



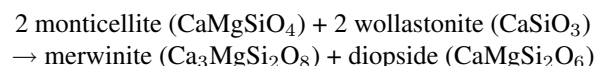
Diffusion-controlled growth of bimineralic merwinite - diopside reaction rims between wollastonite - monticellite interfaces

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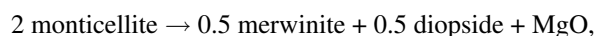
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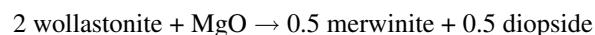
At temperatures of 800 °C to 900 °C and 1.2 GPa, monticellite and wollastonite react to form merwinite and diopside after the reaction:



We synthesized bimineralic merwinite - diopside reaction rims along the interfaces of cylindric crystals of monticellite and wollastonite. The samples were loaded in a platinum capsule and annealed at 800 °C to 900 °C and 1.2 GPa in a piston cylinder apparatus for 5 to 65 hours. Natural CaF₂ was used as pressure medium and the charges were nominally dry. In all experiments, a single layer consisting of bimineralic aggregates of merwinite and diopside was produced in about equal molar amounts. Time series revealed that rim growth is parabolic, indicating that the reaction kinetics is controlled by component diffusion. SEM analysis of the microstructure showed that the original monticellite-wollastonite interface is located in the centre of the reaction rim. This implies that rim growth primarily occurred by transfer of the mobile component MgO from the rim-monticellite interface to the rim-wollastonite interface. The bulk reaction is thus divided into two half reactions occurring at the two reaction fronts. At the rim-monticellite interface the reaction is:



and at the rim-wollastonite interface, it is:



Using the model of Abart et al. (2009), the effective diffusion coefficients D_{MgO} at 800 °C are estimated at $1.55 \cdot 10^{-16} \pm 2.18 \cdot 10^{-17} \text{ m}^2/\text{s}$, and at 900 °C at $2.46 \cdot 10^{-16} \pm 3.45 \cdot 10^{-17} \text{ m}^2/\text{s}$. This yields an activation energy of $E_a = 45.6 \pm 16.4 \text{ kJ/mol}$ and a pre-exponential factor $\log D_0 = -13.59 \pm 1.26$ for the Arrhenius relations to describe the temperature-dependent effective diffusivity of the MgO component in the bimineralic aggregate. IR-spectra revealed distinctive OH-contents in the nominally dry phases monticellite and wollastonite after the experiments, which had not been present in the reactants. Obviously, some hydrogen released by the natural, water-containing CaF₂ pressure medium diffused into the capsule, thus producing traces of water inside. The presence of minute amounts of water may strongly enhance the kinetics of the reaction. In fact, if completely waterfree Al₂O₃-powder is used as pressure medium, no significant reaction occurred, and accordingly, reactants remain OH-free. An Al₂O₃-layer of 3 mm thickness between the capsule and the CaF₂ surrounding delays the onset of rim growth for about one hour. However, once initiated, the reaction progress is the same in instantaneous and delayed reactions.

References: Abart R., Petrishcheva E., Fischer F.D., Svoboda J. (2009), Thermodynamic model for diffusion controlled reaction rim growth in a binary system: application to the forsterite-enstatite-quartz system, American Journal of Science, Vol. 309, pp. 114-131