

Quantitative and Qualitative Correlation of CL and X-ray Signals in Cr-bearing Jade from Chichén-Itzá Archaeological Zone, Mexico

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Jade has always been highly prized in Maya culture. Early Spanish accounts following the European invasion confirm that precious stones were sacrificed in cenotes (water-filled sinkholes) with other items of great value [1], along with burial offerings. Jadeite jade ($\text{NaAlSi}_2\text{O}_6$) is found associated with a limited number of tectonic settings around the globe and was available to the Maya in present day Guatemala [2-5]. In this study we examine a virtually monomineralic jadeite ceremonial bead from Chichén-Itzá Archaeological Zone, Mexico using correlated cathodoluminescence (CL) imaging and spectrometry, electron-induced X-ray microanalysis, and micro-X-ray fluorescence imaging to gain an improved understanding of the origin of jadeite luminescence.

The jade specimen examined in this study (JA092) was described and analyzed by neutron activation as part of large-scale study of jadeite in Mesoamerica [6]. Multispectral CL and backscattered electron (BSE) image montages were collected using an Hitachi S3700N SEM equipped with a Gatan ChromaCL2 imaging system. Hyperspectral CL data were collected via stage scanning using an xCLent system integrated into a JEOL 8530F Plus electron microprobe equipped with Probe for EPMA software. Wavelength dispersive spectrometry (WDS) images and energy dispersive spectra were captured simultaneously during hyperspectral CL imaging, where the WDS Cr signal was summed from four spectrometers to enhance sensitivity. Images of prominent CL peaks in the sum spectrum were derived, and the image with the greatest contrast was used to select positions for quantitative WDS point analysis, where signals from two spectrometers were aggregated for Cr, Ca, Ti, Mn, Fe, and Ni. Micro-X-ray fluorescence (μXRF) element maps were obtained using a Bruker M4 TORNADO equipped with a Rh X-ray source and two XFlash 6|60 X-ray EDS detectors.

The major element compositional range of pyroxene in the bead is limited with a mean jadeite (NaAl) component of $95.1\% \pm 1.6\%$ ($n=58$), and the balance is represented by minor diopside (CaMg) and aegerine (NaFe) along with trace kosmochlor (NaCr) components. As such, grains display little variability in BSE images. In contrast, multispectral CL images show striking core to rim oscillatory zoning patterns in red-green-blue (RGB) channels and the near ultraviolet (NUV) band (Figure 1a). The most prominent feature in the CL sum spectrum is a low energy peak at 1.6 eV (775 nm) that represents the majority of luminescence. Fixed position peak fitting of the sum spectrum results in a constellation of minor peaks around the 1.6 eV feature which may suggest peak position shifts (Figure 1b), in addition to three higher energy peaks at 2.3 eV (539 nm), 2.8 eV (443 nm), and 3.8 eV (335 nm). Zoning in the 1.6 eV CL image show an increase in intensity toward the rim in most crystals, while one aggregate displays high intensity at, or near, the core of crystals (Figure 1c). Chromium concentrations exhibit a positive correlation with 1.6 eV CL intensity and can be divided into two groups: 1) Trace Cr (<400

ppm) forming a highly correlated ($R^2=0.97$) linear array with a regression yielding a Y axis intercept value near zero (Figure 2a), and 2) Minor Cr ($800 < \text{Cr} < 3,000$ ppm) forming a more poorly correlated array ($R^2=0.50$). Other cations are also positively correlated with 1.6 eV CL feature, including: Fe, Ca, Mg, Mn, Ti, with R^2 correlation coefficients ranging from 0.46 to 0.11.

The 2.3 eV and 3.7 eV CL images display reduced contrast relative to the 1.6 eV feature and are negatively correlated with Cr and Fe respectively, with R^2 values of 0.83 and 0.84 (Figure 2b). This negative trend extends to the Y axis intercept for the 2.3 eV feature where Cr concentrations greater than $\approx 2,000$ ppm result in non-luminescence. The 2.8 eV feature has contrast showing coarse-scale core to rim zonation and is negatively correlated with respect to Cr and Fe concentrations. Micro-XRF element maps of the entire bead fragment show little to no chemical zoning in major elements (Na, Al, and Si), with modest jadeite zoning for minor and trace elements (Ca, Cr, Mn, and Fe) (Figure 2c). A higher resolution μXRF image of the area examined by CL indicates Cr qualitatively covaries with the 1.6 eV CL (Figures 2d).

Chromium plays a dominant role in the spectral and microstructural CL characteristics of a Mesoamerican jadeite bead found at Chichén-Itzá Archaeological Zone, Mexico and has been reported in earlier CL studies of jadeite [7, 8]. The 1.6 eV peak represents extrinsic luminescence activated by the substitution of trace Cr within the jadeite structure. Higher concentrations of Cr, in addition to Fe-Ca-Mg-Ni and Mn, produce a poorer correlation with 1.6 eV luminescence potentially due to the increased defect density. Correlation between 1.6 eV CL and high sensitivity Cr images obtained by μXRF are consistent with the quantitative WDS point analysis finding. The WDS data also suggest that the 2.3 eV, 2.8 eV and 3.7 eV CL features are consistent with intrinsic cathodoluminescence, as their intensities are anticorrelated with increasing concentrations of elements substituting into the jadeite structure (e.g. Cr, Fe, Ca, Mg, Mn, and Ti). While the 2.3 eV and 3.7 eV images have reduced contrast relative to the 1.6 eV feature, the coarse-scale zoning in the 2.8 eV feature, relative to the oscillatory 1.6 eV zoning, may represent crystal growth-induced imperfections in the jadeite structure. These microscale imaging and analytical results show significant promise for forging links between archaeological dedicatory jadeite offerings that are often difficult to group [9]. CL and X-ray microanalysis may also aid archaeologists seeking to determine the relationship between such cultural objects and the ancient trade networks responsible for transportation from their point of origin to the site of discovery.

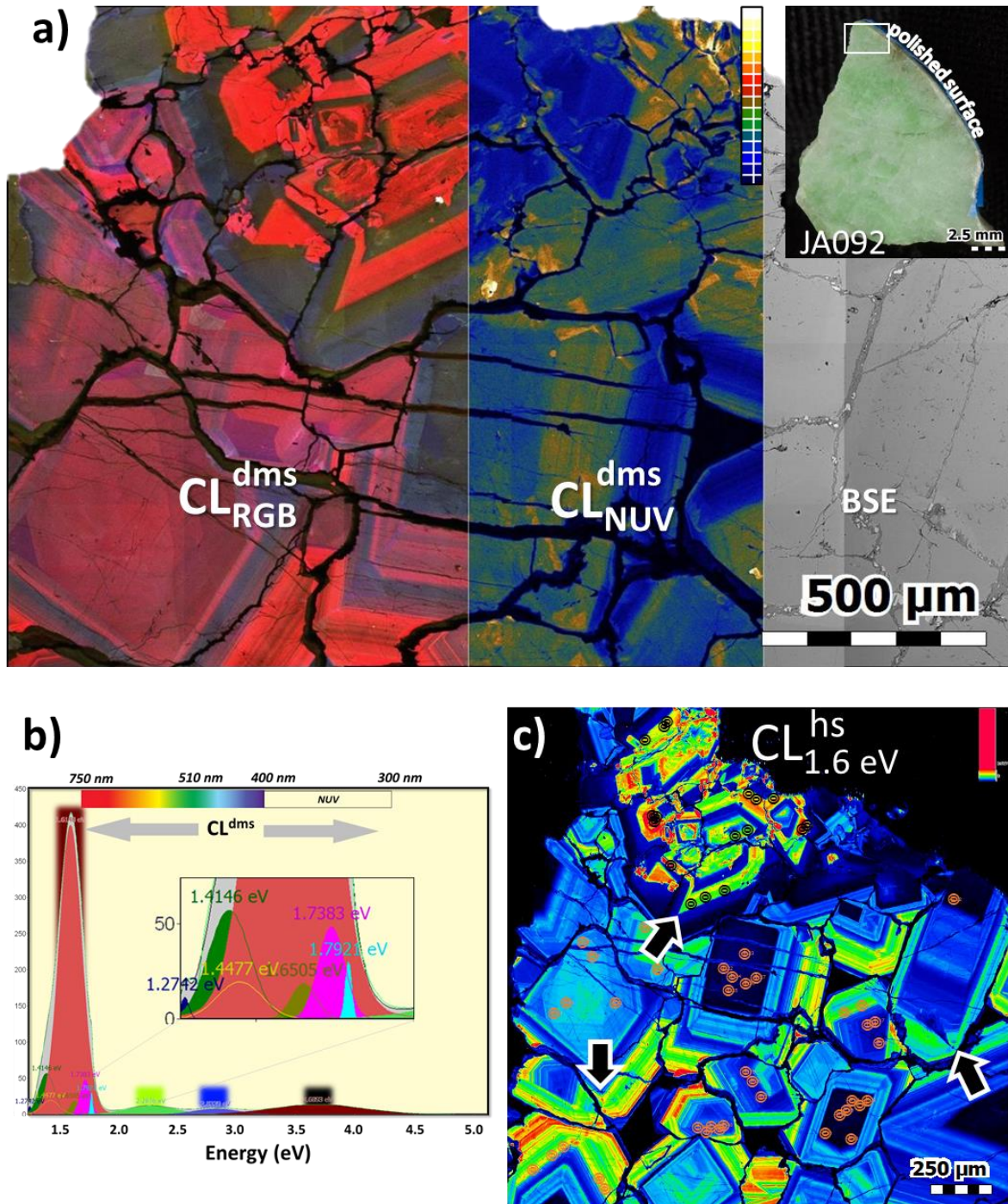


Figure 1. Cathodoluminescence imaging and spectrometry of jadeite bead JA092. a) Dispersive multispectral CL signals (RGB color-NUV false color) and BSE split montage of specimen. Inset: object scale photo showing cultural polished surface and area highlighted for analysis by white rectangle. b) CL sum spectrum showing Gaussian fits, and the overlap between the multi- and hyper-spectral CL systems in energy range. Inset: expanded view of multiple peaks in the NIR-red region. c) Oscillatory core to rim zoning for 1.6 eV CL shown in rainbow false colors, with nested orange and nested black

circles indicating the position of point analyses (black arrows represent points of correlation with μ XRF in figure 2d).

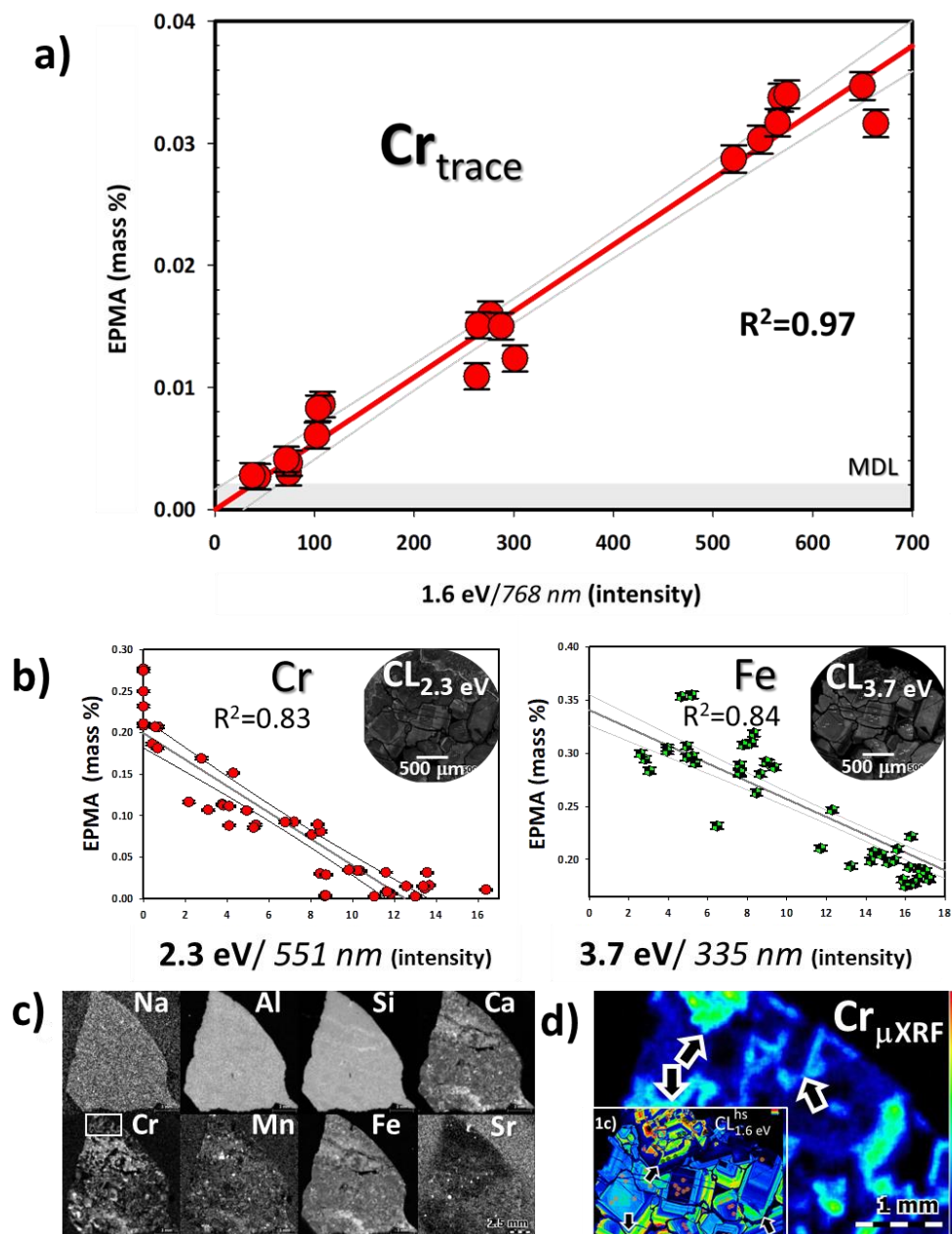


Figure 2. Quantitative and qualitative elemental correlations with CL in jadeite. a) Positively correlated Cr concentration with 1.6 eV CL intensity where the linear regression is shown as solid red line with 95 % uncertainty hyperbolae as light gray lines, and values below the minimum detection limit (MDL; 99 % confidence) are represented by a shaded gray rectangle. b) Negatively correlated Cr (filled red circles) and Fe (filled green and black hexagons) with 2.3 eV and 3.7 eV CL spectral features respectively, with associated CL image insets. c) Major, minor, and trace element μ XRF images of the entire jadeite bead. d) Higher resolution Cr μ XRF image of area in white rectangle shown in (c). Black filled arrows

highlight correlated CL microstructural features displayed in figure 1c and repeated in 2d inset. Note: Error bars represent one sigma uncertainty.

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