 ns. These source corrections, along with the time resolution, were added to the spectra fitting prior to initially considering from one to three lifetime components as fitting possibilities (and selecting the best possible fit).

Same Fe reference samples used to determine the time resolution were used to test the system reliability, resulting in 113(1) ps lifetime that can be compared to the perfect Fe lattice lifetime 110 ps [27, 28].

3 Results and Discussion

Reference values for S lifetime are limited in current literature (present in [6] and not reported in intensive work [27]). In order to check the reliability of S results, Se measurements have been used as a test for the setup and analysis when compared to published results (corresponding to different crystalline structures and preparation states of the samples).

3.1 Selenium

Se XRD pattern is shown in Fig. 2 (a), where some main Miller indices have been labelled. It perfectly fitted to pattern 00-006-0362 evidencing the sample was crystalline with hexagonal structure. PALS measurements of the annealed samples (see Fig. 2 (b) for an example of data fit) resulted in a single component, and no positronium contribution was observed. Fitting with more lifetime components resulted in non-reliable results, discarding the presence of a second component. Three measurements were performed to ensure the reliability of the results resulting in analogous results each time. The average of the three measurements (see Table 1) is presented as result, considering the deviation with respect to the average as uncertainty along with the error bar provided by the fit. The resulting value for this lifetime component was 308(1) ps.

Table 1 Se fitted lifetime for three different measurements

Element	Measurement 1	Measurement 2	Measurement 3	Average
Se	308(1) ps	309(1)	308(1)	308(1) ps

Initial semiconductors PALS work [6] reported several semiconductors associated lifetimes. Se powder was used in that reference as a studied sample and no annealing process is reported (or another sample processing either). A single lifetime component, 366(10) ps, is reported in addition to a longer lifetime (1.42 to 2.72 ns) associated with spurious effects (according to the reference) such as positronium or annihilation in the supporting foil. The short lifetime component is associated to the annihilation in Se in [6], but there is not a mention to an assignation to the annihilation in the bulk or in other positron trap such as vacancies (lifetime is assigned to pure ideal samples without any reference to the annihilation site), so the result should be considered as an average lifetime that could include several components that were not distinguished by the absence of more

components in the fitting process. This result (366(10) ps) is considerably higher than the obtained in this work (308(1) ps), but this should be expected by the difference in the used samples. As the used samples in [6] were powder in as-received state with no thermal treatments (or any other process) to decrease the possible presence of vacancy-type defects, it is unlikely the samples could be considered as defect-less ideal solids, so the presence of defects is almost guaranteed. As the vacancy lifetime is higher than the lifetime associated to the annihilation in the bulk, the average lifetime must therefore increase. In this work crystalline samples have been annealed so the presence of defects should have been reduced or even eliminated. Passivation of single vacancies caused by Hydrogen (H) filling them has been reported to decrease the lifetime associated to the annihilation on them [29-31], nevertheless this cannot explain any reduction in the lifetime associated to the annihilation in the bulk.

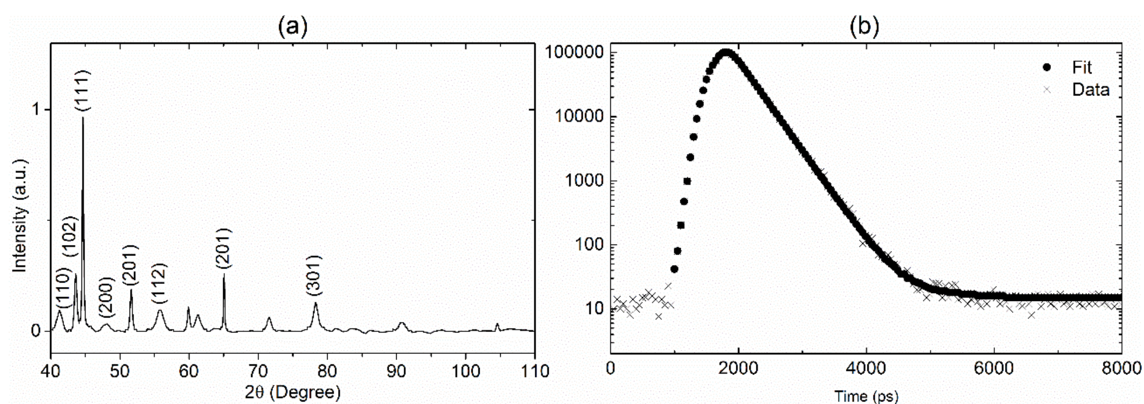

Fig 2 (a) XRD pattern corresponding to Se (pattern number 00-006-0362) and (b) example of PALS data and its corresponding single component fit

Later PALS study [32] analyses the dependence of the positron lifetime on the crystalline structure. They report three different values for Se positron annihilation lifetime, 301.5(15) ps for trigonal structure, 304.2(13) ps for monoclinic structure, and 331.2(32) ps for amorphous structure. These results are significantly lower than the previously reported value in [6] and crystalline (trigonal and monoclinic) samples lifetimes are

comparable with the value from this work corresponding to hexagonal structure (308(1) ps).

A more recent study [13], amorphous and *poly-crystalline* Se (that is indeed crushed small size crystalline Se compacted into pellets) are used. Even when the absence of defects in the samples cannot be guaranteed, the preparation method (well described in reference) grants a reduced (or negligible) number of vacancy-type defects. The PALS results were performed in the temperature range 50 K to 340 K. Lifetime associated with amorphous and *poly-crystalline* Se was reported to be significantly different in the whole range of temperature. Even when this difference decreases as the temperature increases (moreover above room temperature), this means that the Se structure influences the annihilation lifetime. Room-temperature PALS reported results were ~288 ps for amorphous Se, and ~299 ps for *poly-crystalline* Se. When these results are compared with the values reported in [32] it is noticeable that lifetime corresponding to amorphous Se differs significantly (331 ps against 288 ps), but the results for *poly-crystalline* (no details about the crystalline structure are provided in the reference) are similar (299 ps against 301 and 304 ps). Compared with this work result, 308(1) ps, corresponding to hexagonal crystalline Se, it can be affirmed that crystalline Se presents lifetimes in the range 300–310 ps depending on its structure.

After the comparison with the results present in [32] and [13], and considering that only a single lifetime component was determined after annealing the samples (reducing or eliminating the defects presence) lead us to assign the measured value, 308(1) ps, to the annihilation in crystalline hexagonal Se bulk. Results for Se reported in [13] could also confirm that results in [6] (significantly higher) were indeed an average lifetime more than a realistic single-component lifetime.

3.2 Sulphur

S XRD pattern is shown in Fig. 3 (a). It perfectly fitted to pattern 00-008-0247 evidencing the sample was crystalline with orthorhombic structure. As in the case of Se, fitting with more than one lifetime components resulted in non-reliable results for S (see Fig. 3 (b) for an example of data fit). Three measurements were performed (see Table 3) and a single component was determined on each of them. No positronium component was observed either. The average of the values, 300(1) ps, was considered as the final reported value.

Table 2 S fitted lifetime for three different measurements

Element	Measurement 1	Measurement 2	Measurement 3	Average
S	299(1) ps	300(1)	300(1)	300(1) ps

The only reported value for the lifetime associated with pure S is [6]. In this case they measured S in two different states, powder (with no crystalline state information, probably amorphous) and rhombohedral crystal (hexagonal crystal family). The reported lifetimes associated with those samples were 342(10) ps for powder and 350(10) ps for rhombohedral crystal. As in the previous case, the reported results are significantly higher than the lifetime obtained in this work (300(1) ps), and no information about the annealing or preparation of the samples is provided. Again, this might be attributed to the value being an average lifetime that included several annihilation components. It is also noticeable that even when these lifetimes are higher than expected (based on this works measurements) they seem to present the same dependence on the crystalline structure of the samples observed in the case of Se in references [32] and [13] (even when the error bars are big enough to make them compatible so it cannot be assured). It is worth mentioning that results corresponding to Se and S in [6] are not the only that are higher

than later reported lifetimes. In the case of Silicon, they observed a lifetime of 250(6) ps and 240(15) ps for crystalline and powder state samples, when [27] reports 219 ps. For Antimony powder they report 496(12) ps and [27] reports 214 ps. These additional discrepancies (with the same tendencies) support that lifetimes reported in [6] seem to be the average of at least two components that are not resolved (or at least separated in the fit process) causing them to be higher than the lifetimes reported in this work.

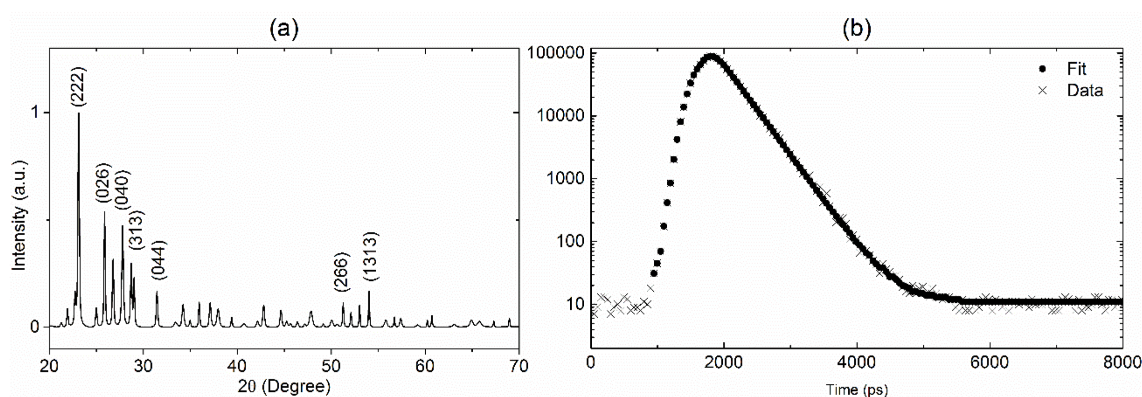

Fig 3 (a) XRD pattern corresponding to S (pattern number 00-008-0247) and (b) example of PALS data and its corresponding single component fit

Once the measurements and analysis have been validated by the comparison of the Se results with some literature values, it is safe considering the obtained value for the S lifetime reliable, and we assign the measured value, 300(1) ps, to the annihilation in the bulk crystalline hexagonal orthorhombic S as defects are supposed to be annealed out.

3.3 Comparison with theoretical calculation

PALS theoretical calculation can be found in [27] including Se bulk lifetime that is not included in classic literature [33-36]. An experimental Se bulk lifetime is included (335 ps) but no details are provided about the measurement. A wide range of values (from 244 ps to 357 ps) are obtained from calculation using different methods and parametrizations

(shown in Table 3), so experimental values are required to determine the methods and parametrizations that provided an accurate result.

Comparing the lifetime obtained in this work, 308(1) ps, with Table 3 it can be observed that LMTO-ASA (*linear muffin-tin orbital method* within the *atomic-spheres approximation*) [33] with GGA parametrization (*generalized gradient approximation*) [36] provides the best theoretical approach, and the rest of them are significantly different. It is worth to mention that AT-SUP method (*atomic superposition approximation*) [33] with BN [34] parametrization (interpolation formula by Boroński and Nieminen) is the best approach to the bulk lifetime obtained in [13] (288 ps) for amorphous Se. As it has been observed that bulk lifetime depends on the crystalline structure of the sample, it is reasonable that different theoretical methods fit the experimental results for different structures as they make different considerations about the electron density distributions. A better comparison with the different experimental results from the different crystallographic structures would be possible if the structure information would be included in the AT-SUP method.

Table 3 Se bulk lifetime calculation for different methods [27]

Method	Parametrization	Bulk lifetime (ps)
AT-SUP	BN	286
AT-SUP	GGA	355
AT-SUP	LDA	244
LMTO-ASA	BN	281
LMTO-ASA	GGA	313

No S PALS theoretical calculations are present in [27] or have been reported in any other reference so no comparison can be made at this point. This suggests that theoretical

calculations should be performed in the future and use the new experimental information as feedback to complete them.

4 Conclusions

High-purity crystalline S and Se have been investigated by PALS spectroscopy. After eliminating the defects on the samples by annealing for 3 hours, a single lifetime component has been determined. This lifetime has been associated with the annihilation in the bulk of the samples. Se obtained lifetime value have been compared with results in [32] and [13] validating the measurements and analysis in order to support the results corresponding to S with reduced literature about it. Lifetime associated with hexagonal Se has been established as 308(1) ps and for orthorhombic S as 300(1) ps. Se results have been also compared to theoretical calculations in [27] allowing to narrow the wide range of values that theoretical models provide, being LMTO-ASA with GGA parametrization [33, 36] the best theoretical approach to the obtained experimental results.

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Data Availability The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Conflict of interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Code Availability (Not Applicable)

Ethics approval (Not Applicable)

Consent to participate (Not Applicable)

Consent for publication (Not Applicable)

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