

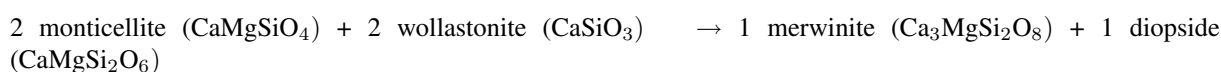


The effect of water on the internal organization of bimineralic diopside-merwinite reaction rims

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Bimineralic diopside + merwinite reaction rims were produced in piston-cylinder experiments along the interfaces of cylindrically shaped single crystals of monticellite and wollastonite at 900 °C, 1.2 GPa and run durations between 5 and 65 h according to the reaction:



IR-spectra of periclase that was also loaded into the capsule show OH-defects after the experiments that initially were not present. This indicates that H₂O, released by natural, water-containing CaF₂ used as solid pressure medium, diffused into the Pt-capsule during the experiment. The amount of water in the capsule increased with increasing run duration, as indicated by an increase of the OH-defect concentration in periclase with time.

During the first stage of rim growth, the reaction products form a cellular-microstructure with palisade shaped merwinite and diopside microcrystals alternating at regular intervals, whereby the long axes of the grains are oriented about normal to the original monticellite-wollastonite interface (cellular type). At longer run durations, diopside and merwinite start to segregate into layers with diopside accumulating in the centre and merwinite at both sides of the reaction rim (multilayer type). After 65 h, segregation of the product phases is almost complete and a triple layer rim with the sequence mtc / mw / di / mw / di is produced.

The two kinetic regimes where the multilayer and the cellular rim types are preferred are separated in the λ versus L_{CaO}/L_{MgO} parameter space by the condition

$$\lambda = \sqrt{\frac{24\delta H m}{q \frac{L_{CaO}}{L_{MgO}} K}}$$

where δ is the width of the reaction fronts at either side of the rim, H the rim thickness, and q a scaling factor for the grain boundary area fraction (i.e., the GB-density normal to the flux); m and K are constants calculated from the molar volumes and the stoichiometric coefficients. Calculation of this model for different grain widths and mobility ratios of the components show that, if all process parameters are kept constant, rim growth starts with a multilayer structure and is replaced by a cellular microstructure at later growth stages. The reverse evolution is observed, which is only possible by a significant change of the relative mobility ratios, where L_{CaO}/L_{MgO} is increasing from $\ll 1$ at short run durations to > 10 at long run durations. We interpret this effect as resulting from increasing water availability as reaction proceeds, forcing segregation of product phases from a cellular microstructure into monomineralic layers. The availability of traces of water does not only affect overall rim growth kinetics (Yund 1997), but also does change relative component mobilities and, consequently, the internal rim organization. This calls for rim growth experiments at controlled low water activities.

Yund RA (1997), Rates of grain boundary diffusion through enstatite and forsterite reaction rims: Contrib Min and Petrol 126: 224–236