*American Mineralogist, Volume 97, pages 38–51, 2012*

# The mechanism of thermal decomposition of dolomite: New insights from 2D-XRD and TEM analyses

**CARLOS RODRIGUEZ-NAVARRO,* KRZYSZTOF KUDLACZ, AND ENCARNACION RUIZ-AGUDO**

Department Mineralogía y Petrología, Universidad de Granada, Fuentenueva s/n, 18071 Granada, Spain

## ABSTRACT

Despite being studied for more than one century, no consensus exists regarding the ultimate mechanism(s) of the thermal decomposition of dolomite [$(CaMg(CO_3)_2$]. To shed light on such a reaction, dolomite single crystals were calcined in air between 500 and 1000 °C, and in situ, in a TEM (high vacuum), following irradiation with the electron beam. In situ TEM shows that the decomposition involves the initial formation of a face centered cubic mixed oxide ($Ca_{0.5}Mg_{0.5}O$) with reactant/product orientation relationships $[001]_{dolomite}//<111>_{oxide}$, $<\bar{4}41>_{dolomite}//<100>_{oxide}$, $\{11\bar{2}0\}_{dolomite}//\{110\}_{oxide}$, $\{11\bar{2}8\}_{dolomite}//\{110\}_{oxide}$ and $\{10\bar{1}4\}_{dolomite}$^$\{100\}_{oxide}$~12°. This phase undergoes de-mixing into oriented crystals of Mg-poor CaO and Ca-poor MgO solid solutions upon long-term e-beam exposure. Ex situ TEM, XRD, 2D-XRD, and FESEM analyses show the formation of porous pseudomorphs made up of oxide nanocrystals with similar parent/product orientation relationships, but with limited Ca/Mg substitution (up to ~9–11%) due to de-mixing (spinodal decomposition) of the metastable (Ca,Mg)O precursor. High ion diffusivity at $T > 500$ °C (ex situ experiments) favors the formation of pure CaO and MgO crystals during coarsening via oriented aggregation and sintering. These results show that the thermal decomposition of dolomite is topotactic and independent of $pCO_2$. Formation of Mg-calcite nanocrystals (up to ~8 mol% Mg) during the so-called "half decomposition" is observed at 650–750 °C. This transient phase formed topotactically following the reaction of CaO nanocystals (solid solution with ~9 mol% Mg) with $CO_2$ present in the air and/or released upon further dolomite decomposition. With increasing *T*, Mg-calcite transformed into calcite, which underwent decomposition following the known topotactic relationship: $\{10\bar{1}4\}_{calcite}//\{110\}_{CaO}$ and $<\bar{4}41>_{calcite}//<110>_{CaO}$. These observations solve the long standing controversy on the mechanism of the "two-stage" decomposition of dolomite, which assumed the direct formation of calcite during the so-called "half decomposition."

**Keywords:** Dolomite, lime, periclase, thermal decomposition, half decomposition, (Ca,Mg)O mixed oxide, 2D-XRD, TEM-SAED, topotactic