

## Scanned colour cathodoluminescence establishes a slate belt provenance for detrital quartz in Devonian black shales of the Appalachian Basin

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Abundant Upper Devonian black shales accumulated in the Appalachian Basin. Terrigenous components must have originated in the Acadian orogenic front to the east, but provenance determination is difficult because of the fine grain size. Commonly used approaches, such as ratios of immobile elements, only allow crude provenance assessments. Quartz grains, the most abundant detrital mineral component in shales, should most closely relate to original source rocks because they are mechanical and chemical stable in surface environments. Quartz grains from different source rocks show cathodoluminescence textures that allow source discrimination, but in shales they are too small to show these features reliably.

Samples from eastern Kentucky were examined with scanned colour cathodoluminescence (SEM colour-CL) to determine quartz provenance. The great majority of quartz grains luminesce in the orange region of the visible spectrum. These grains may show bluish-greenish core regions, are elongated, with regions of irregular-contorted growth, and may show fracturing. In contrast, in CL studies of quartz from sandstones the observed orange CL colour is exceedingly rare. Because of the small size of quartz grains we chose to compare our CL signatures to quartz in slates from North America and Europe. Slate quartz grains showed the very same colour and textural features that we observed in Devonian black shales. We conclude therefore that our source area, the Acadian orogenic front, must have been dominated by slates and related rocks during the Upper Devonian.

## Ti in quartz: Cathodoluminescence and thermometry

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Although zoning of cathodoluminescence (CL) intensity in quartz has long been recognized, recent advancements in microbeam imaging and spectroscopy promise to make CL imaging of quartz a valuable petrologic tool. CL imaging should prove especially useful in understanding the thermal histories of igneous and metamorphic rocks, because the CL emission spectrum is influenced by the presence of Ti, which increases in concentration with temperature of quartz crystallization (Wark & Watson; 2004 Goldschmidt).

To characterize the contribution made by Ti to CL spectra, we measured CL emissions in natural and synthetic quartz over the 300-900 nm range using a Gatan MonoCL3 spectrometer on an electron microprobe. Natural quartz included crystals of hydrothermal, metamorphic, and igneous origin; synthetic quartz included Ti-doped and undoped crystals. Although broad peaks are visible in most spectra at ~625, 690, and 770 nm (orange and red), only a ~415 nm (blue) peak correlates well with Ti concentration. The beam-normalized intensity of the 415 nm peak increases by a factor of roughly 10 for Ti concentrations ranging from ~60 to 600 ppm, while all other peak intensities remain relatively constant. In all quartz grains with at least a few ppm Ti, the visible CL spectrum is overwhelmingly dominated by the 415 nm emission.

Because Ti so strongly influences the CL spectrum, monochromatic (415 nm) and even panchromatic images can often be used to qualitatively map quartz crystallization temperatures. Such images should prove valuable to understanding metamorphic parageneses. For example, amphibolite-grade metapelites from New Hampshire have matrix quartz with dark cores and bright rims, in addition to bright (high-T) quartz rimming garnet that was produced at the staurolite isograd. In igneous rocks, quartz preserves clues about the thermal evolution of magma chambers: CL images of Bishop Tuff quartz, for example, document early, low-T crystallization (dark-CL cores) with later growth of quartz at higher T (bright rims), presumably after a recharge event. In all rock types, the sub-micron resolution of the electron beam allows finer spatial resolution of Ti zoning details (using CL intensity as a proxy for Ti concentration) than is possible by X-ray or SIMS microanalysis.