Fast and precise quantitative compositional mapping and its application to the Nové Dvory ultra-high pressure eclogite.

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Rocks often show chemical inhomogeneity in various scales owing to layers, veins, and so on. To evaluate such inhomogeneity, quantitative compositional mapping would be a powerful tool, since ordinary EPMA quantitative analysis takes large time (> 1 min/spot). Lanari et al. (2014) established a fast analytical technique by combining qualitative mapping (> 100 msec/px) and quantitative analyses (ca. 20 spots/phase). To make quantitative map data, they performed mode analysis for the map data by k-means cluster analysis, calibrated the relationship between map intensity and real concentration for each element of each phase, and applied the calibration to the modal composition. Their technique saves great time, but the analysis still takes long time for the large samples due to recommended analytical conditions of spatial resolution (< 10 μm pixel size) and dwell time (> 100 msec/px) for the mapping, e.g. 55 hours for the area of 100mm^2. This study aims to shrink analysis time further.

The mapping time is proportional to the spatial resolution in O(N^2) and the dwell time in O(N). Thus, decreasing the spatial resolutions saves more time than decreasing the dwell time. Yet, it increases the amount of pixels containing multi-phases, especially when a mapping area contains fine-grained minerals. This problem can be solved by modifying methods of (a) clustering, (b) estimating calibration curves, and (c) applying calibration curves after Lanari et al. (2014).

(a) The soft-clustering is preferred to the hard-clustering (k-means) because it explains proportion of phases in pixels. Since compositional distribution of the map data can be approximated by mixtures of Poisson distributions, this study employed the mixture-Poisson-distribution-model clustering.

(b) Calibration curves for trace components of phases, i.e. elements not included in the stoichiometry, tend to contain large errors. For such components, calibration curves are determined by using all phases.

(c) Composition of a pixel containing various phases is obtained from a weighted mean of concentrations estimated by the calibration curves of each phase, which is weighted by the modal composition of the pixel.

The newly developed technique is applied to the Nové Dvory eclogite, containing pyroxene-rich layer (Layer-P) and garnet-rich layer (Layer-G) in mm-scales. Garnet (Grt) between these layers has Mg-richer core (ca. Fe23Mg56Ca21) than Grt in Layer-G (c.a. Fe30Mg32Ca38), and both Grt show similar rim compositions (ca. Fe28Mg44Ca28). The core compositions probably reflect the inhomogeneity of the protolith (Yasumoto & Hirajima, 2015), though the cause of the inhomogeneity is unclear. Compositions of these layers are estimated by our technique. Qualitative mapping is done in the area of 10 mm * 33 mm with 20 μm pixel size and 120 msec dwell time, taking ca. 55 hours. Total wt% of Layer-P is improved by the technique of ours (97 wt%) than Lanari et al. (2014) (91 wt%), while that of Layer-G are comparable (97 wt% and 98 wt%, respectively), probably because fine-grained texture of Layer-P compared to Layer-G.

The estimated compositions show Mg-Cr-rich (XMg = Mg/(Mg+Fe) = 0.79; Cr2O3 = 0.14 wt%) for Layer-P and vice versa for Layer-G (XMg = 0.64; Cr2O3 = 0.07 wt%). One possible explanation is that Layer-P and G are metamorphosed from pyroxene-rich and plagioclase-rich layers of gabbro, respectively. However, a large difference in XMg of Layer-P and G is unlikely for the gabbro-origin. Cr content of both layer and Mg/Fe ratio of Layer-P are also unlikely high (e.g. general gabbro: Cr2O3 < 0.01 wt%; XMg ≈0.65). Field occurrence shows dominance of Layer-G with minor Layer-P, indicating that Layer-P was crystallized from pyroxenite melt intruded to gabbroic host (Layer-G), and Layer-G partially reacted with the melt. This idea

is supported by presence of pyroxenite melt intrusions (XMg = 0.80-0.91; Cr2O3 = 0.2-1.7 wt%) in peridotite which hosts the study eclogite (Svojtka et al., 2016).

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