

## **The temperature and compositional dependence of disordering in Fe-bearing dolomites**

**ETTORE FRANZOLIN,<sup>1</sup> MARCO MERLINI,<sup>2</sup> STEFANO POLI,<sup>2,\*</sup> AND MAX W. SCHMIDT<sup>1</sup>**

<sup>1</sup>Institute of Geochemistry and Petrology, ETH Zurich, 8092 Zurich, Switzerland

<sup>2</sup>Dipartimento di Scienze della Terra, Università degli Studi di Milano, 20133 Milano, Italy

### **ABSTRACT**

Dolomite occurs in a wide range of rock compositions, from peridotites to mafic eclogites and metasediments, up to mantle depths of more than 200 km. At low-temperatures dolomite is ordered ( $R\bar{3}$ ), but transforms with increasing temperature into a disordered higher symmetry structure ( $R\bar{3}c$ ).

To understand the thermodynamics of dolomite, we have investigated temperature, pressure, kinetics, and compositional dependence of the disordering process in Fe-bearing dolomites. To avoid quench effects, in situ X-ray powder diffraction experiments were performed at 300–1350 K and 2.6–4.2 GPa. The long-range order parameter  $s$ , quantifying the degree of ordering, has been determined using structural parameters from Rietveld refinement and the normalized peak area variation of superstructure Bragg peaks characterizing structural ordering/disordering. Time-series experiments show that disordering occurs in 20–30 min at 858 K and in a few minutes at temperatures  $\geq 999$  K. The order parameter decreases with increasing temperature and  $X_{\text{Fe}}$ . Complete disorder is attained in dolomite at  $\sim 1240$  K, 100–220 K lower than previously thought, and in an ankeritic-dolomite<sub>s.s.</sub> with an  $X_{\text{Fe}}$  of 0.43 at temperatures as low as  $\sim 900$  K. The temperature-composition dependence of the disorder process was fitted with a phenomenological approach intermediate between the Landau theory and the Bragg-Williams model and predicts complete disorder in pure ankerite to occur already at  $\sim 470$  K.

The relatively low-temperature experiments of this study also constrain the breakdown of dolomite to aragonite+Fe-bearing magnesite at 4.2 GPa to temperature lower than  $\sim 800$  K favoring an almost straight Clapeyron-slope for this disputed reaction.

**Keywords:** Carbonates, high pressure, synchrotron, dolomite