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TL and OSL analyses of natural orange calcite crystal

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ABSTRACT

The study presents Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) characterization of orange calcite. It is known that calcite exhibits TL, however its OSL emission is still unwell studied. The crystalline characterization was done by means of X-rays Diffraction (XRD) technique, and it was confirmed that the sample is a pure calcium carbonate arranged in a rhombohedral crystal system. Total and traces elements were determined using Total Reflection X-Ray Fluorescence (TXRF) technique. Several impurities were found, such as Fe (117 mg/kg), Sr (80 mg/kg), K (79 mg/kg), Mn (34 mg/kg). Furthermore, some trace impurities, such as Ni (3.87 mg/kg), Pb (3.8 mg/kg), Cr (2.1 mg/kg), Zn (1.54 mg/kg) and Hf (1 mg/kg) were also determined, and they may play an important role in the luminescent emission of orange calcite. Samples in powder form were irradiated with crescent doses of beta particles, in the dose range of 0.16-20 Gy. Applying the deconvolution technique of the TL emission curve in Ultraviolet (UV) region, through the general order kinetics model, individuals TL peaks were found at 93, 130, 162, 189 and 227 °C. An OSL response was verified and can be fitted using 3 components with decay constant values of 2.3, 10.0 and 77.4 s. It can conclude that orange calcite exhibits UV luminescence in both TL and OSL emissions, with high sensitivity compared to those found in the literature. Thus, it can be used in dating and dosimetry for doses from 0.3 Gy for TL and 4 Gy for the OSL technique.

Keywords: **Orange calcite, Optically Stimulated Luminescence, Thermoluminescence.**

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1. INTRODUCTION

Calcite has been widely used in thermoluminescence (TL) and Electronic Paramagnetic Resonance (EPR) dating, due to its great abundance in the earth's crust. It can also be easily found in geological and archaeological sites, in the form of secondary depositions of carbonate, corals and shells [1-3].

Initial studies on the TL of calcite assessing its TL peaks lifetimes were carried out by Calderon et al, in 1984 [3]. Some dating works began near this year, such as that of Takatohi et al, 1984, which dated a fish fossil found in Araripe, Ceará, Brazil using TL [4], and Pretti and Watanabe, 1983, that determined the formation of calcite from the Bauru Group, São Paulo, Brazil [5]. Other study by Tatumi et al, 1989, dated speleothems from Caverna do Diabo, Brazil, using TL and Electron spin resonance (ESR) techniques [6]. Khanlary and Townsend (1991) measured the TL spectrum of calcite, and depicted three peaks at 100, 240 and 400 °C [7]. Studies of the effects of heat treatment [8] and irradiation with different Ultraviolet (UV), beta and gamma sources on the TL response were also performed on limestones [9,10]. Determination of the kinetic parameters of the traps responsible for the TL peaks and studies on TL peaks deconvolution were carried out to understand the stability of the centers of samples used for luminescence dating, which is very important, since in dating, the sample must have stable peaks that remain for a few hundred up to million years [11-13]

Calcite samples taken from caves, shells and limestone samples have also been successfully dated by TL in several other studies in the last decades [14-18] which emphasizes its role in the area.

Although the calcite TL has been extensively studied and applied as a natural dosimeter, its OSL emission has not been in-depth elucidated yet. Ugomori and Ikeya, 1980, stimulated a calcite sample with UV (337 nm) and observed an OSL emission at 430nm, also demonstrating that this OSL signal increased with dose and related this emission to the TL peak at 286 °C [19]. On the other hand, Galloway (2002), studied the luminescence of limestones stimulated with UV (370nm) and concluded that the luminescence was weak and did not increase with the radiation dose. It could have occurred because a longer, and then, less energetic wavelength was used [20]. Kalita and Chithambo, (2019) studied the TL and Infrared Stimulated Luminescence (IRSL) of a limestone sample collected from Maswsmai Cave, India. They noted that the IRSL signal has linear dose response behavior between 10-100Gy and 200-1000 Gy [21].

Guilheiro et al, 2021, observed the OSL emission of a yellow calcite, whose intensity was reasonable to be used in dating, managing to observe an OSL decay curve from the dose 4.3 Gy. The OSL signal was detected in the UV region and excited with blue light (470nm) [1].

Nowadays, articles about the OSL of calcite are still scarce. Therefore, the main objective of this work is to perform a detailed study of the OSL of orange calcite. It will also be shown the study of the crystallinity by using X-ray diffraction (XRD), the determination of its trace impurities through Total Reflection X-Ray Fluorescence (TXRF) and its TL emission.

2. MATERIALS AND METHODS

The calcite sample from the State of Minas Gerais, Brazil was used in the present investigation. To the analyses, the mineral was ground with an agate mortar and pistil, to get the powder fraction (around 100 μm). For the crystallographic characterization, the sample was analyzed with XRD technique, with a Rigaku diffractometer, model Miniflex 300, with Cu-K_α which X-rays tube operates at 30 kV and 10 mA, the measurements were made at an initial angle of 5° to 75°, in steps of 0.02° and for a period of 0.20 s per step.

The concentrations of impurities found in the sample were determined by means of total TXRF analysis using S2 PICOFOX equipment. The sample was weighed on a precision semi-analytical scale, obtaining a weight of 107.3 mg, homogeneously diluted in a pattern solution, and then, dried in an oven at 60 °C for 15 min in a quartz plate. The time of measurement was 300 s. The results identified the main and trace elements in the calcite crystal.

The powder sample was subjected to TL and OSL measurements using a TL/OSL automated reader RISØ, model DA20. A thermal cleaning up to 500 °C, with a rate of 5°C/s, was performed before TL measurements, to eliminate the natural TL. Irradiations with beta particles were carried out using a ^{90}Sr / ^{90}Y source (dose rate of 0.081 Gy/s), at doses ranging from 0.16 to 19.44 Gy. TL as measured in the interval between 0-500 °C, with a heating rate of 5 °C/s, and in a N_2 atmosphere. For the OSL process, the sample was stimulated with blue light (470nm) during 40s at a temperature of 60 °C in the Continuous-wave OSL (CW-OSL) mode. For TL, the emission was measured in the

Visible (VIS) and UV regions, using the optical filters Schott BG-39 and Hoya U-340, respectively; in the case of OSL, it was detected in the UV.

To better investigate the TL and OSL emissions, measurements were made to construct the TL and OSL growth curves in relation to the radiation dose and the curves were adjusted. The experimental curves of TL and OSL emissions were theoretically fitted with the general order kinetics model. In this way, the amount of TL peaks, the kinetic order and the parameters of the E and s traps thereof can be determined. In relation to the OSL curve, we can determine the number of individual components present in the curve, their kinetic orders, and lifetimes.

3. RESULTS AND DISCUSSION

3.1. Crystallinity and composition study

XRD diffractogram obtained with the powder sample proved that it is a calcium carbonate net and arranged in a rhombohedral system (ref. cod. 01-072-1652), as shown in the figure 1. The most intense peaks were associated with their respective Miller Indices. Calcite crystal is a natural polymorphic mineral, belonging to the carbonate group, found in sedimentary rocks and may present itself as the predominant mineral. It is chemically formed by $CaCO_3$ and it can be found in different crystalline arrangements such as rhombohedral or hexagonal structures according to the literature [22]. The crystallite size is estimated by the Scherrer Equation [23], and it was of 45.6 ± 6.3 nm. This value is quite to that found for Guilheiro et al, (2021) [1], who found a value of 46.9 for another sort of calcite.

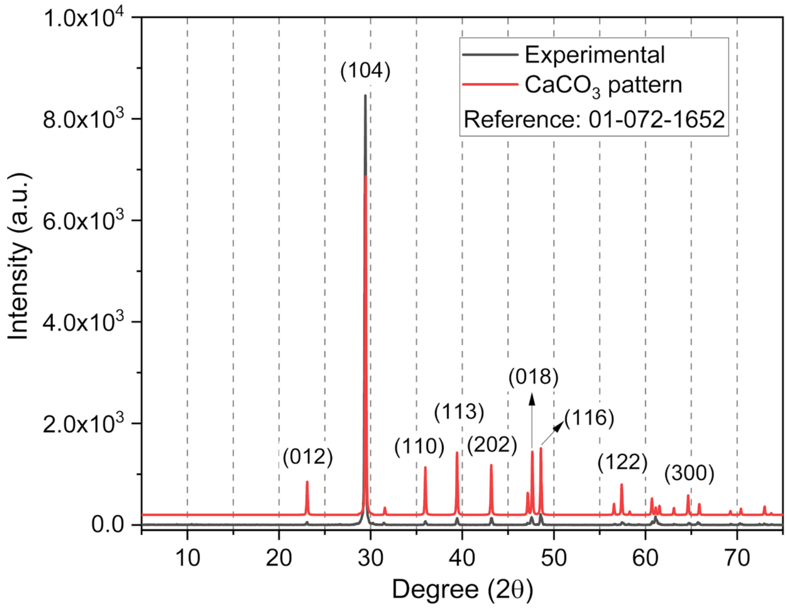


Figure 1: *XRD diffractogram for orange calcite from Brazil (black line) and pattern for $CaCO_3$ mineral in the rhombohedral system (red line).*

The results obtained from the TXRF technique identified the impurities present in the calcite as shown in Table 1. There is a predominant presence of element Calcium (Ca), which is related to matrix, and the trace elements such as Iron (Fe), Strontium (Sr), Potassium (K), Manganese (Mn), Nickel (Ni), Lead (Pb), Chromium (Cr), Zinc (Zn) and Hafnium (Hf), some of them could be related to luminescence centers.

Calcites normally incorporate various impurities during their crystallization, and traces of these impurities, such as Mn and Cr, can form color centers in the crystal, promoting luminescent properties. Depending on the content of its impurities and genesis, the sample may present different TL emission behaviors, since the phenomenon is related to the defects in the material [11]. Rezier, 2017, analyzed impurities from an orange calcite sample using the Energy Dispersive X-rays Fluorescence (EDXRF) with an Ampetk system and noticed the presence of Ca, Fe, Mn, Zn and Silicon (Si); and with the EDXRF Artax system, they found Ca, Fe, Zn, Sr, Mn, Sr, Germanium (Ge) and Bromine (Br). These impurities changed depending on the analyzed point. Some elements such as Fe, Sr, Mn, and Zn were found in the present work as well [24].

Table 1: Concentration of elements found by TXRF in orange calcite.

Elements	Concentration ± σ (mg/kg)
Ca	44522 ± 12
Fe	117 ± 7
Sr	80 ± 10
K	79 ± 12
Mn	35 ± 2
Ni	3.87 ± 0.02
Pb	3.8 ± 0.5
Cr	2.1 ± 0.3
Zn	1.54 ± 0.02
Hf	1 ± 0.05

3.2 Luminescence study

To luminescence characterization the powder sample was submitted to TL detected at VIS and UV and, also with OSL analysis.

In the figure 2a it is possible to observe the TL glow curves from the sample, detected at VIS region. The samples were previously irradiated with doses from 0.324 to 19.44 Gy. It is clearly observed a broad TL peak at 93 °C being initiated in the temperature of 50 °C, and other smaller ones in the region between 100 to 200 °C. In order to analyze with more details, TL glow curve was deconvoluted with general order kinetics equation [25], and 5 single peaks were determined at 93, 109, 162, 189 and 227 °C, as is shown in fig. 2b and in the inset (fig 2c). All the parameters found in the deconvolution process, such as the activation energy (E_a), frequency factor (s), and kinetic order (b), are listed in Table 2. In the literature, we usually find works approaching colorless and white calcites; these calcites often exhibit three TL peaks at 150, 240, and 320 °C, approximately [6,16,17]. These peaks are clearly different from those found in the present work, indicating that the color centers responsible for orange calcite are different from those responsible for white or colorless calcite. Kalita and Chitambo (2019), studied the TL of a limestone that exhibited two peaks at 92 and 239 °C, but observed that the emission became appreciable after 10 Gy. The study was performed with a dose interval from 10 to 1000 Gy, which is higher than the one used in this work. Thus, we can conclude that our sample is much more sensitive to the radiation dose [21].

Figure 2d shows a TL growth curve obtained with 93 °C peak. It was noticed that the TL intensity increases linearly up to 1 Gy, and then, there is another linear region with a different slope up to a dose of 14.58 Gy though.

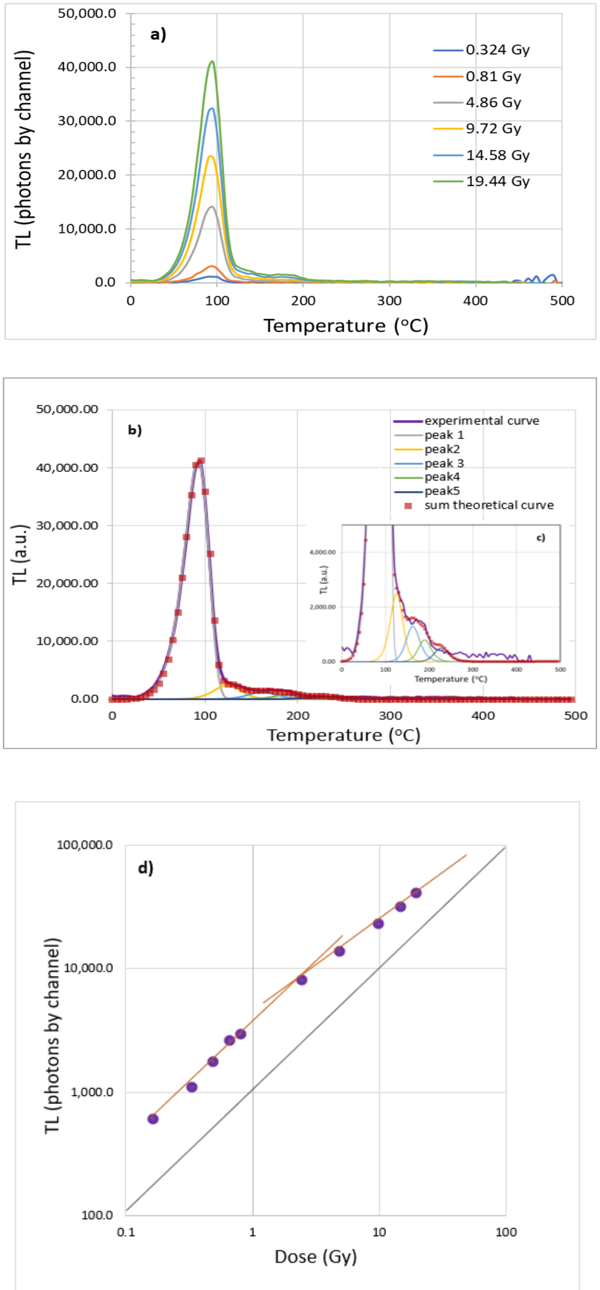


Figure 2: *a) TL glow curves detected at VIS region, b) TL glow curve deconvoluted using general order kinetic equation and c) inset and d) TL growth curve of 93 °C TL peak (purple points are the experimental ones; orange lines indicate the two linear regions).*

Table 2: Parameters obtained using a general equation for TL emission, recorded in VIS region of orange calcite, I_m is the maximum intensity, T_m is peak temperature, E_a activation energy, *b* the kinetic order and *s* the frequency factor.

	Peak 1	**Peak 2**	**Peak 3**	**Peak 4**	**Peak 5**
I_m (a.u.)	41.3	2.5	1.3	0.8	0.5
T_m (°C)	93	109	162	189	227
E_a (eV)	0.85	1.2	1.5	1.8	1.9
b	1.0	1.6	2	2	2
s (s^{-1})	$1.9x10^{11}$	$6.7x10^{14}$	$1.0x10^{17}$	$2.0x10^{19}$	$6.0x10^{18}$
F.O.M. = 8.8 %					

Figure 3 shows an example of a TL curve detected in the UV region; the curve is similar to that obtained in the VIS spectrum. Using the general order deconvolution equation, we also find 5 peaks, which have practically the same parameters, except for the peaks 2 and 4. All the evaluated parameters in the deconvolution process are listed in Table 3.

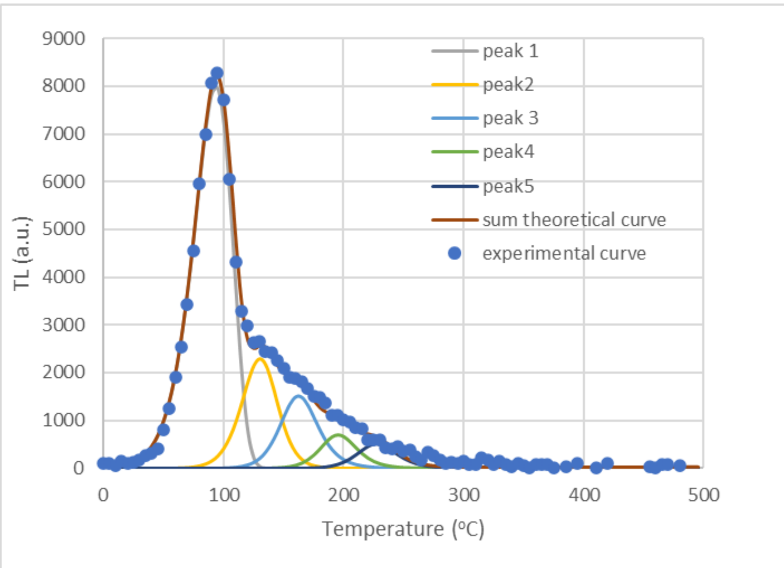


Figure 3: *TL glow curve detected in UV region and deconvoluted using general order kinetic equation.*

Table 3: Parameters obtained using a general equation for TL emission, recorded in UV region of orange calcite, I_{max} is the maximum intensity, T_m is peak temperature, E_a activation energy, b the kinetic order and s the frequency factor.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
I_m (a.u.)	8	2.3	1.5	0.7	0.5
T_m (°C)	93	130	162	195	227
E_a (eV)	0.7	1.2	1.5	1.8	1.9
b	1.0	1.6	2	2	2
s (s^{-1})	1.3×10^{9}	4.2×10^{14}	1.1×10^{17}	1.1×10^{19}	6.0×10^{18}
F.O.M. = 9 %					

The calibration curve of 93 °C peak increased linearly with the dose in the range of approximately 0.081 to 19.44 Gy, as is shown in figure 4.

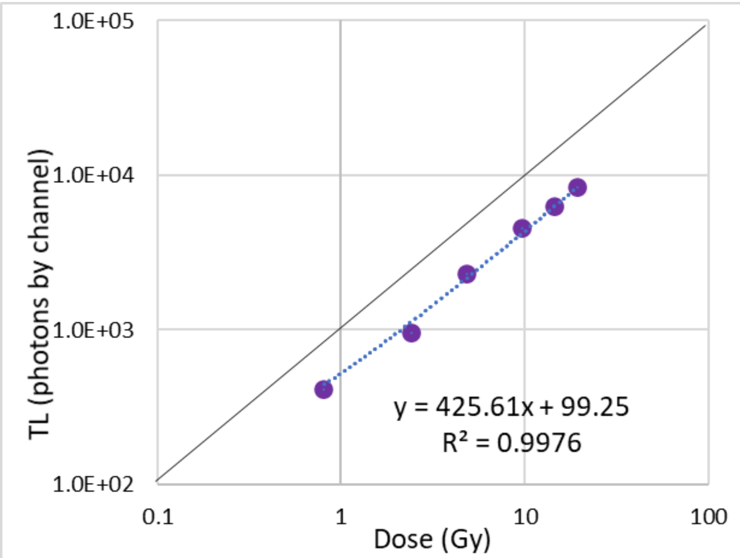
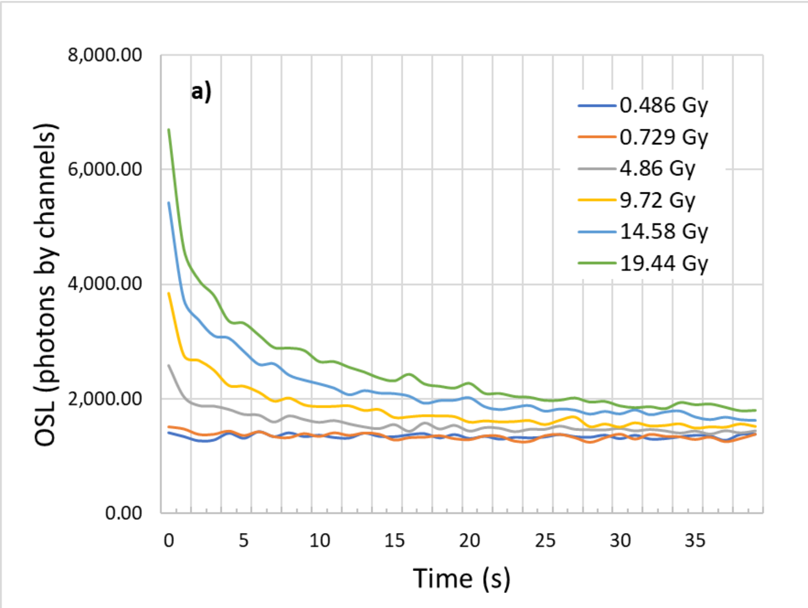


Figure 4: *TL growth curve of 93 °C TL UV peak.*

Fig. 5a shows OSL decay curves previously irradiated with doses between 0.486 and 19.44 Gy. The maximum OSL signal intensities as a function of dose increases, however, at low doses the signal starts to grow slowly and begins to increase substantially after 10 Gy, as shown in figure 5b, showing a sublinear behavior at the beginning. In the case of yellow calcite (Guilheiros et al, 2021) [1], the growth obtained was linear in the region of 4.3 to 21.5 Gy. The present sample exhibited a more sensitive response, emitting OSL at doses lower than 4 Gy.



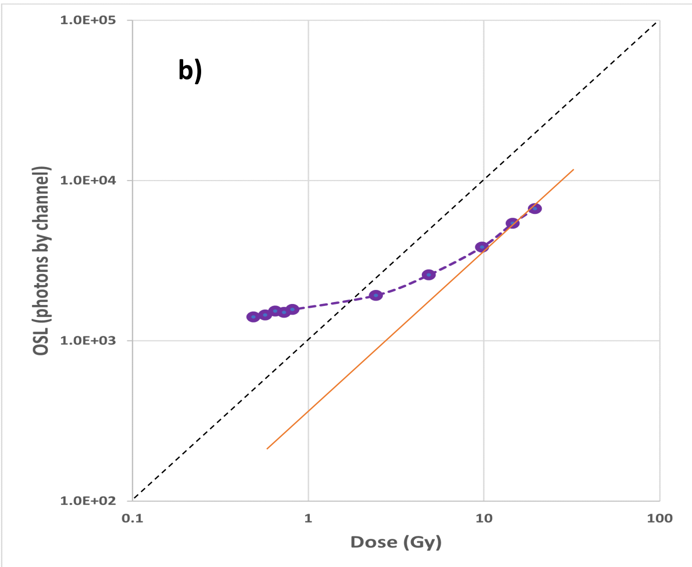


Figure 5: a) *OSL emission curves of yellow calcite with crescent beta dose, b) OSL dose response curve (purple points represent the experimental curve; orange line is the linear curve).*

The OSL signal was deconvoluted into 3 individual components (Fig. 6), using the General Order Kinetics (GOK) equation (eq. 1) [25]:

$$I(t) = I_0\left(1 + (b-1)\frac{t}{\tau}\right)^{\frac{b}{b-1}} \qquad (1)$$

Where *I(t)* is the OSL intensity of signal as a function of the initial intensity (I_0), the time (*t*), τ is the lifetime, and *b is* the kinetic order. The parameters found in the adjustment are presented in Table 4. Figure 6 shows the deconvolution process results, three components are found as a fast component with lifetime of 2.3 s, a medium one with 10.0 s and a long one with 77.4 s. The adjustment was successful using *b* equal 1.9 for fast component and 1 for medium and long ones. The FOM value found about 3.7% proves the quality of the fit. Similar results of OSL curves deconvolution of calcite were not found in the literature, so these results are unprecedented.

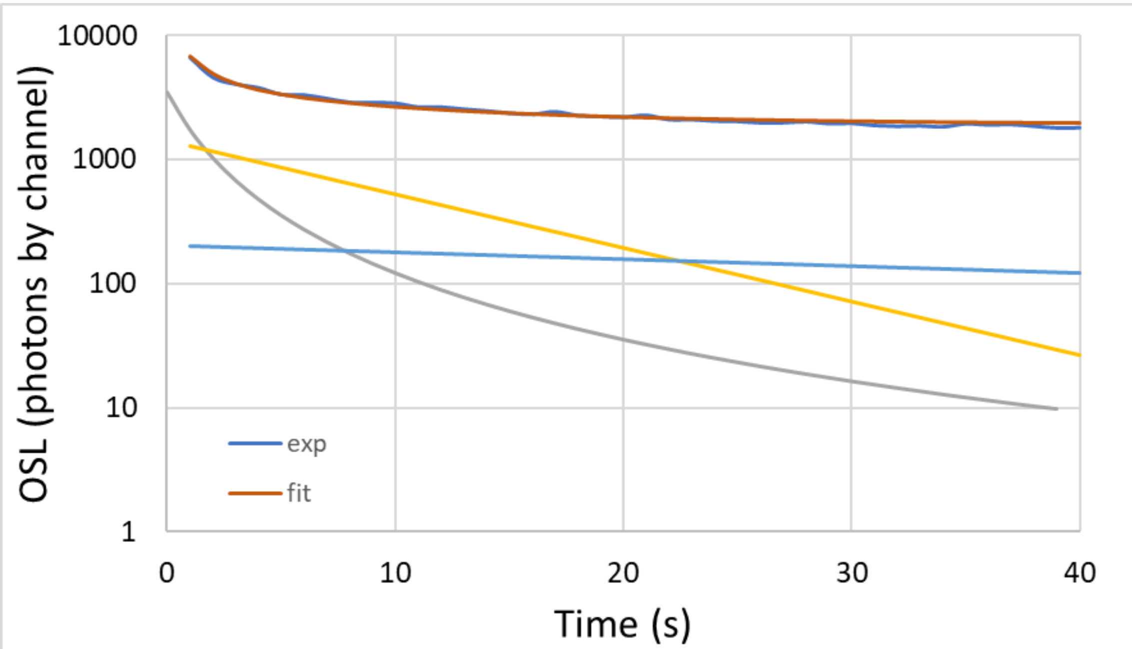


Figure 6: *CW-OSL curve deconvoluted with general order kinetic.*

Table 4: General order kinetic parameters for OSL emission of orange calcite, where I_0 is the maximum intensity, *b* the kinetic order and τ is the lifetime.

	FAST	MEDIUM	SLOW
I_0 (a.u.)	3500	1300	200
b	1.9	1.0000001	1.0000001
τ (s)	2.3	10.0	77.4
FOM = 3.7 %			

The presence of three components is an indication that there are different trap levels in the orange calcite which are blue light sensitive and responsible for the OSL emission. Moreover, the medium and slow components should be more stable, which can be convenient for dosimetry and dating.

4. CONCLUSIONS

The studied sample is a calcite which has a rhombohedral system and the crystallite size of approximately 45.6 nm. It has several impurities, such as Mn and Fe, which could be associated with its orange color. TL emission was detected in the UV and VIS spectrum, both presenting response with beta irradiation in the range between 0.3 and 19.4 Gy. The TL glow curves presented 5 peaks in the temperature range of 90 to 227 °C.

The OSL of the sample rises with the radiation dose and it can be decomposed into three components with a mean life span of 2.3, 10.0, and 77.4 s, and has a good response after 4 Gy, approximately. Calcites generally do not emit UV light, in this case, we observe these emissions in both TL and OSL measurements, which point out the existence of different centers for the mineral. Therefore, it makes the sample unique in relation to that, and usable in the dating and in of ionizing radiation dosimetry.

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