



## Assessing the origin of diagenetic quartz in organic-rich mudstone via in-situ geochemical and hyperspectral characterization

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### Summary

Quartz is one of the major constitutive minerals of sedimentary rocks where it can be present in at least two forms: i) as a detrital component and ii) as an authigenic phase precipitated during diagenesis. Assessing the relative proportion of quartz of different origins is critical to understand the petrophysical and mechanical properties of mudstones and their distribution in sedimentary basins and ultimately to plan cost-effective exploration and production strategies.

Focusing on samples of post mature, organic-rich Marcellus shale we developed an analytical workflow combining high-resolution scanning electron microscopy (SEM), quantitative trace element analysis and hyperspectral cathodoluminescence (CL) at sub-micron spatial resolution to demonstrate that quartz occurs in a dominant detrital component and a volumetrically less abundant authigenic fraction. The latter includes minute pore filling, euhedral overgrowths on detrital quartz grains and agglutinated foraminifera amounting to ca. 5 % of the analyzed area in SEM-CL images. Detrital and diagenetic quartz are distinguished based on i) the intensity and spectral characteristics of their cathodoluminescence signal and ii) trace element contents, specifically aluminum content being consistently higher in diagenetic quartz and reaching values in the thousands of ppm (e.g. Figure 1).

The analytical data, supported by mass-balance arguments, suggests the main source of diagenetic silica in the Marcellus shale is locally derived, the high content of Al in the diagenetic quartz is inferred to result from late diagenetic reactions (advanced illitization of detrital smectite and albitization of K-feldspar) releasing Al and Si in the pore fluid that are then precipitated in the form of quartz overgrowth.

In this context, the abundance of authigenic quartz and its porosity reduction capacity are limited by temperature conditions the sediments are exposed to and the preceding mechanical compaction reducing the available pore space. Authigenic quartz occurs is engulfed by porous pyrobitumen, indicating that the organic matter migrated into a palaeo-inter-crystalline pore network after the onset of quartz overgrowth. It can be therefore be inferred that migration of organic matter postdates and potentially limits the extent of quartz cementation in the Marcellus shale by displacing the pore water and reducing the pore space necessary for precipitation of authigenic quartz.

This study provides a first documentation of in-situ trace element composition of diagenetic quartz in organic-rich mudstone shale and provides a microstructural framework to understand geochemical fluid-rock interactions and their effects on the petrophysical properties of organic rich sediments during burial and thermal maturation.

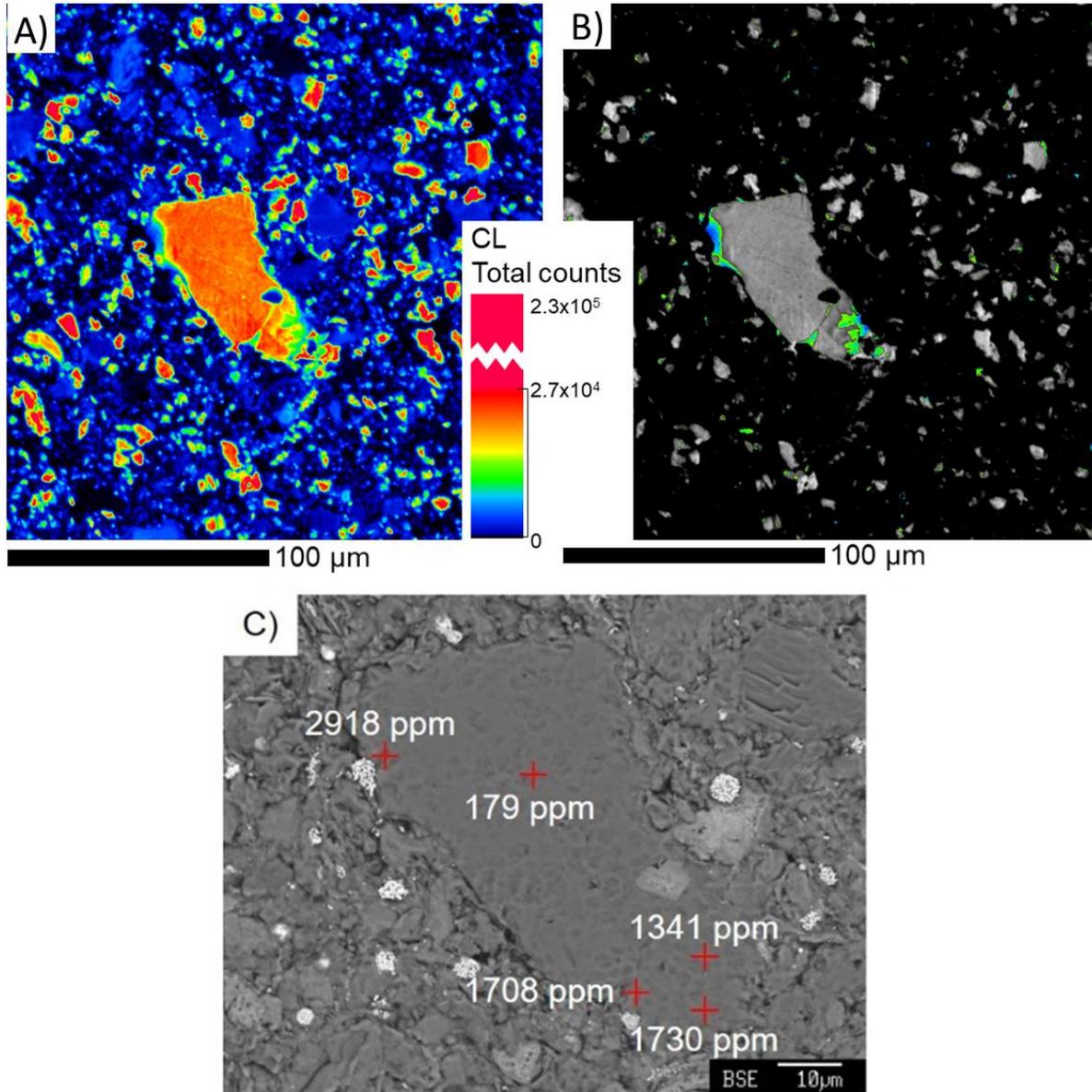


Figure 1 A) Panchromatic cathodoluminescence (CL) image showing a relatively large quartz grain with heterogeneous CL colour: orange to red on the inside and blue to green along the rims. B) Distribution of authigenic quartz (blue to green colours) around and within detrital quartz grains. C) Back-scattered electron image of the quartz grain shown in A and B with overlay of trace element quantification points (red crosses), also shown are the measured values (in ppm) of aluminium in quartz. Note the contrast in aluminium levels between the centre of the detrital grain and the diagenetic overgrowths.

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