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The kinetic effect induced by variable cooling rate on the crystal-chemistry of spinel in basaltic systems revealed by EPMA mapping

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Abstract

The crystal-chemical variations of spinels grown as a function of cooling rate ($\Delta T/\Delta t$) were analyzed via X-ray electron-microprobe (EPMA) maps. Maps were collected serially by using a fixed distance. Spinels solidified from a tholeiitic MOR basaltic liquid (B_{100}) cooled at cooling rates ($\Delta T/\Delta t$) of 1, 7, 60, and 180 °C/h, between 1300 and 800 °C and at ambient P and f_{O_2}. As $\Delta T/\Delta t$ increases, the amount of spinel is invariably <5 area% and its size decreases. Compared to the previous data set collected by common single and selected EPMA analytical points (112 analyses), the kinetic effects induced by $\Delta T/\Delta t$ are here quantitatively captured by a large number of analyses (2052).

The TiO_2, Al_2O_3, MgO, and FeO^{tot} show large compositional variations at low cooling rates (from 1 to 60 °C/h), and only the average TiO_2 concentration shows a well-defined trend as a function of $\Delta T/\Delta t$. However, calculated average cation amounts (apfu) unveil quantitative kinetic effects. When $\Delta T/\Delta t$ increases (from 1 to 180 °C/h), only Ti^{4+} shows a linear decreasing trend, whereas the other major Al^{3+}, Fe^{3+}, Fe^{2+}, and Mg^{2+} cations alone are scattered. Conversely, the sums of trivalent ($Al^{3+}+Fe^{3+}$) and divalent ($Mg^{2+}+Fe^{2+}$) cations quantitatively capture the effect of the $\Delta T/\Delta t$. These new outcomes could be the base of novel geospeedometers with significant implications in volcanology, geophysics, and material sciences in regard to silicate melt rheology on Earth. They should be extended to high-pressure, hydrated, and low oxygen fugacity conditions. Furthermore, the analytical approach used here to capture kinetic effects on spinel growth and compositions can be also applied to other crystalline phases grown from silicate liquids.

Keywords: Spinel, crystal-chemistry, kinetic, cooling rate ($\Delta T/\Delta t$), EPMA maps