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An overview of the luminescence of minerals: a review and a tribute to Prof. Dr. Javier García Guinea

Una visión general de la luminiscencia de los minerales: una revisión y un homenaje al Prof. Dr. Javier García Guinea

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ABSTRACT

Luminescence emission is observed from many minerals and it provides important information about the physical and chemical processes taking place in both inorganic and biogenic materials (silicates, carbonates, phosphates, etcetera). It is equally valuable for geological and archaeological dating, detection of irradiated foods, or retrospective applications. Examples described here emphasize some of the career successes of Prof. Dr. Javier García Guinea who has advanced the topic with major contributions to the fields of physics and chemistry of minerals by the study of luminescent emission from natural materials. Geological materials are particularly challenging, as they are highly variable, thus, it has been an achievement to understand the underlying processes and his dedication and expertise have greatly influenced the fields of luminescence spectroscopy and its applications in geosciences, material sciences, retrospective dosimetry and biomedical engineering. He has inspired and guided many researchers, and will undoubtedly continue to do so into his retirement.

Keywords: Luminescence; Mineralogy; Spectroscopy.

RESUMEN

La luminiscencia observada en muchos minerales proporciona información importante sobre los procesos físicos y químicos que tienen lugar tanto en materiales inorgánicos como biogénicos (silicatos, carbonatos, fosfatos, etc.). Es igualmente valiosa para la datación geológica y arqueológica, la detección de alimentos irradiados y aplicaciones retrospectivas entre otras. Los ejemplos descritos aquí resaltan las contribuciones más significativas de la carrera del Prof. Dr. Javier García Guinea, quien ha avanzado en el tema con importantes aportes a los campos de la física y la química de los minerales mediante el estudio de la emisión luminiscente de materiales naturales. Los materiales geológicos son particularmente desafiantes, ya que son altamente variables; por lo tanto, ha sido un logro comprender los procesos subyacentes, y su dedicación y experiencia han influido enormemente en los campos de la espectroscopia de luminiscencia y sus aplicaciones en geociencias, ciencia de materiales, dosimetría retrospectiva e ingeniería biomédica. Ha inspirado y guiado a muchos investigadores, y sin duda seguirá haciéndolo en su jubilación.

Palabras clave: Luminiscencia; Mineralogía; Espectroscopía.

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Introduction

Prof. Dr. Javier García-Guinea's contributions have been significantly linked to interdisciplinary studies related to the physics and chemistry of minerals, combining knowledge in mineralogy and spectroscopic techniques. Luminescence spectroscopy emerged as a powerful analytical technique capable of providing information on complex materials across many different fields including mineralogy, materials science, environmental monitoring, and biomedical engineering. His input has encompassed diverse luminescence processes, including:

- Thermoluminescence (TL): Light emission induced by heating following prior exposure to ionizing radiation, widely used in geochronology, retrospective dosimetry, and archaeological dating.
- Cathodoluminescence (CL): Excitation via an electron beam, allowing high-resolution mapping of compositional variations and crystal defects in minerals.
- Radioluminescence (RL): Emission produced by X-ray excitation, providing insights into charge recombination efficiency and impurity effects.
- Photoluminescence (PL): Photon-excited luminescence, used for analysing electronic band structures, defect centres, and impurity distributions.
- Ionoluminescence (IL): Luminescence induced by ion bombardment, particularly useful for studying temperature-dependent luminescence properties.

These familiar methodologies provide sensitivity to the most subtle variations in composition, structural disorder, and external influences (e.g., ionizing radiation, mechanical stress, or thermal treatment) at the atomic and molecular scale. They evolved from work with idealized simple synthetic materials whereas Professor García-Guinea's extensive research work has included the far more challenging use of natural materials which are highly non-uniform and often heavily doped with a very wide range of impurities. His ground breaking approach has bridged mineralogy, spectroscopy, and luminescence research, with profound impact across multiple scientific and technological disciplines. Characterized by rigorous research and a synergistic integration of advanced analytical methods with theoretical interpretations, his work has provided critical insights into the luminescent properties of diverse materials such as calcium carbonates, alkali feldspars, hydrated minerals, oxalates, and phosphate minerals, among others, linking their complex chemical structures and compositions (Garcia-Guinea et al., 2007, 2011, 2015, 2018).

This article, directly inspired by García-Guinea's career includes illustrative examples from his extensive research, and emphasises many benefits of luminescence spectroscopy. However, an obvious problem for a brief overview is to select representative examples as he has published ~450 articles and books with ~340 co-authors from ~50 countries since 1987. The references on this short article merely highlight a few examples from the last 25 years to offer an overview of his more recent research.

Fundamentals of Luminescence in Minerals

Luminescence arises from the emission of photons following excitation of a material by an energy source which may be thermal or external. Many excitation processes promote electrons to higher energy levels and their subsequent return to the ground state can occur radiatively. The wavelength and intensity of the emitted light provide information about the electronic structure of the material, its defect states, and the nature of radiative recombination processes. Beyond the fundamental aspects, electron-phonon interactions play a critical role in modulating luminescence efficiency, particularly in minerals exposed to extreme thermal or irradiation conditions. Understanding these interactions is challenging as historically, discussions were generally made in absolute terms of highly localised interactions. Nevertheless, this is simplistic as in many systems there is unequivocal evidence for association of impurities and electronic interactions extending over tens, to thousands, of neighbouring ions (Townsend and Wang, 2024). In natural minerals such complexity is exacerbated by non-uniformity of the samples and highly variable presence of impurities. Despite this complex challenge application of luminescence techniques

has been a defining, and successful, feature of Prof. Dr. García-Guinea's scientific career. Through meticulous experimentation and theoretical modeling, he has significantly contributed to both advancement of luminescence-based research in materials science and to major advances in mineralogy.

Research with Feldspars and Geochronological Applications

Prof. Dr. Garcia-Guinea's early research was dedicated to understanding the luminescent properties of alkali feldspars, such as adularia and sanidine. His investigations focused on how mechanical and thermal treatments affect UV luminescence emission bands, revealing that:

- Grinding processes consistently reduce UV luminescence intensity, which he attributed to an increase in lattice disorder and defect density (Garcia-Guinea and Correcher, 2000).
- The 340 nm luminescence emission band in tectosilicates correlates with structural disorder, alkali ion mobility, and external stress fields (Garcia-Guinea et al., 2007).
- The application of TL and RL spectroscopy has highlighted the chronometric potential of feldspars, making them invaluable for geological and archaeological dating, as well as retrospective radiation dosimetry (Can et al., 2011). Additionally, feldspar-based materials exhibit long-lasting luminescence properties, making them potential candidates for optoelectronic applications, including phosphors for display technologies and persistent luminescence in emergency signage (Ucar et al., 2020).

Professor Dr. Garcia Guinea developed a collaboration with Professor Townsend and Dr Hole in Sussex which offered access to multi-wavelength TL equipment simultaneous spectral detection resolved TL with a sensitivity some 800 times better than any other system then in use elsewhere (Finch et al., 2019), The Sussex lab also used on-line optical equipment for changes induced by ion beam analysis. These unique systems opened new perspectives on luminescence processes as the IPD detectors simultaneously record all wavelengths at the same temperature offering a 3D TL display of wavelength, intensity, and spectra. Some examples of such spectra are included later in figures 1 and 2. During this period in Sussex he met Prof. Dr. Nurdogan Can, with whom he formed a strong professional and personal bond, leading to a long-lasting scientific collaboration.

The fundamental physicochemical principles governing luminescence in feldspar are complex, but after months of meticulous analysis, García-Guinea unravelled key processes and analysis benefitted from the unique Sussex facilities with ion beams and very high performance TL spectra. This was evidenced with spectral data of TL not only with carbonates, but also with phosphate minerals such as variscite, turquoise and apatites, where he focused on:

- Radiation-induced damage in variscite, particularly discolouration and structural modifications caused by ionizing radiation (Garcia-Guinea et al., 2008).
- The luminescence characteristics of turquoise, providing valuable insights into its spectroscopic properties. (Crespo-Feo et al., 2010)
- The effects of chemical impurities on luminescence emissions in apatites, revealing how trace elements influence optical behavior (Roman-Lopez et al., 2014a).

His investigations extended to biogenic materials, particularly natural bone, commercial hydroxyapatite, and collagen, where he conducted comprehensive studies on thermally and electronically stimulated luminescence. His approach integrated both CL and blue TL, supported by XRD, Raman spectroscopy, XRF, and FTIR analysis, offering a multidimensional approach to studying biominerals (Iordanidis et al., 2011).

- *Materials Science and Engineering*
  Ca-rich phosphates, especially hydroxyapatite (HAP), were analysed using TL and CL methodologies, which are instrumental in evaluating their structural properties and defect chemistry (Roman-Lopez et al., 2014b).

These findings have significant implications for biomaterials and bone tissue engineering, where synthetic HAP is used in medical applications. (Roman-Lopez et al., 2014b)

- *Environmental Monitoring and Dosimetry*
  Retrospective dosimetry: His research on the TL properties of quartz and feldspar demonstrated their suitability for dose reconstruction in areas affected by nuclear accidents and radiological events (Correcher et al., 1999a). Moreover, the growing interest in bioluminescent nanomaterials has led to the investigation of mineral-derived phosphors for biomedical imaging and targeted drug delivery systems. (González-Enguita et al., 2024)
  UV dosimetry: He highlighted the potential of TL as a fast and reliable technique for detecting UV-irradiated samples. This application extends to food irradiation detection and the assessment of UVC exposure, whether from artificial sources (e.g., welding electrodes) or natural origins (e.g., regions beneath the ozone hole). (Garcia-Guinea et al., 2004).

- *Biomedical Applications*
  Ca-rich oxalates extracted from the human body were shown to exhibit significant luminescent properties, opening the door for luminescence-based biomedical diagnostics.
  This approach has implications for early disease detection and personalized medicine.
  His work on kidney stones, analysed using XRD, SEM, Raman spectroscopy, and CL, enabled a comprehensive characterization of these surgically extracted biogenic materials. (González-Enguita et al., 2024)

The latter item marked a significant departure from his geological work, although the equipment was remained the same. The luminescent properties of calcium-rich oxalates extracted from the human body have significant potential in biomedical applications, opening the door to the use of luminescence as a highly sensitive technique for detecting subtle changes in the composition and structure of biogenic materials with implications for early disease detection and personalized medicine. In particular, kidney stones analysed using by X-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy, and cathodoluminescence (CL) enable a comprehensive characterization of these surgically extracted biogenic materials and he pioneered the combined application of these techniques for the study of complex biominerals such as kidney stones, leading to major advancements in understanding the interaction between chemical, biological, and environmental factors in the formation of oxalates, uric acid, phosphates, and cystine. The research aimed to establish correlations between these findings and patient's lifestyle and dietary habits as this provides critical insights into the etiology of stone formation and informing strategies for treatments (González-Enguita., 2024).

Carbonates

Expanding his research scope to calcium-rich carbonates (calcite and aragonite), key constituents of rocks and biogenic materials, Prof. Dr. García-Guinea demonstrated the potential of TL and CL in dosimetric applications, particularly in radiological emergencies. His studies on carbonates also explored the role of intrinsic defects in luminescence and the modulating influence of hydroxyl groups on the TL properties of carbonate surfaces. The sensitivity of CL to Mn^{2+} activators in calcites was also extensively investigated. Additionally, his research on the influence of water on mineral properties led to the discovery of green CL spectral emission from insulating surfaces characterized by metal-hydroxyl bonds. This expanded the known range of luminescence phenomena in minerals and highlighted the role of surface chemistry in optical properties. The 3DTL plots demonstrated the effect of hydroxyl groups on their TL behavior, establishing a new spectroscopic approach to investigate the hydration state of mineral surfaces (Garcia-Guinea et al., 2017). His approach of using many diverse materials with a variety of experimental techniques is clear from the studies of natural bone, commercial hydroxyapatite and collagen which were comprehensively characterised thermally and electronically via not only luminescence, but with input from XRD, Raman spectroscopy, XRF and FTIR analyses (Roman-Lopez et al., 2014b).

In hindsight it is obvious that a consistent feature of the research has been to use a very wide range of detection and analysis techniques with state of the art equipment, not only in his laboratory in Spain, but also with many other research partners. These included studies from Mangualde, Portugal, a region within the Central Iberian Zone of the Variscan Belt, characterized by extensive carbonate formations associated with metamorphic and granitic areas, plus microcline samples from Zarzalejo (Madrid, Spain), an area known for its coarse-grained Hercynian granites.

Results and discussion

As illustrated in Figure 1, CL and TL emission from carbonate minerals such as calcite, aragonite, smithsonite and strontianite show similar luminescence spectral characteristics and are strongly influenced by both their chemical composition (impurities, trace elements, presence of water/hydroxyl groups) and their crystal structure (defects, lattice distortions). (Garcia-Guinea et al., 2009a, 2009b, 2015, 2017, 2018; Boronat et al., 2017).

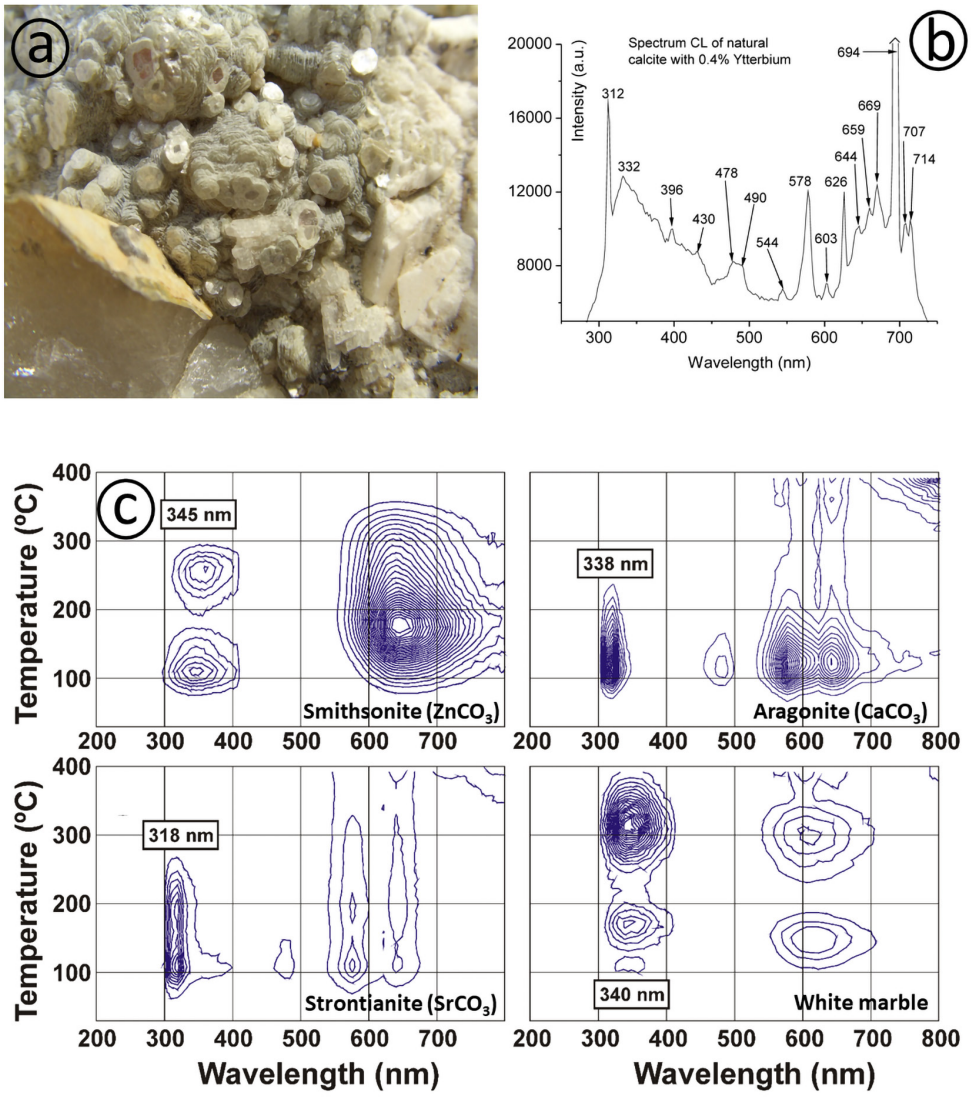

Figure 1.— (a) Sample of Ca-rich carbonates collected in Mangualde (Portugal). (b) CL emission of a natural calcite observed in the Mangualde sample containing 0.4% of Yb^{3+}. (c) TL contour plots carried out in Sussex comparing a mineral phase of aragonite detected in the Portuguese sample and smithsonite (from Aliva mine in Picos de Europa, Santander, Spain), strontianite (from the Whitesmith mine in Strontian, Scotland, UK) and white marble (from Macael in Almería, Spain).

Elements like Ga, In, Tl, Ni, Ba, Bi, Ge, Al, Fe, and Na can enhance the green CL emission in carbonates, although Mn is the most significant contributor. Thus, Mn^{2+} can be identified as a common activator in carbonates, replacing Ca^{2+}, usually associated with green-yellow luminescence emissions. The specific wavelengths of these emissions are attributed to transitions within the Mn^{2+} ion (e.g., $^4T_{1g}(^4G) \rightarrow {}^6A_{1g}(^6S)$) and are sensitive to the crystal field strength, which is determined by the coordination environment around the Mn^{2+} ion within the carbonate lattice and the metal-oxygen bond distances (Valle-Fuentes et al., 2007; Garcia-Guinea et al., 2009a). Different carbonate phases (rhombohedral or orthorhombic) may exhibit variations in Mn^{2+} emission wavelengths due to these structural differences. The spectral position and intensity of the Yb^{3+} luminescence depend on the local crystal field and the symmetry of the carbonate host lattice of the mineral, calcite collected in Mangualde (Portugal) (Figs 1a and b). The rhombohedral structure in calcite, where Yb^{3+} can substitute for Ca^{2+}, can induce a sharp infrared luminescence signal due to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition (Fig 1b). In carbonate minerals, quenching mechanisms such as energy transfer to lattice vibrations (phonons) play a role in determining the efficiency of Yb^{3+} luminescence. Differences in phonon energy between these carbonates influence the efficiency of Yb^{3+} luminescence, with lower phonon energy hosts generally enhancing emission efficiency (Garcia-Guinea et al., 2015).

The data reveal the presence of both UV-blue (approx. 315–360 nm) and orange-red (approx. 620–650 nm) TL and CL emissions. These may be due to both surface and structural hydroxyl groups and water molecules (Garcia-Guinea et al., 2009b, 2017, 2018). These emissions are usually attributed to dehydration processes, the formation of non-bridging oxygen hole centers (NBOHCs), and stressed C-O bonds, influenced by these hydrated species. The intensity of these bands can be affected by preheating treatments that induce dihydroxylation processes. Modelling of sites is difficult as the presence of hydroxyl groups or structural defects can variously enhance or quench the luminescence signals. Fe^{3+} is also readily found in the carbonate lattice and often acts as a luminescence inhibitor, but iron-containing materials may still display CL bands associated with hydroxyl and water (Garcia-Guinea et al., 2017). Oxidized iron surfaces may exhibit luminescence associated with hydrated compounds. Strontium (Sr) and Barium (Ba)-rich carbonates can exhibit blue coloration and luminescence, potentially linked to specific point defects or trace element activation and the presence of rare earth elements (e.g., Dy^{3+}, Tb^{3+}, Sm^{3+}, Gd^{3+}, Ce^{3+}) present as impurities can also contribute to specific luminescence bands (e.g., Dy^{3+} at 480 and 580 nm, Tb^{3+} at 540 nm, Sm^{3+} at 640 nm, Gd^{3+} at 320 nm, Ce^{3+} at 355 and 370 nm) (Valle-Fuentes et al., 2007; Garcia-Guinea et al., 2015).

Luminescence detection and characterization of impurity sites in insulators is enabled by high sensitivity detectors but modelling of the sites is inevitably speculative without corroborating signals from say electron spin resonance (ESR) or electron nuclear double resonance (ENDOR). Further, crystal defects such as oxygen vacancies, dislocations, planar defects, and grain boundaries play a crucial role in luminescence by acting as trapping and recombination centers for charge carriers (Garcia-Guinea et al., 2017). The type and concentration of these defects, which are influenced by the crystallinity, formation conditions (e.g., hydrothermal vs. biogenic), and post-formation treatments (e.g., irradiation, heating), affect the intensity, spectral distribution, and thermal stability of the luminescence (Garcia-Guinea et al., 2017; Boronat et al., 2017). For instance, lattice stress due to temperature changes can affect the UV-blue CL region in calcite. Different polymorphs like aragonite and calcite can show variations in luminescence spectra due to differences in their crystal structures and defect types (Boronat et al., 2017). The carbonate anion itself can act as a precursor for luminescence related to intrinsic structural defects. In this sense, stressed C-O bonds, potentially influenced by water or hydroxyl groups, can contribute to emissions around 360 nm.

In summary, the luminescence spectra of carbonates ensue from complex interactions between the chemical impurities, the presence of water-related species, and the nature and distribution of defects within their crystal lattice. Nevertheless, the wavelength emission and intensities of luminescence bands can provide information about the compositional characteristics, structural imperfections, and history of geological or, even artificial carbonates.

The luminescence spectra of aluminosilicates exhibit several emission bands in the range of UV-infrared regions (Figure 2). The assignment of these bands is often linked to both the chemical composition, particularly the presence of specific metal ions and hydroxyl groups, and the crystal structure, including defects and structural features like twinning.

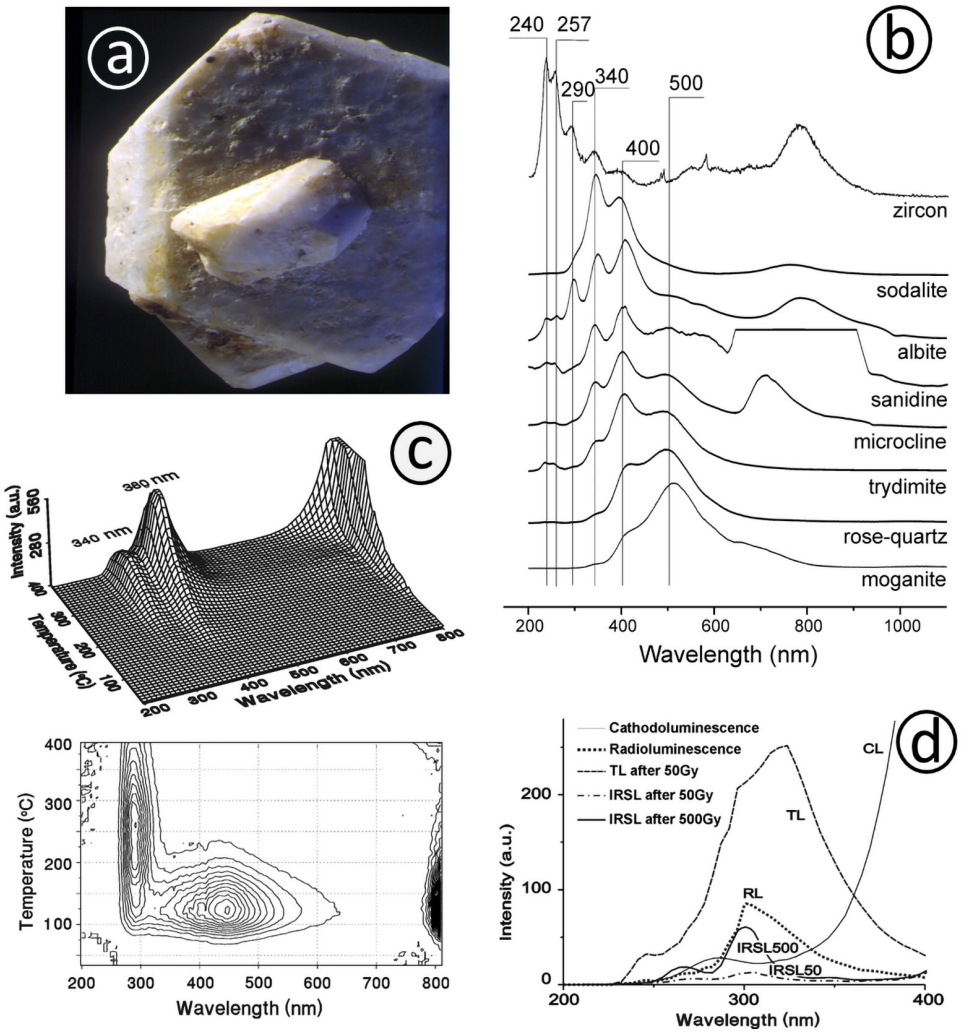

Figure 2.— Luminescence response of: (a) K-rich feldspar microcline sample from Zarzalejo (Madrid, Spain). (b) Comparison of the CL emission of different Si-rich minerals in the UV-IR range. (c) 3D-TL emission of microcline sample (upper part) and the corresponding contour plot where is possible identify the main groups of components at 340 and 390 nm respectively (lower part). And (d) Comparison of the IRSL, TL, RL and CL emission of the microcline sample.

Figure 2b shows that Si-rich minerals display UV bands (280-290 nm) that have been associated with defect sites linked to the presence of Na in the K aluminosilicate lattice (Correcher et al., 1999a, 2011). This band in Na-rich feldspars (albite) and can be potentially useful for retrospective dosimetry (Correcher et al., 1999b). It can also show a multi-order kinetic glow curve related to a dynamic continuous trapping-detrapping process. The 340 nm emission band in tectosilicate lattices (Fig 2c), including feldspars and Si-rich minerals, has been correlated with stressed Si–O bonds and structural defects related to features like albite-pericline twinning in microcline. It can also be enhanced in stressed silicates under cryogenic conditions (Correcher et al., 1999a; Garcia-Guinea et al., 2007). The 380 nm UV waveband is characteristic of mineral phases containing SiO_4 tetrahedral (quartz and silicates) and can be related to intrinsic defects in the lattice, potentially $[AlO_4]^0$ centers. This band in sanidine is thought to be linked with thermal alkali self-diffusion mechanisms and anomalous fading of TL. Preheating can reinforce this blue TL emission in alkali aluminosilicates (Garcia-Guinea et al., 2001, 2007; Correcher et al., 1999a). The broad blue emission band at 400 nm is commonly observed in aluminosilicates and is often used for dating and dosimetric purposes. This emission is linked to $[AlO_4]^0$ centers (aluminum-hole centers) formed by the recombination of electrons with holes trapped adjacent to Al-M^+ centers after irradiation, involving alkali self-diffusion (Correcher et al., 2004). Specific bands at 420 and 480 nm,

are typically observed in aluminosilicates. These peaks, along with a 460 nm band, have been seen in chrysotile and jade (Garcia-Guinea et al., 2018). The 430 nm emission band could be associated with Cu(II) ions near hole traps or recombination on a center formed from a hole-oxygen atom adjacent to two Al atoms (Al–O–Al). The 480 nm band in feldspars can be due to the presence of Ti^{4+}. The presence of alkali and earth alkali elements in aluminosilicates can enhance UV-blue broad emissions (around 360-380, 420, and 480 nm), sometimes masking the green emission (Garcia-Guinea et al., 2017).

Green spectral CL emissions peaked at circa 550-570 nm and are often associated with manganese impurities (Mn^{2+}) in aluminosilicate lattices, specifically the spin and parity forbidden $^4T_1 \rightarrow {}^6A_1$ transition, although Mn^{2+} is not the exclusive cause of this green emission. Other metals such as Ga, In, Tl, Ni, Ba, Bi, Ge, Al, and Fe can also enhance this green emission, albeit with varying intensities (decreasing order: Mn > Ga > In > Tl > Ni > Ba > Bi > Ge > Rb > Al > K > Fe > Na) (Garcia-Guinea et al., 2017). Iron, while showing a clear 600-700 nm peak, exhibits much less intensity, possibly acting as a luminescence killer. The presence of OH^- groups on the surfaces of insulators with metal-hydroxyl bonds is proposed as another essential origin of these UV-green emissions. The proposed mechanism involves a nonspecific reaction: electron-beam + 2 (Metal-OH) → H_2O + O + photons. This mechanism agrees with radiolytic models but not with ligand field theory. Quartz with 570 nm bands is associated with low-temperature hydrothermal environments related to fast crystallization with oxygen deficiency (Garcia-Guinea et al., 2017). Lower energy emissions at 640 nm in K-rich feldspar and amazonite is associated with the presence of Fe^{3+} ions, possibly due to the reduction of Fe^{3+} to Fe^{2+} by irradiation. A near-infrared emission at 700 nm in volcanic sanidine is attributed to Fe^{3+} substituted for Al^{3+} (Garcia-Guinea and Correcher, 2003, Correcher and Garcia-Guinea, 2011).

Figure 2d shows the IRSL, TL, RL and CL emission of the microcline sample where is possible to observe that TL of 50 Gy-irradiated microcline reveals UV and blue emission bands, with specific wavelengths linked to structural defects at 340 nm and 380 nm (Correcher et al., 1999a; Garcia-Guinea et al., 2007). The 400 nm TL emission in K-rich feldspar demonstrates a linear dose dependence (Correcher et al., 2000, 2004), and the overall TL behavior is governed by continuous trap distributions (Garcia-Guinea and Correcher, 2003). The characteristic 380 nm UV emission is associated with $[AlO_4]^0$ centers (Garcia-Guinea et al., 2007), while crushing can reduce UV emission intensity (Garcia-Guinea and Correcher 2000). RL spectra of K-feldspar display UV (290 nm), green (570 nm), and red-IR (640 nm) components, with intensity ratios differing from CL TL and IRSL, indicating radiation-dependent recombination center efficiency. CL of microcline also shows 290 nm (UV), 570 nm (green), and 640 nm (red-IR) emissions, where the UV band is linked to twin-domain boundary defects involving Na^+ diffusion, and green/red bands to Mn^{2+}/Fe^{3+} impurities. Stressed tectosilicates, including feldspars and quartz, often exhibit a 340 nm CL band, attributed as aforementioned to non-bridging oxygen silicon vacancy-hole centers (Garcia-Guinea et al., 2007). IRSL in microcline displays emission spectra similar to TL and RL (290 nm, 440 nm, 720 nm). In summary, while UV and blue luminescence are common across these techniques in K-rich feldspars, often stemming from intrinsic defects, and green/red emissions are tied to impurities, the relative intensities and specific behaviors vary based on the stimulation method and the intricate defect structure of the material (Correcher & Garcia-Guinea, 2011).

The study of luminescence in oxalates and phosphates using techniques such as CL and TL reveal complex spectral features that are mainly linked to their chemical composition and crystal structure (Garcia-Guinea et al., 2017). In oxalates, the luminescence characteristics are related to their chemical and structural properties. Studies on Ca-rich oxalates from the human body (renal and gallbladder calculi) and synthetic $CaC_2O_4 \cdot H_2O$ have shown complex CL and TL emissions that are influenced by radiation effects (Garcia-Guinea et al., 2018). The presence of different phases of calcium oxalate (e.g., whewellite and weddellite) within renal calculi can lead to distinct spectral behaviour (González-Enguita et al., 2024). Studies performed on sodium oxalate has explored the effect of thermal annealing on its crystal structure and TL emission, highlighting the relationship between lattice changes and luminescence behaviour (Garcia-Guinea et al., 2011). Optical and spectral observations on cystine, oxalate, and apatite renal calculi further underscore the diverse luminescence properties arising from different chemical compositions within these biological materials (Iordanidis et al., 2011).

The luminescence emission bands in phosphates are often associated with the presence of impurities and structural defects within their crystal lattices. For example, in natural apatites, various CL wavebands have been observed, and their characteristics are influenced by chemical impurities. Emissions around 360 nm have been linked to Ce^{3+}, blue emissions (410–430 nm) to Eu^{2+}, orange-red emissions to Sm^{3+}, and additional lines to Dy^{3+} (480 and 570 nm) and Nd^{3+} (870–900 nm). These trivalent Rare Earth Elements (REEs) generally occupy Ca(I) sites, while divalent REEs substitute in the lower symmetry Ca(II) sites (Roman-Lopez et al., 2014b).

The luminescence spectra of phosphates and oxalates are highly sensitive to their chemical composition, including the presence of trace elements, impurities, and hydrous components, as well as their crystal structure and the presence of structural defects (Roman-Lopez et al., 2014a; Garcia-Guinea et al., 2011). Techniques like CL and TL serve as powerful tools for probing these relationships, providing insights into the nature of luminescence centres and the influence of the material's local environment on its optical properties. The analysis of luminescence spectra can therefore be crucial for characterizing these materials and understanding their formation and history (Garcia-Guinea et al., 2008; González-Enguita et al., 2024).

As mentioned earlier, Garcia-Guinea has also expanded his research from geological materials into material of biological interest, such as kidney stones. Here the luminescence data (e.g. figure 3) are surprisingly valuable as there are spectral differences between variously doped and shaped aspects of the biological material. Such data may be a precursor to clues as to the origin of the kidney stone formation and hence their non-surgical reduction.

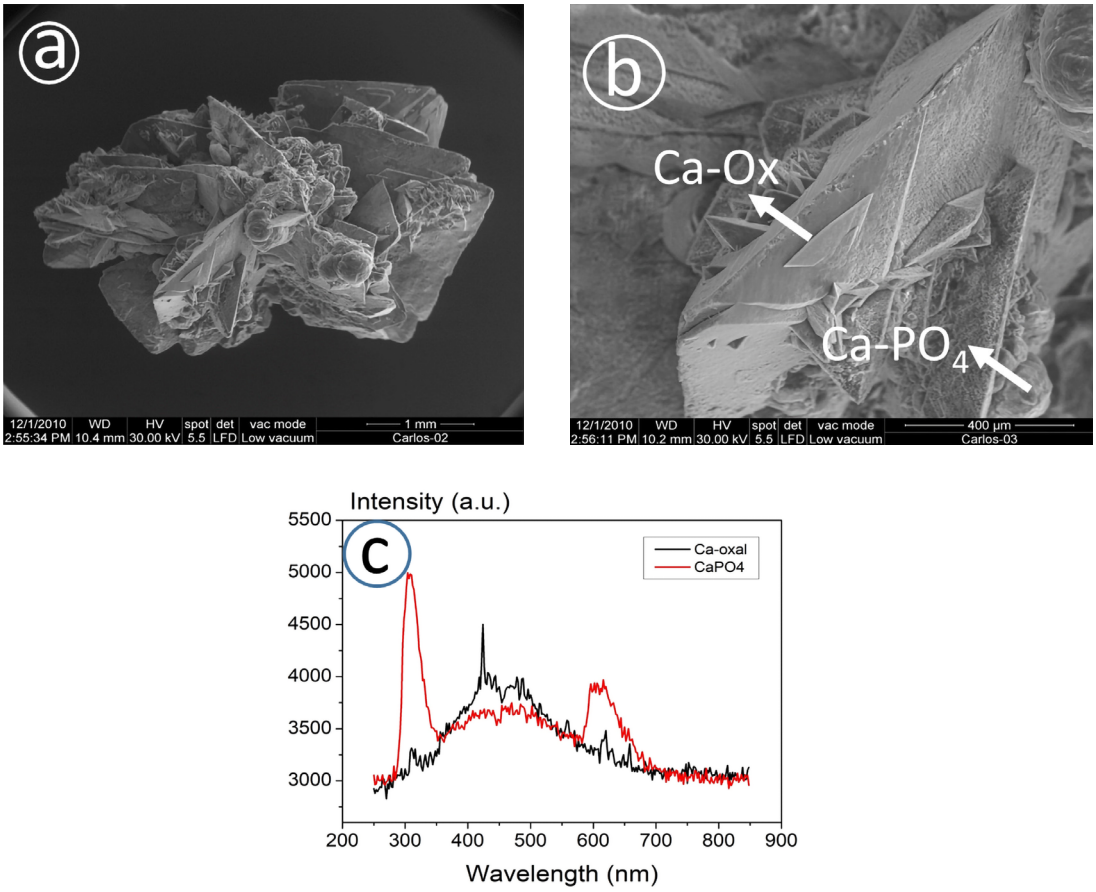

Figure 3.— Images of (a) renal calculi obtained naturally (without surgery) size over 4 mm. (b) The ESEM image displays the 'knife' structure corresponding to Ca-oxalate crystals and 'spheres' structure linked to Ca-rich phosphates. (c) Comparison of the CL emission corresponding to 'spheres' and 'knives'.

The preceding examples focus on laboratory based mineralogical analyses of samples collected from mineral sites. This exploratory aspect of a geologists career has not been emphasized here but is nevertheless a significant factor. Thus to conclude figures 4a and 4b offers a picture of Garcia-Guinea *inside* an extremely large gypsum geode in Pulpí (Almería, Spain) that he and his friends had pioneering, studied and protected.

Figure 4.— (a) Prof. Dr. J. Garcia-Guinea (back-right), Prof. Dr. J. M. Calaforra (in red), Dr. P. Lopez-Arce (in pink) and Angel Romero (front) inside a very large gypsum geode which they had studied (Townsend, 2022). (b) Prof. Dr. J. García-Guinea inside of the gypsum geode

Conclusion

This short article offers a very brief indication of the contributions of Prof. Dr. Javier García-Guinea to his progress in geological analyses and characterization of different minerals. The focus here has been on his use of luminescence and related techniques, which emphasize that one can discriminate between nominally similar specimens via differences in spectra that link to alternative variations in crystallography and the impurity content of the minerals. There are equally significant changes as consequences of the historical variations of the minerals from pressure and their thermal history. In principle, this may make it feasible to recognize changes between nominally the same mineral found at different sites. Nevertheless, one cannot over emphasize the inherent complexity and challenge associated with these scientific advances, and progress in such characterization, that are vastly more complex in natural geological materials than the equivalent studies with synthetic manufactured examples of commercial crystals and phosphors.

For those of us who have worked with him he has been an inspiration, a mine of knowledge, and a truly good scientist and friend. We wish him well in his retirement.

DECLARATION OF COMPETING INTEREST

The authors of this article declare that they have no financial, professional or personal conflicts of interest that could have inappropriately influenced this work.

AUTHORSHIP

Virgilio Correcher: Conceptualization, Investigation, Methodology, writing-original draft, writing-review & editing; **Nurdogan Can**: Conceptualization, Investigation, Methodology, writing-review & editing; **Peter D. Townsend**: Conceptualization, Investigation, Methodology, writing-review & editing.

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