

**KINETICS OF COMPOSITIONAL AND STRUCTURAL MATURATION OF DOLOMITE AND MAGNESITE (150 - 220 °C) – AN EXPERIMENTAL APPROACH**Kell Duivestein, I.<sup>1</sup>, Baldermann, A.<sup>1</sup>, Mavromatis, V.<sup>1,2</sup> & Dietzel, M.<sup>1</sup><sup>1</sup>Institute of Applied Geosciences, Graz University of Technology, Rechbauerstrasse 12, A-8010 Graz, Austria<sup>2</sup>Géosciences Environnement Toulouse (GET), CNRS, UMR5563, 14 Avenue Edouard Belin,

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Dolomite is an abundant Ca-Mg-carbonate phase throughout ancient carbonate platforms, however, is scarce throughout modern carbonate-depositional environments and seemingly impossible to precipitate experimentally at ambient temperature; this summarizes a geological enigma commonly referred to as “the dolomite problem”. A similar “problem” exists for the much less abundant Mg-carbonate mineral magnesite ( $\text{MgCO}_3$ ), which is often associated with dolomite. Natural and synthetic dolomites exhibit significant differences in their compositional and structural properties of stoichiometry (i.e., the relative abundance of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  occupying cation sites within the crystal lattice) and cation ordering degree (i.e., “COD”: a measure of the distribution of the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions within the crystal lattice). The physicochemical parameters controlling these properties along with the absence of or the presence and abundance of magnesite precipitation, however, are still poorly understood.

In this study, dolomite and magnesite were synthesized in batch reactors at temperatures of 150 °C, 180 °C and 220 °C by reacting  $\text{CaCO}_3$  (aragonite or calcite) with an artificial solution containing  $\text{MgCl}_2$  and  $\text{NaHCO}_3$  over a 360-day reaction period. The obtained results on the maturation of the stoichiometry of dolomite and magnesite and on the COD of dolomite indicate that the formation of ideal, stoichiometric and well ordered, dolomite and of stoichiometric magnesite follow a ripening process and proceed through dissolution and re-precipitation of a sequence of intermediate phases, such as Ca-magnesite, huntite, very-high-Mg-calcite and disordered dolomite. The occurrence and metastability of the precursor phases formed are dependent on temperature and the  $\text{CaCO}_3$  phase being altered. Temperature is the major rate-controlling parameter of the maturation of dolomite and magnesite stoichiometry and COD of dolomite, corroborating results from prior experiments and natural deposits.

From our data, we determined kinetic rates for the stoichiometric ripening of magnesite and dolomite and for the COD of dolomite for the first time using a first-order reaction kinetic approach. The kinetics increase with temperature following the linear Arrhenius equation, in turn allowing for activation energies of the respective processes to be determined (44.0, 57.4 and 9.3  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively). Interestingly, we found the reaction rate for magnesite stoichiometric ripening is approximately one third of that for dolomite regardless of the temperature, carbonate alkalinity or  $\text{CaCO}_3$  phase used for reaction. Extrapolation of the obtained dolomitization rates indicates that about 1.4 and 6.8 Myr are required to approach ideal dolomite at 50 °C and 25 °C, respectively, explaining the large absence of ordered dolomite in modern sedimentary successions. The present dataset provides new insights into dolomitization pathways and rates and contributes to a better understanding of the wide range of stoichiometries and COD values of dolomite and its evolution versus magnesite observed in the geological record and in laboratory studies.