



Cation disordering in dolomite: theoretical and experimental approach.

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Cation distribution over crystallographic sites strongly affects the physical-chemical properties of dolomite and the geological processes connected with them, i.e. fluid reservoir properties, fault weakening, and dolomite stability under subduction conditions.

A wide group of scientists has studied disordering in dolomite as mixing of Mg in Ca crystal structure sites. Through both in-situ [1] and ex-situ [2] experiments a temperature range of about 1200-1400K has been assigned to the disordering process. Variations in stacking sequence, which are a consequence of the cation (dis)ordering processes, have been experimentally documented both in thermally disordered stoichiometric samples [3] and in non-stoichiometric dolomites as a result of cation ordering processes [4].

In order to study disordering evolution in dolomite as well as the thermodynamic stability of disordered dolomite structures, we have used both theoretical and experimental approaches.

First principles total-energy calculations of different stoichiometric disordered dolomite structures were performed at the hybrid Hartree-Fock/Density-Functional-Theory (HF/DFT) level [5] using a development version of CRYSTAL software [6]. The WC1LYP Hamiltonian [7] was used for the calculations, which includes a non local exact Hartree-Fock exchange contribution. Both substitutional and polytypic defects in cation distribution were observed, and quantum-statistical calculations based on the theoretically calculated energies allowed us to obtain the probability of specific disordered configurations at given temperatures.

In particular, results from ab-initio calculations showed that at room temperature a fully-ordered dolomite is the most favoured configuration. As the temperature (T) increases, the probability of the ordered configuration decreases and at $T \sim 460\text{K}$, the probabilities related to the ordered and stacking-disordered dolomites become the same. Polytypic dolomite is the most favoured configuration at higher temperatures. We can preliminarily state that defects in the cation distribution in dolomite seem energetically stable not only at high temperature conditions.

In the experimental waypart, we performed single crystal X-ray diffraction on ordered and thermally treated dolomite samples. Heating processes were carried out using a piston cylinder apparatus under a pressure of 3GPa and temperatures of about 1273K, 1373K and 1473K. While X-ray powder diffraction data indicated a disordering occurring during heat treatment, i.e. through an increase of the intensity ratio (006)/(015) [8], single crystal X-ray refinements with the {1120} twinning law showed evidence of twinning structures instead of the main mechanism of disordering. A successful structure refinement, obtained only with the assumption of the twinning, suggested a high density of twin domains with internally highly ordered structure.

We therefore conclude that polymorphic cation substitution in dolomite seems not to be the main disordering process which affects the mineral.

Studies are in progress in order to connect theoretical and experimental results, developing calculations on different supercell sizes as well as further crystal structure refinements of different sets of thermally treated dolomites and careful inspection for possible superstructure reflections.

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