

Quantitative Compositional Stage Mapping and Cluster Analysis

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Research on rock samples uses both wavelength-dispersive (WDS) and energy-dispersive spectrometry (EDS) for fixed-beam stage mapping on the electron microprobe (EPMA). Recent efforts center on fully quantitative compositional mapping [1]. Conventional EPMA spot analysis uses probe current of 1 – 25 nA and count times of 10's of sec for major elements, and 50 – 250 nA with times up to 1000 sec for trace elements. These ranges of 1 – 250 nA and 10 – 1000 sec represent a total dose range of 10 – 250000 nA-sec. Quantitative EPMA map runs typically use 50 – 250 nA to compensate for shorter count times of 10 – 50 msec per pixel, representing a dose range of 0.5 – 12.5 nA-sec, several orders of magnitude lower than for spot analysis. This nA-sec metric is useful for evaluating the precision and detection limit for conventional vs. map analysis, and reveals that mapping measurements have significantly lower precision and therefore higher detection limits. Here the precision and accuracy dependence on mapping conditions, and the effect on downstream clustering operations is discussed.

A comb-layered xenolith is used for demonstrating these parameters, and contains multiple layers of mm-length dendritic plagioclase, sector-zoned Ca-pyroxene, euhedral to granular olivine, and quenched basaltic glass (Fig. 1). Spot analyses of the core and rim of the Ca-pyroxene sector zones shows the zones are defined by elements Mg, Al, Ti, and Cr (Table 1). Analyses at conventional conditions of 750 nA-sec have lower standard deviation of all elements, compared to those at mapping conditions of 1 nA-sec. The core and rim compositions, clearly discriminated at 750 nA-sec, are not statistically different at the mapping condition of 1 nA-sec for trace elements Ti and Cr, which at 3 standard deviations overlap in composition. This illustrates that spot analyses are required to intelligently select measurement conditions for mapping runs, as a dose greater than 1 nA-sec is required. Quantitative EPMA stage maps were acquired on a 1-inch round polished section using a 2.25 mm square map area at 800 x 800 pixels, using procedures described previously [1]. Three map runs were conducted at 15kV with a “fast run” acquired at 1 nA-sec (100 nA and 10 msec per pixel), a “slow run” at 10 nA-sec (200 nA and 50 msec), and a reference run at 37.5 nA-sec (250 nA and 150 msec). The Cr concentrations and detection limit for the sector zones are shown in Fig. 2A and B. In order to statistically detect Cr above background at 0.3 – 0.5 wt. %, it is necessary to acquire maps at dose \geq 10 nA-sec. The analytical sensitivity is also critical for discriminating the two sector zone compositions.

Cluster analysis is ideal for exploring the compositional variations in rock samples. The result of supervised cluster analysis using ENVI is illustrated in Fig. 2 C, where Al vs. Mg data exhibits a trend between core and rim compositions [2]. Pixels gradational to the two end points represent both sampling at zone boundaries and the dispersion of measurements due to counting statistics. In n-element space the clear separation of the sector zones requires counting statistics which discriminate the sectors for major and trace elements at better than 1 standard deviation. Results from unsupervised cluster analysis using the Fiji Xlib plug-in are shown in Fig. 2 D for the 10 nA-sec mapping run, where the sectors are clearly and accurately discriminated [3]. Cluster analysis using the 1 nA-sec run data exhibits poor discrimination of core vs. rim, resulting in pixels assigned to a single cluster. In summary, an evaluation of phase chemistry, counting statistics, and required calculated dose is important for cluster analysis. This approach can be

used for both EDS and WDS-based compositional mapping and illustrates the complementary nature of each.

References

- [1] P Carpenter, T Hahn, *Microsc. Microanal.* **23** (Suppl 1) 2017.
 [2] ENVI software, <http://www.harrisgeospatial.com>
 [3] Fiji Xlib plug-in, <http://imagej.net/Xlib>

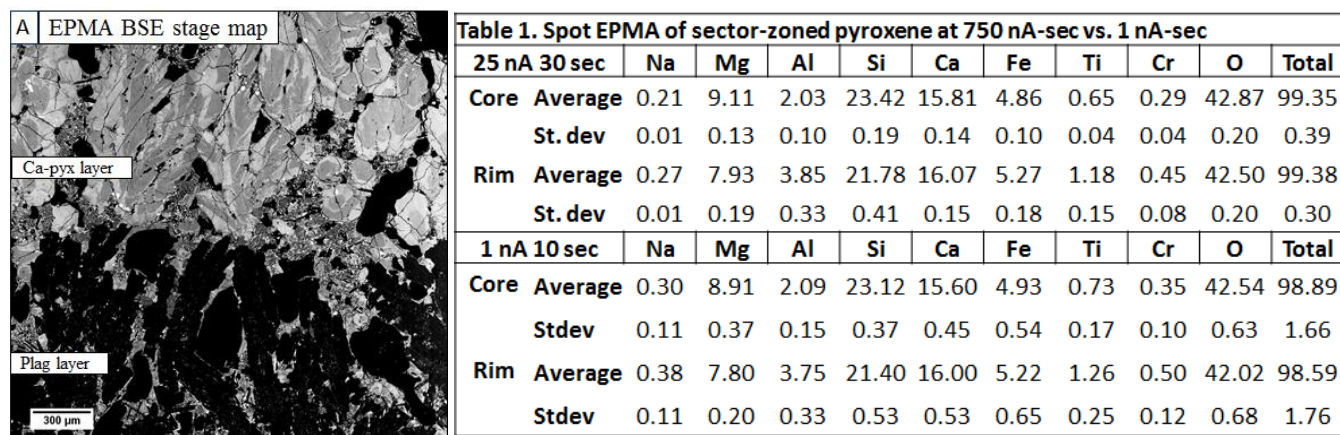


Figure 1. (A) BSE stage map with upper sector-zoned Ca-pyroxene layer. **Table 1.** EPMA spot analyses of pyroxene core and rim, obtained at 25 nA, 30 sec (750 nA-sec) vs. 1 nA, 10 sec (1 nA-sec).

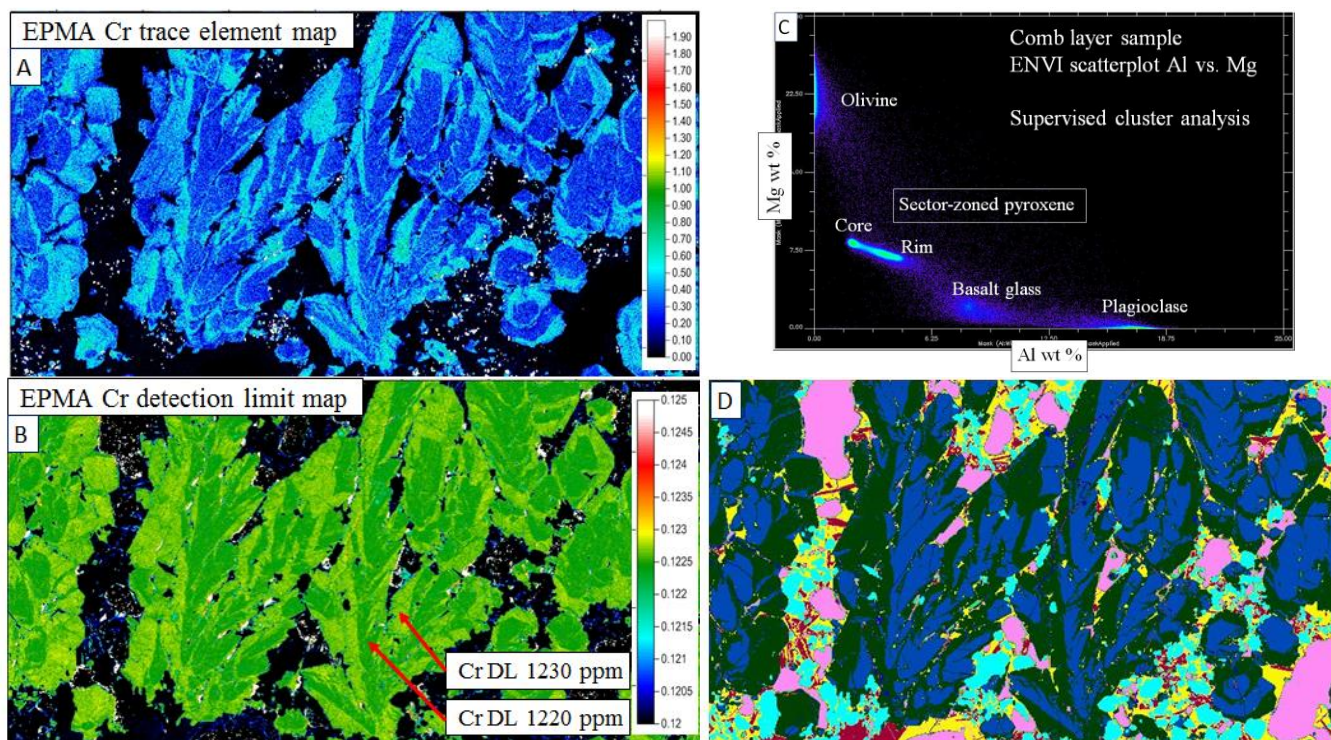


Figure 2. (A) Quantitative Cr concentration map of sector-zoned Ca-pyroxene, acquired at 250 nA, 150 msec (37.5 nA-sec). (B) Cr detection limit map. (C) ENVI supervised cluster analysis and core vs. rim discrimination. (D) Fiji Xlib unsupervised cluster analysis on map run using 10 nA-sec dose (colors are cluster classification).