

Phase transformations and reaction kinetics during the temperature-induced oxidation of natural olivine

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ABSTRACT

This work describes the sequence of transformations and their reaction kinetics during the oxidation of olivine in air at high temperature. A natural olivine sample from the layered series of the Ivrea-Verbano igneous complex (Western Alps, Italy) was heated in the temperature range 25–1300 °C in air and investigated by in situ, real time powder X-ray diffraction (PXRD). The evolution of the peaks (measured integrated intensities) was followed in non-isothermal conditions using variable heating rates ($b = 20, 22, 25, 27,$ and 30 °C/min). The total time of the experiments ranged from about 256 ($b = 30$ °C/min) to 277 ($b = 20$ °C/min) min including the time for the data collections. An additional isothermal run was performed at 800 °C. The analysis of the kinetic data was attempted with the use of different equations including the classical Avrami theory for solid-state reactions. The kinetic results were confirmed by independent experimental data from electron microscopy (SEM, TEM).

In the transformation sequence, hematite appears at about 600 °C producing amorphous segregations of silica that later recombine with forsterite to form pyroxene. Hematite is stable up to 1130 °C where it is transformed into magnetite. The rate limiting step for the formation of hematite is a two-dimensional diffusion with constant or decelerating nucleation rate and apparent activation energy of 15 kcal/mol. The concentration of Fe³⁺ in Fe-rich regions favors the heterogeneous nucleation of hematite, which may take place on existing defects or at the grain boundaries with impurity phases such as serpentine. At 1130 °C, magnetite is formed at the expenses of hematite, with a contracting volume interface-controlled reaction in two or three dimensions with an apparent activation energy of 30–31 kcal/mol. The hematite to magnetite transformation is direct, without a metastable amorphous intermediate. It is described by the “shrinking core model,” with the formation of a magnetite outer layer at the surface of the hematite particles that proceeds toward the core of the reacting hematite by diffusion of the oxygen throughout the newly formed magnetite layer. Its rate is limited by the advancement of the reaction front. The rate-limiting step for the formation of pyroxene is two-dimensional diffusion with decelerating nucleation rate with an apparent activation energy of 29 kcal/mol.