Photoluminescence Imaging of Whole Zircon Grains on a Petrographic Microscope—An Underused Aide for Geochronologic Studies

Ryan J. McAleer 1,*, Aaron M. Jubb 2, Paul C. Hackley 2, Gregory J. Walsh 3, Arthur J. Merschat 1, Sean P. Regan 4,5, William C. Burton 1 and Jorge A. Vazquez *

1 U.S. Geological Survey, Florence Bascom Geoscience Center, 12201 Sunrise Valley Dr., Reston, VA 20192, USA; amerschat@usgs.gov (A.J.M.); bburton@usgs.gov (W.C.B.)
2 U.S. Geological Survey, Eastern Energy Resources Science Center, 12201 Sunrise Valley Dr., Reston, VA 20192, USA; ajubb@usgs.gov (A.M.J.); phackley@usgs.gov (P.C.H.)
3 U.S. Geological Survey, Florence Bascom Geoscience Center, 87 State Street Room 228, PO Box 628, Montpelier, VT 05602, USA; gwalsh@usgs.gov
4 Department of Geosciences, University of Alaska Fairbanks, Fairbanks, Alaska 99775, USA; sregan5@alaska.edu
5 Geophysical Institute, University of Alaska Fairbanks, Fairbanks, Alaska 99775, USA
6 U.S. Geological Survey, 345 Middlefield Road, Mail Stop 910, Menlo Park, CA 94025, USA; jvazquez@usgs.gov

* Correspondence: rmcaleer@usgs.gov

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Abstract: The refractory nature of zircon to temperature and pressure allows even a single zircon grain to preserve a rich history of magmatic, metamorphic, and hydrothermal processes. Isotopic dating of micro-domains exposed in cross-sections of zircon grains allows us to interrogate this history. Unfortunately, our ability to select the zircon grains in a heavy mineral concentrate that records the most geochronologic information is limited by our inability to predict internal zonation from observations of whole grains. Here we document the use of a petrographic microscope to observe and image the photoluminescence (PL) response of whole zircon grains excited under ultraviolet (UV) light, and the utility of this PL response in selecting grains for geochronology. While zircon fluorescence has long been known, there is limited documentation of its utility for and application to geochronologic studies. Our observations of zircon from an un-metamorphosed igneous rock, two meta-igneous rocks, and a placer deposit show that variations in the PL color are readily observable in real-time, both among grains in a population of zircons and within single grains. Analyses of cross-sections of the same grains demonstrate that the changes in PL correlate with zoning in backscattered electron (BSE) and cathodoluminescence (CL) images as well as with changes in U + Th concentration and spectroscopic proxies for radiation damage. In other words, the whole grain PL provides a low-resolution preview of the U + Th zoning expected in a cross-sectioned grain. We demonstrate the usefulness of this “preview” in identifying and selecting the subset of zircon grains in a heavy mineral separate that has metamorphic rims of sufficient width to date by secondary ionization mass spectrometry (SIMS). The data are also used to place preliminary constraints on the age and U + Th concentrations at which a yellow PL response is observed in natural samples. The PL response of zircon is well-known among spectroscopists, and these simple applications demonstrate several ways in which the response might be more effectively used by geochronologists.

Keywords: cathodoluminescence; geochronology; photoluminescence; radiation damage; thermochronology; U/Pb; ZHe; zircon
1. Introduction

In cross-section, zircon grains commonly exhibit complex and intricate zoning patterns in backscattered electron (BSE) and cathodoluminescence (CL) images, and this zoning reflects a rich history of magmatic, metamorphic, and hydrothermal processes. Although the exact cause of zoning may not be known, superposition and crosscutting relationships demonstrate relative time relationships, and these textural relationships inform spot placement for microanalytical and isotopic dating methods (e.g., secondary ionization mass spectrometry (SIMS), LA-ICP-MS). Isotopic, trace element, and spectroscopic data provide additional information on the geochemical variance among dated zones and help to link the ages to processes. Practically, however, it is the textural relationships observed in CL and BSE images that are critical for analytical spot placement and so these images are universally used for U/Pb dating of micro-domains in zircon.

Prior to mounting zircons in epoxy and cross-sectioning by mechanical polishing, the grains of interest for isotopic dating must be selected from a zircon mineral separate. A typical approach for an igneous or metamorphic rock is to select a subset of grains (~50–100) based on their appearance under incident and/or plain polarized light. The vast literature on zircon morphology ([1] and references therein), the objective of the particular study, and the geochronologist’s experience help to define the grain selection criteria. The selected grains are then mounted and cross-sectioned, and BSE and CL images of the selected grains reveal new and sometimes surprising information. In some cases, this information may leave the geochronologist wishing they had mounted more or different grains. For example, electron microscopy may show that only a small subset (e.g., 2 of 50) of the selected grains has metamorphic rims thick enough to date by spatially resolved methods. Here we demonstrate the utility of an additional dataset at the grain selection stage—imaging/observation of whole zircon grains excited under ultraviolet (UV) light on a petrographic microscope.

It has long been known that zircon luminesces under visible and ultraviolet light excitation (e.g., [2,3]). This property made zircon attractive to mineral collectors and found practical use as a tool to estimate the quantity of zircon in heavy mineral sands (e.g., [2,4]), and as a grain identification aid in some geochronology laboratories [5]. Early observers noted that zircon grains excited by UV light could exhibit some variance in photoluminescence (PL) color, but grain populations from igneous samples exhibited fairly uniform PL, and grains with the most intense response typically luminesced in shades of yellow [2]. Spectroscopic studies showed that this yellow response was broadband (e.g., [6,7]) even under laser excitation [8], but the causes of this broadband luminescence remained controversial and were ascribed to both impurities and defects [7–9].

Gaff [8] used a combination of time-resolved spectroscopy, thermal treatment, and neutron and alpha irradiation to demonstrate that the yellow broadband luminescence was due to many luminescence centers, and that in natural zircon the centers were dominantly radiation-induced. Specifically, it was shown that yellow PL with a decay time of 30–35 μsec could be removed by heating to ~700 °C and then be restored by neutron or alpha irradiation. This result has been confirmed by irradiation experiments on synthetic zircon samples [5,10,11]. In these experiments it was found that irradiation with alpha particles [5,10], neutrons [10], and oxygen ions [5] induced broadband yellow PL, while irradiation with X-rays and gamma radiation did not [10]—indicating that the broadband PL is related to the creation of point defects rather than irradiation-associated ionization [5,10]. In detail, the relative contribution to the yellow PL of alpha particles versus the recoil of heavy atoms during alpha particle ejection is not known [5]. Regardless, in natural samples, the source of alpha particles and related recoil effects (i.e., radiation damage) is dominated by the decay of U and Th atoms, and so the yellow PL is intimately related to the U + Th concentration and the thermal history—making this response particularly relevant to geochronology and thermochronology.

Much research over the past two decades has focused on the development of a zircon thermochronometer that is spectroscopy-based. Most of this pioneering work has been done using laser excitation at wavelengths in the visible to near-infrared, because at these wavelengths the broadband yellow PL response is muted-to-absent, and many other spectral lines are apparent under the high intensity of laser excitation. As a result, it is now well documented that linear correlations can exist
between the full-width-at-half-maximum (FWHM) of the \( v_3(\text{SiO}_2) \) Raman stretching mode and the alpha dose in artificially and naturally irradiated samples (e.g., [12–19]). A similar correlation has been documented between the FWHM of narrow PL lines from the rare earth elements (REEs) Dy and Sm and the alpha dose [20]. Laser-based spectroscopy and these relationships have now been applied in a variety of studies to evaluate radiation damage in polished zircon grains, and hyperspectral PL/Raman mapping is now used to produce 2D images of radiation damage of these polished surfaces (e.g., [14,21–23]). The above responses are very useful for quantitative work, but the measurements require expensive laser-based systems and the images derived from sets of spot analyses are time-consuming to collect and not observable in real-time. Most importantly, all of the measurements are made after the zircon grains have been mounted and cross-sectioned. There is no opportunity to select grains based on the spectroscopic response.

Because we are interested in a qualitative tool for the evaluation of whole zircon grains in real-time we return to the intense and broadband PL response observed under conventional (vs. laser-based) UV excitation. We find this PL response is a valuable tool when selecting zircon grains for U/Pb geochronology.

2. Materials and Methods

The original purpose of this research was to determine the U/Pb isotopic age(s) of igneous and meta-igneous zircon grains. The samples were not selected because they were anticipated to have unique PL characteristics. The three studied samples are the Paleozoic (kyanite-grade Nonnewaug Granite (PB515) from Connecticut, USA [24], the Mesoproterozoic granulite facies charnockitic gneiss at Pharaoh Mountain, from the Adirondacks, New York, USA (GP1104), and an unnamed and weakly metamorphosed Neoproterozoic granitoid from North Carolina, USA (HD18-1). A sample with detrital zircons from the Hickory Mine, Virginia, USA placer deposit was later examined in PL (but not dated). Collectively, these samples provide a sample set exhibiting wide variance in PL response in mineral separates of igneous, meta-igneous, and sedimentary zircon grains.

2.1. Whole-grain Microscopy and Spectroscopy

Several kilogram samples were collected and crushed in a Sturtevant jaw crusher, ground to < 250 micrometers in a Bico disk mill, and then passed over a Willfley table. Zircon was further concentrated from the heavy mineral fraction by passing the sample through lithium heteroplytungstate (LST) heavy liquid (\( \rho = 2.85 \text{ g/cm}^3 \)), methylene iodide (\( \rho = 3.3 \text{ g/cm}^3 \)), and a Frantz L-1 magnetic separator. The separated zircon grains were poured into a Petri dish or dispersed onto a glass slide with a rectangular grid drawn on the back side and examined and imaged while illuminated with incident (IL) and plain polarized light (PPL) on a Leica Z16 stereoscope, that is, using standard illumination methods for grain picking. Grains were then observed and imaged under PL on a Zeiss AxioImager petrographic microscope fitted with an EXFO 120 series X-Cite tin-halide bulb (Excelitas, Waltham, MA, USA), a AxioCam MRc5 camera (Zeiss, Oberkochen, Germany), long-UV (~365 nm) and blue (~470 nm) excitation filters, and long pass filters of ~420 and 520 nm, respectively. Spectral data from a subset of undated grains (~25 x 25 micrometer spot size) were also measured using a MSP400 photodiode array (JM-microsystems, Essingen, Germany) coupled to the AxioImager with a fiber liquid light guide, using a procedure similar to that described by Baranger et al., [25].

The grains dispersed on the gridded glass slide could be directly examined in PL and the slide navigated with a stage micrometer. The Petri dish did not fit under the objectives of the petrographic microscope used and so the grains were transferred from the Petri dish to a 1 cm diameter carbon sticky tab prior to PL observation. This transfer was accomplished either by pressing the tab onto a region of grains or by hand picking a subset of grains and placing them on the tab. The gridded slide was found to be the preferred method of grain examination under PL because it allowed for correlative imaging (PPL, IL, PL) of a large number of grains, although the lack of grain fixation required careful sample handling. We were unable to find a clear adhesive that did not strongly
luminesce under UV illumination. The glass slide and carbon sticky tape exhibited no visible luminescence.

2.2. Cross-sectioned grain microscopy and spectroscopy

Approximately 80 zircon grains from each of the three bedrock samples were selected based on their optical (PPL, IL, PL) characteristics for isotopic analysis by sensitive high-resolution ion microprobe reverse geometry (SHRIMP-RG) methods. Grains were mounted in Struers EpoFix epoxy and polished (1 μm finish) to expose a cross-section of the zircon grains. The polished grains were then coated with carbon and imaged in BSE and panchromatic CL modes using a SU5000 FE-SEM (Hitachi, Tokyo, Japan). Following electron microscopy, the carbon coat was removed and PL spot analyses were recorded using a Xplora Plus confocal Raman microscope (Horiba, Kyoto, Japan) with the minimum pinhole setting of 100 μm. The spot size of these analyses was ~1 μm in diameter and ~2 μm in depth. FWHM measurements of the 1000 cm⁻¹ Raman ν₁(SiO₂) stretching band were made using both a 473 nm and 532 nm laser and a 2400 lines/mm grating. The Raman measurements made with the 532 nm laser were less affected by fluorescence and are reported in Table 1. FWHM and peak position measurements of the Dy luminescence peaks were made using the 473 nm laser and a 2400 lines/mm grating. Extended spectra were collected with the 473 nm laser and 600 lines/mm grating. All spectra were fit using a sum of Lorentzian profiles with a linear or cubic baseline in the Igor Pro software suite (v. 7.08). No fit parameters were fixed during the spectral deconvolution and the peaks were fit concurrently with the baseline.

PL of the polished grains was not recorded using the Zeiss AxioImager. This instrument is not confocal, thus, out of focus light originating from the strong blue PL response of the mounting epoxy obscured the zircon PL signal.

2.3. SHRIMP-RG U/Pb and trace element analysis

Polished mounts of zircon grains were analyzed by SIMS on the Stanford-U.S. Geological Survey SHRIMP-RG ion microprobe (ASI, Fyshwick, Australia). The U–Pb isotopic age was determined with a ~20 μm diameter by ~1 μm depth spot using the methods of Williams et al., [26], and using R33 as the primary age standard [27] and a primary crystallization age of 419 Ma. Raw isotopic data were collected in five cycles and were reduced using Squid 2 [28]. The second round of SHRIMP-RG analyses were done to determine trace element concentrations for a subset of spot locations from sample PB515 and GP1104. A ~10 × ~1 μm spot was analyzed directly adjacent to the U/Pb spot analysis with MAD-559 [29] as the concentration standard and using the analytical methods outlined in Coble et al., [29]. Trace element concentrations are accurate to about ±20% [30].

3. Results

3.1. Hickory Mine detrital sample

The detrital zircon grains from the Old Hickory Mine, Virginia placer deposit exhibit a variety of morphologies and clarity in PPL, as expected for detrital grains that have been subject to sedimentary transport. Many grains are opaque in PPL. The grains also exhibit a wide range of PL colors and intensity (Figure 1a,b), and most grains are various shades of yellow-orange with a few deep red grains. There is no obvious correlation between the appearance of grains in PPL and in PL. For example, grains that are clear in PPL (circles in Figure 1a,b) exhibit the entire range of observed PL colors.
3.2. Nonewaug Granite (PB515)

Zircon grains from the Nonewaug Granite are generally subhedral and have aspect ratios of 3:1 or greater. A large number of grains are opaque in IL and PPL, but rare grains of high clarity are present (Figure 2a). Under UV excitation the opaque grains typically appear red and the clear grains are yellow (Figure 2b). Notably, with increased magnification, zoning in the PL response becomes apparent in some grains (arrows in Figure 2b, Supplemental Figure S3). The most common are yellow tips on grains with red cores (Figure 2b,f), but veins that exhibit yellow PL are also observed (Figure 3b, Supplemental Figure S3). In some optically clear grains, concentric and oscillatory zoning defined by variations in the intensity of yellow PL is observed (Supplemental Figure S3). Altered feldspar appears bright blue, and titanite shows very weak red luminescence (Supplemental Figure S1). Observation of the same grains in 470 nm light yields a severely muted to absent PL response in zircon. However, it also reveals zircon grains with wispy zones of brilliant green luminescence (Figure 3c,d). Altered feldspar grains are yellow, and titanite grains are deep red under 470 nm excitation (Supplemental Figure S1). Spectroscopy of UV-excited and unpolished zircon grains records a maximum intensity at ~570 nm in both yellow and red PL zones (Figure 2c). However, the absolute intensity at 570 nm is ~4x lower in the red PL zone than the yellow. Additionally, a broad shoulder with intensity extending out to 850 nm is present in the red zone, but absent in the yellow zone, and a small peak at 480 nm is present. The green luminescent zone exhibits a maximum intensity at ~540 nm (Figure 2c).

Electron microscopy of cross-sections of these grains shows a strong correlation between the unpolished grain PL and BSE and CL images. Zones that are red in PL images correspond to zones that are bright in BSE and dark in CL images, and PL-yellow zones correspond to zones that are dark in BSE and bright in CL images (Figure 2d–g). The brightest CL zones occur at grain rims and embay oscillatory-zoned cores, but also form veins that transect grains. A high clarity grain that was yellow and unzoned in the PL image exhibits intermediate CL intensity and oscillatory zoning in the core and a very narrow bright CL rim (Figure 2d). Grain cores that are red in PL images can also exhibit oscillatory zoning in BSE and CL, however, chaotic zoning within these cores is also common (Figure 2e,f). The wispy zone that displays brilliant green PL in blue light (Figure 3c) does not show cathodoluminescence (Figure 3d,e). In BSE this zone is bright, but slightly darker “islands,” are present. Energy dispersive spectroscopy (EDS) analyses show that the bright band and the islands are anomalously high in U relative to the rest of the grain, but the islands also have an elevated Ca content.

SHRIMP-RG analyses of bright CL-yellow PL tips yield 206Pb/238U isotopic ages of ~380 Ma. Grain cores, including medium CL-yellow PL and dark CL-red PL zones, yield 206Pb/238U isotopic ages of ~430 Ma. Concentration data show that the dark CL-red PL zones have higher U, Th, P, and REE contents than bright CL-yellow PL zones (Table 1, Supplemental Table S1) and higher Th/U ratios. The yellow zones are notably low in U (<30 ppm) and especially low in Th (<1 ppm). However, the
PL-yellow zones are enriched in Hf resulting in a similar heavy trace element concentration for 4 of the 5 analyses. All zones have low Fe (<20 ppm) and Ti (<10 ppm) contents.

**Figure 2.** (a) PPL image of heavy mineral separate from the Nonewaug Granite dispersed on a glass slide. (b) PL image of grains shown in (a). Pink arrows highlight grains with distinct yellow tips on red cores. (c) Spectral data from points indicated in (a) and (b). (d–g) Grains selected for U/Pb geochronology. The whole grain PL image is shown with correlative backscattered electron (BSE), cathodoluminescence (CL), and PPL images of the grains in cross-section. Spot locations, U/Pb ages (in Ma), and U, Th, Dy, and Fe concentrations (in ppm) are given. ttn = titanite, fsp = feldspar.

Laser-based (473 nm) luminescence spectra from the red PL core and yellow PL rim of the grain in Figure 2e are shown in Figure 4 and are typical of other grains. The rim spectrum has families of sharp peaks at ~480 and ~580 nm attributed to Dy$^{3+}$ [10,21], and a sharp peak at 495 nm—the 1000 cm$^{-1}$ Raman $\nu_3$(SiO$_4$) stretching band. The spectrum from the grain core is similar, but the Dy$^{3+}$ peaks are broader, the Raman peak is lower in intensity relative to the adjacent Dy$^{3+}$ peaks, and two peaks attributed to Sm$^{3+}$ are present at 603 and 615 nm [10,21]. The FWHM values for Raman and Dy$^{3+}$ sublevel I and II peaks from the grains in Figure 2d–g increase with increasing U + Th content (Table 1, Supplemental Figure S6), as expected for these radiation-damage proxies [12,20].
Less common PL response of zircon grains from the Nonewaug Granite. (a) The incident light image of an opaque zircon grain from the Nonewaug Granite. (b) PL image of the grain shown in (a). The majority of the grain appears red, but a narrow yellow vein and a diffuse green zone are also present. (c–d) The same grain excited under blue light. The yellow and red luminescence are muted, and wispy zones of green luminescence are more apparent. (e–g) BSE and CL images of the same grain after cross-sectioning. The green luminescent zone appears to be partially recrystallized, and semi-quantitative energy dispersive spectroscopy (EDS) analysis shows this zone is strongly enriched in uranium and calcium.

Spectra from a red PL core and yellow PL rim of a whole zircon grain shown in Figures 2e and 5b (photodiode array, 5 nm bins). (b) Spectroscopic data collected on the Horiba Explora Plus confocal Raman system (473 nm laser, 600 lines/mm grating) for the core and rim of the cross-sectioned zircon grain. Peak identification after [14,21,31], and references therein. (c) Panchromatic CL image showing laser spot locations of spectra in (b).
Table 1. Rare earth element (REE) concentrations, U/Pb isotopic age, and select spectroscopic parameters for zircons in Figures 2 and 5. All element concentrations in ppm.

| Elemen| PB515 (Figure 2) | GP1104 (Figure 5) |
|-------|------------------|-------------------|
|       | 2d   | 2e   | 2f   | 2g   | 5d   | 5e   | 5f   | 5g   | 5g   |
| Al    | 8    | 57   | 4    | 4    | 15   | 7    | 7    | 35   | 6    | 40   | 12   | 6    | 9    |
| P     | 1000 | 380  | 14   | 16   | 1800 | 250  | 280  | 280  | 70   | 300  | 43   | 270  | 67   |
| Ca    | 0.9  | 1    | 0.9  | 1    | 0.7  | 2    | 2    | 2    | 2    | 1    | 2    | 2    | 2    |
| Sc    | 220  | 68   | 23   | 27   | 790  | 10   | 9    | 18   | 2    | 19   | 10   | 20   | 1    |
| 48Ti  | 6    | 10   | 0.7  | 6    | 5    | 4    | 4    | 6    | 4    | 2    | 3    | 3    | 3    |
| 49Ti  | 6    | 11   | 0.7  | 5    | 5    | 4    | 4    | 6    | 3    | 3    | 4    | 2    | 3    |
| Fe    | 1    | 6    | 1    | 1    | 2    | 6    | 7    | 3    | 20   | 3    | 7    | 1    | 18   |
| Y     | 1500 | 1500 | 28   | 20   | 2900 | 1100 | 920  | 840  | 220  | 1200 | 180  | 1000 | 170  |
| Nb    | 5    | 29   | 3    | 2    | 14   | 20   | 14   | 9    | 3    | 5    | 5    | 4    | 2    |
| La    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    |
| Ce    | 13   | 38   | 0    | 10   | 22   | 23   | 12   | 1    | 5    | 2    | 4    | 3    | 9    |
| Nd    | 2    | 1    | 0    | 0    | 1    | 0.9  | 0.5  | 0    | 0    | 3    | 0    | 0.7  | 0    |
| Sm    | 6    | 4    | 0    | 0    | 6    | 2    | 2    | 0    | 8    | 0    | 3    | 0    | 0    |
| Eu    | 0.9  | 0    | 0    | 0.9  | 0    | 0    | 0    | 0    | 1    | 0    | 0    | 0    | 0    |
| Gd    | 55   | 35   | 0    | 0    | 81   | 22   | 18   | 19   | 1    | 51   | 4    | 27   | 2    |
| Ho    | 59   | 64   | 0.9  | 6    | 110  | 44   | 35   | 30   | 7    | 55   | 7    | 41   | 5    |
| Tb    | 17   | 13   | 0    | 0    | 32   | 8    | 7    | 7    | 0.7  | 15   | 1    | 9    | 0.7  |
| Dy    | 170  | 160  | 2    | 2    | 330  | 110  | 80   | 78   | 14   | 160  | 18   | 100  | 11   |
| Er    | 250  | 270  | 5    | 3    | 410  | 200  | 160  | 140  | 45   | 220  | 25   | 160  | 36   |
| Tm    | 53   | 58   | 1    | 0.6  | 82   | 46   | 33   | 27   | 14   | 43   | 5    | 32   | 11   |
| Yb    | 440  | 470  | 8    | 5    | 630  | 380  | 270  | 210  | 150  | 330  | 37   | 250  | 130  |
| Lu    | 82   | 92   | 2    | 1    | 120  | 70   | 47   | 36   | 41   | 65   | 7    | 45   | 37   |
| Hf    | 10,30| 11,20| 12,40| 13,50| 11,10| 15,20| 13,10| 9,90| 12,60| 8,90| 11,90| 9,40| 10,70|
| Pb    | 12   | 87   | 1    | 0.5  | 47   | 120  | 65   | 21   | 150  | 8    | 59   | 11   | 88   |
| Th    | 120  | 470  | 0    | 0    | 130  | 180  | 120  | 48   | 8    | 27   | 8    | 25   | 5    |
| U     | 180  | 1300 | 27   | 17   | 690  | 720  | 390  | 130  | 920  | 52   | 390  | 69   | 590  |

Age: 430 ± 435 ± 381 ± 390 ± 442 ± 1167 ± 1116 ± 1132 ± 1083 ± 1129 ± 1034 ± 1222 ± 1116

Dy^3+(I): 17 ± 30 ± 17 ± 14 ± 38 ± 40 ± 35 ± 19 ± 35 ± 15 ± 29 ± 16 ± 36 ± 1

Dy^3+(II): 27 ± 32 ± 31 ± 25 ± 35 ± 28 ± 30 ± 28 ± 36 ± 25 ± 30 ± 26 ± 32 ± 2

vSiO2: 5 ± 8 ± 5 ± 1 ± 9 ± 9 ± 3 ± 8 ± 7 ± 12 ± 5 ± 10 ± 5 ± 13 ± 4

Notes: U/Pb ages are the 206Pb/238U age for PB515 and 207Pb/206Pb for GP1104. Ages are in Ma and uncertainties are 1σ. FWHM values and precision uncertainties (2σ) are in cm⁻¹ and have been rounded up to the nearest cm⁻¹ for a conservative estimate. v3 = Raman v3(SiO2) stretching band, Dy^3+(I) = Dy^3+ sublevel I, Dy^3+(II) = Dy^3+ sublevel II.

3.3. Charnockite Gneiss at Pharaoh Mountain (GP1104)

Zircon grains from Pharaoh Mountain are typically subhedral and have aspect ratios of 3:1 or greater (Figure 5, Supplemental Figure S4). In PPL and IL many more high-clarity grains are present than in the Nonnewaug Granite sample, but most grains are nearly opaque in PPL (Figure 5a). Grains that are opaque in PPL can appear either red or yellow under UV excitation and clear grains appear bright yellow at their tips, and colorless to a light yellow away from grain tips (Figure 5b, point 4). At higher magnification intra-grain PL zoning is readily apparent. The zoning is the inverse of that found in the Nonnewaug Granite, with grains commonly having yellow cores and red rims (Figure 5e,f, Supplemental Figure S4). Additionally, red zones also occur along fractures and in grain cores that are opaque in PPL. In some high clarity grains, oscillatory zoning between yellow and faint yellow PL is observed (Supplemental Figure S4). Whole-grain spectroscopy of zircon records a maximum intensity at ~570 nm regardless of the color observed in PL images (Figure 5c). The absolute intensity at 570 nm is again lower in the red PL zone than the yellow. The intense yellow tips and the faint yellow grain cores yield similar intensities at 570 nm, but the width of the 570 nm peak is much narrower in the faint yellow zone, and a 480 nm peak is present. A grain with a “dark red” zone
(Figure 5b, point 3) has increased intensity at >700 nm as compared to the more commonly observed red PL response. Apatite grains are blue under UV excitation and orange under blue light (Supplemental Figure S2).

Electron microscopy of cross-sectioned grains again show that red PL zones correspond to zones that are dark in CL and bright in BSE images, and yellow PL zones corresponding to zones that are relatively bright in CL and dark in BSE images. Yellow PL cores exhibit oscillatory zoning in BSE and CL (Figure 5f,g, Supplemental Figure S4), and these cores are commonly transected by CL-dark veins. Red PL cores, rims, and veins are only weakly cathodoluminescent and do not appear zoned, however, within these CL-homogenous zones there is some variation in brightness in BSE images that highlight sinuous zones of zircon comprised of different compositions.

SHRIMP-RG analyses of grain cores that are yellow in PL images and bright in CL images and exhibit oscillatory zoning, show that these zones have typical U + Th concentrations of <100 ppm and Th/U ratios of ∼0.5 (Table 1). These low concentrations lead to imprecise $^{206}\text{Pb}^{207}\text{Pb}$ isotopic ages for individual spots, but a nominal population age of ∼1150 Ma. In contrast, SHRIMP-RG analyses from red PL/dark CL zones have typical U + Th concentrations of ∼1000 ppm and U/Th ratios of >20. This population yields more precise $^{206}\text{Pb}^{207}\text{Pb}$ isotopic ages for individual spots, but a range of ages that spans ∼1200–1050 Ma. In general, red zones are low in Y and REEs, and high in U and Hf as compared to yellow zones. Both red and yellow zones have a low Fe (<20 ppm) and Ti (<6 ppm) content (Figure 5, Table 1, Supplemental Table S1), though Fe is commonly higher in red zones. Laser-based (473 nm) spot analyses adjacent to SHRIMP-RG spots show a positive correlation between the FWHM proxies for radiation damage and U + Th content (Table 1, Supplemental Figure S6).

3.4. Granitoid at Beauty Spot (HD-18-1)

Zircon grains from the Neoproterozoic granitoid (HD-18-1) are typically fragments, and rare whole grains indicate an initial aspect ratio of ∼2:1. All grains are of fairly high clarity in PPL and IL. In PL images zircon appear bright to faint yellow or non-luminescent—similar to high clarity grains from Pharaoh Mountain. Notably, at higher magnification fine-scale oscillatory zoning between bright yellow PL and non- or more weakly-luminescent zones is apparent in many grains (Figure 6, Supplemental Figure S5). Whole grain spectroscopy was not done on zircon grains from this sample.

As with the above samples, there is a close correlation between the whole grain PL image and CL and BSE images of grain cross-sections (Figure 6, Supplemental Figure S5). Oscillatory zoning is apparent in CL and BSE images of all grains and matches the oscillatory zoning in geometry when it is apparent in PL images. In detail, the bands that exhibit the brightest yellow PL are brightest in CL and darkest in BSE images. Several prevalent and correlative high-intensity PL, bright CL bands are highlighted in Figure 6a,d. Raman spot analyses across this zoning further demonstrate that variations in the Raman and Dy$^{3+}$ FWHM correlate directly with variation in CL intensity (Figure 6f).

SHRIMP-RG analyses of these oscillatory zoned grains from the weakly metamorphosed granitoid yield $^{206}\text{Pb}^{207}\text{Pb}$ isotopic ages of ∼730 Ma regardless of spot location. Trace element data were not collected on these grains, but U and Th concentrations collected during U/Pb analysis averaged 170 and 95 ppm, respectively. The CL and PL zoning occur at a scale finer than the SHRIMP-RG spot analyses (Supplemental Figure S5).
Figure 5. (a) PPL image of heavy mineral separate from a granitic gneiss at Pharaoh Mountain, Adirondacks, New York. Grains are dispersed on a glass slide. (b) PL image of grains shown in (a). (c) Spectral data from points indicated in (a) and (b). (d–g) Grains selected for U/Pb geochronology. The whole grain PL image is shown with correlative BSE, CL, and PPL images of the grains in cross-section. Spot locations, U/Pb ages (in Ma), and U, Th, Dy, and Fe concentrations (in ppm) are given.

Figure 6. (a–c) PL, PPL, and IL image of an optically clear zircon grain from the granitoid at Beauty Spot. White dashed lines in (a) correspond to yellow dashed lines in (e). (d–e) BSE and CL image of the same grain after cross-sectioning. (f) The plot of the full-width-at-half-maximum (FWHM) of the Dy sublevel I photoluminescence peak and the FWHM of the Raman v(SiO4) stretching band along the traverse indicated in (e). Changes in the FWHM of these parameters correspond closely to zoning observed in CL and PL. Note the external grain shape in the PL image is slightly different than the shape in CL and BSE images because the grain was polished to less than ½ depth and so the grain tip was not exposed for electron microscopy.

3.5. Correlations Across Methods:

In the above section and in the supplemental information the external shape of grain may differ significantly between the PL image and the CL/BSE images of a cross-section of the same grain (e.g., Figure 6, Supplemental Figure S3a). There are at least two reasons for this difference: 1. the polishing
depth deviated significantly from half depth (Figure 6, Supplemental Figure S5a,b,d); 2. the grain was placed on a different crystal face for polishing than for PL imaging. (Supplemental Figure S3a,e). Figure 7a,b provide cartoons illustrating each case, respectively.

In general, whole grain PL zoning and BSE/CL zoning in cross-sections of the same grains are strongly correlated (see above). The correlations can be remarkably good (e.g., Figure 6). However, the whole grain imaging and spectroscopy originate from different volumes of material than the cross-sectioned images and spectroscopy. This is true because ~1/2 of the grain has been removed during cross-sectioning, but also because of the different interaction volumes of the sampling methods.

In our whole grain PL images and PL spot analyses, UV light simultaneously illuminates the entire field of view (FOV). The FOV has been stopped down to 25 × 25 μm by a field diaphragm. In both cases, the PL from areas that are in focus is strongest, but out of focus PL is also detected. For images, this contributes to “blurriness,” but also allows PL emitted from internal parts of grains (Figure 7c) to be imaged. Similarly, for the spectroscopic measurements, this signifies that the PL signal comes from a significant volume around the focal plane.

In contrast, confocal Raman spectroscopy (and imaging) uses a pin-hole to reject out of focus light and so the measured signal comes from a volume ~1 μm in diameter and 2 μm in depth. Similarly, the BSE and CL signals come from a volume that is <1 μm³. Therefore, even if the UV excited PL images and measurements could have been made on the polished grain (we could not perform these analyses due to the strong blue luminescence of the epoxy) the sampling volume would be significantly different for each method.

The SHRIMP-RG measurements sample a zone of ~20 μm in diameter by 1–2 μm in-depth as compared to the 1 μm diameter of Raman measurements. Again, the compositional data and spectroscopic results do not come from exactly the same volume.

**Figure 7.** (a) Cartoon showing how variation in polishing depth results in an external shape mismatch between imaging types as occurs in Figure 6. (b) Cartoon showing a zircon with a rectangular cross-section. Rotation of the grain to a new face during transfer for polishing results in a width difference between PL and BSE images (e.g., Supplementary Figure S3e). (c) Cartoon showing some of the effects that result in the net PL image. Acceptance of out of focus light allows you to “see through” thin yellow PL zones in the center of the grain to perceive a red PL core as faint orange. Blurry oscillatory zoning in the yellow PL is observed at grain margins where interfaces between yellow PL and non-PL zones become steep relative to the direction of illumination.
4. Discussion

4.1. Photoluminescence Response: General Observations

In this study, we have examined whole zircon grains in the air on a petrographic microscope fitted with a tin-halide UV light source. The images demonstrate that the intensity of luminescence from whole zircon grains under long UV excitation is sufficient to allow real-time observation and imaging of PL from zircon at 50—100x magnification (i.e., PL from 10s of grains can be observed and imaged in a single field of view, Figures 1b, 2b, and 5b). Additionally, at these magnifications, wide variance in PL among a population of grains and within single grains is apparent in detrital, igneous, and meta-igneous rocks (Figures 1, 2, and 5). In many cases the grains that are zoned in PL exhibit no obvious zoning in PPL or IL—the typical types of illumination used during zircon grain selection (Figures 2, 3, and 5). That is, through UV excitation of the well-known zircon PL response, it is possible to extract useful information during the examination of whole zircon grains that is not available from common PPL or IL imaging.

Correlative imaging demonstrates that the PL response of whole zircon grains correlates with the BSE and panchromatic CL response of cross-sections of the same grains (Figures 2, 3, 5, and 6). In general, zircon grains or parts of grains that appear red under UV excitation are relatively bright in BSE and dark in CL, and grains or parts of grains that appear yellow are relatively dark in BSE and bright in CL. In other words, the PL imaging provides a preview of the BSE and CL zoning expected in a cross-sectioned grain. In that the BSE and CL images are universally used to determine spot locations for U/Pb analysis, the PL response is useful, regardless of its origin, in selecting grains for cross-sectioning that are most likely to record the geochronologic information of interest. For example, in the zircon separate from the Nonewaug Granite a subset (~5%) of whole grains clearly had red-cores and yellow-rims under UV excitation (Figure 2). This observation allowed us to preferentially select grains for cross-sectioning that had sufficiently thick rims for U-Pb analysis with the SHRIMP-RG ion probe.

As mentioned previously, leveraging the PL response of zircon to UV excitation is not a new idea—industry and some geochronology labs [5] use UV illumination on a binocular microscope to identify and select zircon grains. The long working distance of the binocular scope is advantageous because it allows zircon grains to be picked (using proper safety precautions) while under UV illumination. Unfortunately, the long working distance also results in inefficient light collection, and only grains with the most intense (typically yellow) response are observable [5]. For example, in our own attempts using a gooseneck LED UV light source (360–380 nm) delivering ~150W/m² at a distance of 4 cm, a 415 nm long pass filter, and a Leica Z16 stereoscope the PL response of zircon from both the Nonewaug Granite and the charnockitic gneiss from Pharaoh Mountain was negligible and could not be imaged. Although examination on a petrographic microscope does not allow for direct grain picking under UV light, the increased intensity of the PL signal and the availability of higher magnification can reveal a variety of details not apparent otherwise—and these details are useful in a number of applications (see below).

4.2. Origins of the Visible PL Color

The above correlations between PL and electron microscopy (BSE, CL) demonstrate the potential utility of the PL imaging of whole zircon grains, but the images are more powerful if the origins of the PL are understood. A number of studies have explored the origins of PL in natural and synthetic zircon excited by UV light [5–8,10]. These studies demonstrated that the luminescence spectrum of a typical natural zircon can include sharp peaks from REE centers and broad peaks from metal-ion complexes, but that the spectrum is typically dominated by broadband luminescence centered at ~570 nm, and this yellow PL is radiation-induced. The irradiation experiments of [5] also showed that in synthetic zircon the intensity of the 570 nm peak initially increases with radiation dosage, but that at moderate doses the response is suppressed upon further irradiation. In this context, the results presented here are more easily interpreted and also allow us to offer a few observations regarding
the interpretation of the visible PL. In our PL images, we observe four zircon PL responses: yellow, red, colorless, and brilliant green. Here we focus on the first three responses.

Comparison of trace element analyses from Noneau and Pharaoh Mountain samples with PL images shows that intra-grain variance from yellow to red PL most closely correlates with an increase in the U + Th concentration. However, these intra-grain red and yellow zones also have drastically different trace element concentrations and U/Pb isotopic ages (Table 1), and so the correlation of PL color with U + Th concentration is only one of many relationships that are present. In contrast, the analyses of grain cores (Figure 2d,e,g) from grains in from the Noneau granite have similar trace element patterns and overlapping U/Pb ages, but significantly different U + Th concentrations—and a different PL response. The yellow core (Figure 2d) has a U + Th concentration of 300 ppm, while the red cores have concentrations of 820 and 1770 ppm (Figure 2e,g), respectively. These analyses, though limited, are consistent with radiation damage (from the decay of U and Th) being the major contributor to the visible PL color and with the quenching of yellow PL and/or a redshift in PL beyond some radiation damage threshold. The fact that red zones in the Noneau zircons have higher Dy concentrations than yellow zones (Table 1, Figure 2d–g) also demonstrates that the Dy\(^{3+}\)-luminescence center, so dominant under 473 nm laser excitation (Figure 4b), is a minor contributor to the total PL intensity under tin-halide UV excitation.

The spectral data collected on whole grains provide some additional insight into the origin of the shift from yellow to red PL observed in some samples. These spectra (Figures 2c and 5c) show that for both yellow and red grains in the Noneau and Pharaoh Mountain samples the maximum PL intensity is at \(\approx 570\) nm, but in red grains, the absolute peak intensity at 570 nm is lower. Gaft [8] noted that in some natural zircons, annealing of radiation damage by heat treatment removed the broad and intense 570 nm component and revealed poorly understood blue and red spectral components that were tentatively attributed to defects related to Ti-O complexes and Ti\(^{3+}\) and Fe\(^{3+}\), respectively (but see also [10]). Similarly, in a natural setting, the quenching of the yellow response due to increasing radiation damage—as has already been documented in synthetic samples for PL [5] and CL [11,32]—could increase the relative contribution of a weaker red component. In this way, variation from yellow to red in our PL images may indirectly reflect increasing radiation damage and U + Th concentration.

Spectroscopic proxies for radiation damage support the hypothesis that red PL, although present in zones of high U + Th concentration, does not result solely from radiation damage. Spot analyses show that CL-dark/Red PL zones have relatively wide FWHM values for both the Raman \(\nu(SiO_4)\) and luminescent Dy I and II sublevel peaks as compared to CL-bright/yellow PL zones (Table 1, Figures 2, 3, and 5), indicating greater radiation damage in the red PL zones (e.g., [12,20]). However, the high clarity grain from granitoid at Beauty Spot (Figure 6) oscillates between yellow PL and little to no PL response (i.e., colorless), and here the colorless zones are more damaged (Figure 6f). This observation coupled with the whole grain spectroscopy indicates that in natural zircon increasing radiation damage does result in quenching of the yellow PL, but does not, by itself, result in red PL. A lack of trace element data for this sample prohibits us from speculating further on the cause of the red PL.

Undoubtedly, directly linking the observed PL color under UV illumination to U + Th concentration and radiation damage is an oversimplification. For example, a detailed spectroscopic study has documented a number of non-radiation induced luminescence centers that can contribute to the visible PL color of zircon, some of which remain poorly understood [10]. Nevertheless, for most grains studied here correlations exist between U + Th concentration, radiation damage, and visible PL color. Therefore, we suggest that in many samples, changes in the visible PL color of zircon, as observed under UV illumination, will track changes in radiation damage, i.e., the U + Th concentration and the cooling (annealing) history of the zircon. In zircon grains with a common cooling history (e.g., zircons separated from an igneous rock or single zircon grains), variation in this PL response is therefore a proxy for changes in the U + Th concentration.
4.3. Implications

The ability to determine the gross U + Th zoning of a zircon grain without physically exposing the core of the grain is a powerful tool for geo and thermochronology. The primary application demonstrated here is the use of PL in selecting grains that record metamorphic recrystallization or overgrowth in addition to igneous crystallization (Figures 2 and 4). In many rocks, metamorphic recrystallization/overgrowth of zircon is heterogeneous at a local scale and so only a subset of zircon grains in a mineral separate will have metamorphic rims — and only a subset of those grains will have rims that are > 20 μm in width and sufficiently thick to date. The PL images allow for the preferential selection of grains with datable rims. For example, in addition to selecting optically clear grains from the Nonewaug Granite (Figure 2d,g) we also selected grains that were opaque in PPL because they exhibited zoning under UV-light (Figure 2e,f). These grains were selected because they had thick yellow PL rims distinct from red PL cores. Following grain cross-sectioning it was apparent that these opaque grains were the only grains with rims of sufficient thickness to allow for SIMS analysis and for determination of the age of metamorphic zircon growth. These grains would not have been selected using only PPL and IL and therefore the age of the low U rims could not have been determined. In general, the PL images provide a means to look for a partial metamorphic replacement of metamict and otherwise opaque grains (Figures 2, 3, and 5).

A priori knowledge of U + Th zonation would also be especially useful in the U-Th/He dating of zircon (ZHe). The long ejection distance (~15–20 μm) of alpha particles in zircon makes ZHe ages strongly affected by zonation in the parent nuclides (e.g., [33,34]). Many ZHe studies assume a uniform parent distribution when calculating an alpha ejection correction. This assumption is never strictly correct and, in extreme cases, can lead to ZHe ages that are incorrect by >30% [33]. PL imaging could be used to select grains with limited zoning in PL or to at least document the zonation (or lack thereof) and the expected effect on the resultant ZHe age for any given grain. In an ideal case, it may be possible to use an image similar to the one in Figure 6a along with spectroscopic and LA-ICP-MS depth profiles [35] to model the correction.

Our observations also allow us to place some rough constraints on the age and U + Th concentrations at which these whole-grain PL observations might be “illuminating.” In Figure 8 we plot the age vs cumulative alpha dose for our unknown analyses, with data points coded as red or yellow based on the color observed under tin-halide UV illumination (Figures 2 and 5, Supplemental Table S2). The alpha dose was calculated using both our U/Pb ages (assumes no recovery of PL inducing defect centers after crystallization) and the nominal ZFT age (assumes complete recovery of the relevant defects up to the temperature of fission track recovery or ~250°C) based on regional thermochronologic data [36–38]. The U/Pb-based calculation indicates that a rough alpha dose range of ~2 × 10¹⁴ to 6 × 10¹⁷ α/g yields visible yellow PL on this petrographic microscope. The ZFT based dose yields a lower and narrower range of ~1 × 10¹⁶ to 2.5 × 10¹⁷α/g. Given that zircon grains in samples commonly show significant variation in U + Th concentration [39], either dosage range is likely to include some grains or parts of grains in zircon populations that are Proterozoic to Tertiary in age (Figure 8). In grains where the alpha dose zoning straddles either bound of the yellow PL range, yellow vs. non-yellow zoning should be observable (Figure 6). In cases where the alpha dose is outside of this range, other luminescence centers may be observable. In either case the PL image places constraints on the spatial pattern of accumulated radiation damage and the associated U + Th concentration in the zircon grain. Figure 8 shows the relationship between these variables.

The observation of whole zircon grains under UV illumination on a petrographic microscope is simple, rapid, and inexpensive, and reveals zoning patterns that are not apparent using standard methodologies. Given the expensive and laborious nature of arriving at U/Pb and ZHe isotopic ages, it is easy to justify the additional step of observing the heavy mineral separate and/or individual zircon grains under UV illumination.
Supplementary Materials: The following are available online at www.mdpi.com/2075-163X/10/10/876/s1, Figure S1: Correlative microscopy of heavy mineral separate from sample PB515; Figure S2: Correlative microscopy of heavy mineral separate from sample GP1104; Figure S3: Additional correlative whole-grain PL and CL+BSE images from cross sections of the same zircon grains from sample PB515; Figure S4: Additional correlative whole-grain PL and CL+BSE images from cross sections of the same zircon grains from sample GP1104; Figure S5: Additional correlative whole-grain PL and CL+BSE images from cross sections of the same zircon grains from sample HD-1-18; Figure S6: Full width at half max (FWHM) of the Dy\textsuperscript{3+} sublevel I peak vs. cumulative alpha dose for the data presented in Table 1 and Figures 2 and 5; Table S1: Rare earth element concentrations and U/Pb isotopic age for zircons in Figures S3 and S4; Table S2: Data plotted in Figure 8 of the main text. All tabular data are also available in an associated U.S. Geological Survey data release [40].

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