

## DOLOMITE STABILITY AS A FUNCTION OF P, T, $p\text{CO}_2$ AND CATION ORDERING. APPLICATIONS TO NATURAL PROCESSES

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### INTRODUCTION

Carbonates are among the main sedimentary rock-forming minerals and primary components of both igneous carbonatite deposits and metacarbonates covering 7% of the land surface. Dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] is the most abundant double carbonate in nature and its stability field extends from sedimentary up to high temperature (HT)-high pressure (HP) conditions as shown by phase equilibria experiments (Biellmann & Gillet, 1992; Luth, 2001; Zhu & Ogasawara, 2002; Buob *et al.*, 2006; Hammouda *et al.*, 2011).

Many geological processes are influenced by the physical and chemical features of dolomite. The physical evolution of reservoirs for fluids (water, oil and gasses) strongly depends on the thermodynamic and kinetic properties of the dolomite dissolution process, which is itself dependent on the mineralogical and chemical characteristics of the mineral together with the pressure, temperature and  $\text{CO}_2$  partial pressure ( $p\text{CO}_2$ ) conditions. Dedolomitization, *i.e.* the dissolution of dolomite accompanied by the precipitation of calcite, has recently attracted interest because of its importance in the fault weakening processes as induced by incongruent dissolution of dolomite (Collettini *et al.*, 2009). It is also well known that dolomite contributes to the transportation of carbon into the deep upper mantle by subducting lithospheric plates (Kerrick & Connolly, 2001; Zhu & Ogasawara, 2002; Hammouda *et al.*, 2011). The mineral was found to be stable at mantle conditions down to approximately 250 km ( $\sim 8$  GPa) depending on the rate of subduction as well as on the crystallographic characteristics of the mineral, *i.e.* the dolomite stability field is contracted as cation distribution approaches a random configuration (Hammouda *et al.*, 2011 and references therein).

The aim of this study was to improve knowledge on cation distribution over crystallographic sites in dolomite structure by focusing on back-reaction processes and quenching characteristics of cation disordering. Additionally, cation distribution in dolomite structure was studied as influencing the physical and thermodynamic properties of the mineral in natural systems. Two different systems were studied; the first characterized by high pressure/temperature (P/T) conditions and the second by low P/T conditions. In particular, the baric behaviour of dolomite under HP conditions and the dissolution behaviour of dolomite in aqueous solution were analysed in order to clarify the effect of cation disordering with respect to the other external parameters (P, T and  $p\text{CO}_2$ ).

### CATION DISTRIBUTION OVER DOLOMITE CRYSTALLOGRAPHIC SITES – EXPERIMENTAL STUDY

The influence of the temperature on cation distribution in dolomite structure has commonly been attributed to intra-layer type disordering by *in situ* X-ray powder diffraction experiments (Luth, 2001; Antao *et al.*, 2004; Hammouda *et al.*, 2011).

Cation distribution in dolomite structure was studied in the present work as a consequence of *ex situ* thermal treatments. This approach allowed us, on the one hand, to determine the ordering state of *ex situ* annealed dolomites and then to clarify the quenchability/unquenchability of thermally induced disordering in dolomite. On the other hand, to investigate the back-reaction processes which occur during the quench from high temperature to room conditions. Additionally, *ex situ* thermal treatments allowed to reproduce observations on natural geological materials by avoiding *in situ* effects.

The dolomite collections of the Natural History Museums of London and Florence were analysed and a fully-ordered stoichiometric dolomite sample from Eugui (Spain) was chosen for the study. Thermal treatments

were carried out in collaboration with Bayerisches Geoinstitut (University of Bayreuth, Germany). Experiments were carried out by means of the piston cylinder techniques at 1000 °C, 1100 °C and 1200 °C and 3 GPa pressure.

The thermally treated dolomites were analysed by both single crystal and powder X-ray diffraction analysis (SC-XRD and XRPD) in collaboration with the Natural History Museum of Denmark (University of Copenhagen, Denmark). These two techniques were compared as analytical techniques for cation distribution study in dolomite structure.

#### *X-ray powder diffraction analysis*

XRPD data were refined using TOPAS software (Cheary & Coelho, 1992; Cheary *et al.*, 2004) and the ordering state was quantified dealing with three main approaches: the order parameter  $s$  (Helgeson *et al.*, 1978) (values from 1 to 0 respectively for a fully ordered and a fully disordered dolomite), the  $z$  coordinate for C atom ( $z_C$  approaches 1/4 special position typical of the calcite-like space group as disorder is approached) and the intensity of the ordering-type reflection (Hammouda *et al.*, 2011 and references therein) (015, 015 and 021  $b$ -type reflections intensities decrease as disorder increases). All these investigated parameters showed increasing disordering conditions with the annealing temperature as it is shown in Table 1. However, a broadened peak profile shape was observed for the  $b$ -type reflections of the thermally treated samples as much as  $T$  increases. This observation posed questions regarding a probable underestimation of disordering conditions for the annealed samples.

Table 1 - Selected results from Rietveld refinement of X-ray powder diffraction data.

ID	$a$	$c$	$V$	$x_{Ca,A}$	$s$	$\sqrt{I_{005}/I_{006}}$	$R_p$	$R_{wp}$	Goof	$R_{Bragg}$
EU	4.80777(3)	16.0091(1)	320.468(2)	0.972(5)	0.94(1)	1.03	0.0761	0.1096	2.931	0.0639
EU1000	4.80692(5)	16.0254(2)	320.681(4)	0.909(5)	0.82(1)	0.75	0.0814	0.1044	2.162	0.0521
EU1100	4.80557(4)	16.0339(2)	320.671(3)	0.876(5)	0.75(1)	0.79	0.0707	0.0944	2.162	0.0356
EU1200	4.80521(5)	16.0246(2)	320.437(4)	0.752(7)	0.50(1)	0.68	0.0898	0.1222	2.789	0.0385

Cell dimensions (expressed in Å), Ca occupancy on A site ( $x_{Ca,A}$ ) and the order parameter  $s$  are listed together with the square root of intensity ratio  $I_{015}/I_{006}$  (Hammouda *et al.*, 2011 and references therein) (015 and 006 are a  $b$ -type reflection and a common reflection respectively). The raw integrated intensities were calculated by individual profile fitting of the 015 and 006 reflections by the same TOPAS software. Standard reliability factors for Rietveld refinements are listed for all the samples. EU1000, EU1100 and EU1200 mean Eugui samples annealed at 1000, 1100 and 1200 °C, respectively.

#### *Single crystal X-ray diffraction analysis*

As regards the refinement of single crystal data, this was performed by means of SHELX-97 program (Sheldrick, 2008). Results are listed in Table 2. Differently from XRPD, the order parameter  $s$  as well as  $z_C$  atomic position quantified pretty high ordering conditions for all the samples. However, successful structure refinements of samples annealed over 1100 °C came just from the assumption of twinning. Twinned structures, characterized by high internal order, were refined and the ratio of the two twinned components was 25:75 and 48:52 for 1100 °C and 1200 °C thermally treated samples respectively. Thus, at 1200 °C, the expected temperature for complete cation disordering (Reeder & Wenk, 1983; Antao *et al.*, 2004), the two twinned components were found to have approximately 1:1 proportion.

Table 2 - Unit cell parameters (expressed in Å) from single crystal X-ray diffraction analysis and selected results of data refinement.

ID	EU	EU1000	EU1100	EU1200
<b>Cell parameters</b>				
<i>a</i>	4.811(1)	4.827(1)	4.816(1)	4.817(2)
<i>c</i>	16.035(4)	16.003(6)	16.079(4)	16.040(7)
<i>V</i>	321.4(1)	323.9(1)	322.92(9)	322.3(1)
No. refl. used	410	412	452	421
<b>Crystal structure refinements</b>				
$x_{Ca,A}$	0.979(6)	0.952(9)	0.927(8)	0.91(1)
<i>s</i>	0.96(2)	0.90(2)	0.85(2)	0.82(3)
% <sub>twinning</sub>	0	0	25	48
No. param.	20	20	21	21
$R_1$	0.017	0.034	0.037	0.042
No. refl. [ $I > 4\sigma(I)$ ]	144	150	152	154
$wR_2$	0.0441	0.0919	0.0111	0.1275
Goof	1.100	1.131	1.169	1.162
hp	0.17	0.60	0.45	0.58
dh	-0.27	-0.52	-0.60	-0.50

Cell dimensions are listed together with the number of reflections used for unit cell determinations. Ca occupancy on its own site ( $x_{Ca,A}$ ) and disorder parameter *s* are listed together with the twinning percentage within the crystal structure. The number of refined parameters (No. param.) and the accordance parameters, such as  $R_1$ , the number of reflections used for calculating  $R_1$  (No. refl. [ $I > 4\sigma(I)$ ]),  $wR_2$ , goodness of fit (Goof) and highest peak (hp) and deepest hole (dh) in final difference Fourier map, are also listed.

A comparison between ordering conditions refined from XRPD and SC-XRD data shows that disordering is overestimated by the former with respect to the latter. However, the complex structural state refined from single crystal data for the annealed samples, *i.e.* twinned domains internally characterized by high order degrees, is not detectable by powder diffraction data refinements. Therefore, powder diffraction analysis was considered to be an inefficient method to study cation distribution over crystallographic sites in *ex situ* experiments since it may overestimate disordering conditions and cover cation distributions other than the intra-layer type disordering.

As regards the origin of those twinned structures, they may be either a probable quenching derived occurrence or a thermally induced one. In order to clarify the influence of T in producing either twinned domains or intra-layered disordered cationic configurations, experiments were coupled with a theoretical study.

#### CATION DISTRIBUTION OVER DOLOMITE CRYSTALLOGRAPHIC SITES – THEORETICAL STUDY

*Ab initio* calculations were performed by using the CRYSTAL09 code (Dovesi *et al.*, 2009) in collaboration with the University of Turin in order to analyse the disordering mechanism which drives the non-ideal cation distribution over dolomite crystallographic sites and to analyse the thermodynamic stability of differently disordered dolomite structures. Disorder was modelled in fully-stoichiometric dolomite structures by

using a supercell approach. As a compromise between computational strategy/resources and supercell dimensions, calculations were performed at the static level on a conventional cell (CC) and a  $2 \times 2 \times 2$  supercell (SC) built from the primitive cell. Both intra- and inter-layer type disordering were modelled and disordering conditions were quantified by introducing some parameters: the weighted  $s$  parameter ( $s_w$ ) referring to the intra-layer type disorder and the frequency of stacking disorder  $f$  together with the distance of stacking inversion  $d$  as regards the inter-layer type. These parameters were summarized in a total ordering parameter ( $s_t$ ) which takes into account both disordering types and has values between 1 (fully order) and 0 (fully-disorder). In addition, a configurational disorder parameter ( $s_c$ ) was proposed in order to introduce, in disordering quantification, the existence probability for each configuration as a function of temperature  $T$ .

Total static energy calculations showed that ordered dolomite is always the most stable configuration at the static point level being the energy differences between ordered and disordered configurations lower than  $-7$  kJ/mol referring to the primitive cell.

The configurational entropy contribution was taken into account by means of a quantum-statistical thermodynamic approach. Fig. 1 shows results of quantum-statistical thermodynamic analysis. At a very low temperature ( $T < 298$  K), fully-ordered dolomite configuration is the most stable one. At  $T$  of approximately 300 K, SC8 becomes the most probable configuration ( $s_t = 0.75$ ) and at  $T \sim 750$  K, the probability paths cross again and SC4895 becomes the most probable one ( $s_t = 0.50$ ). However, it needs to be pointed out that these temperatures are largely lower than 1200 K, the temperature limit at which the first appearance of disorder was experimentally found (Hammouda *et al.*, 2011), likely due to kinetic reasons. In Fig. 2, the crystal structures of the three most probable configurations are shown.

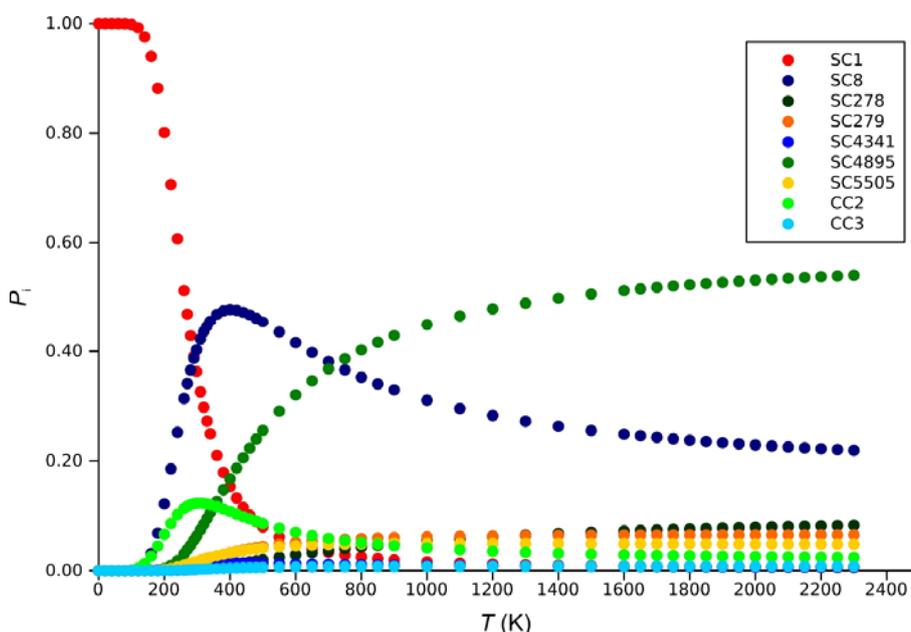


Fig. 1 - Occurrence probability related to each simulated configuration as dependent on temperature. The different atomic configurations are listed in terms of the supercell size (either CC or SC) and a number as it is assigned by CRYSTAL09 (Dovesi *et al.*, 2009).

The theoretical study of cation distribution in dolomite structure shows that an intra-layered type disordering is the main process which drives the thermally induced cation distribution over crystallographic sites. Coupling experiments and calculations, two main observations can be made:

1. The driving mechanism of the thermally induced cation distribution over crystallographic sites was found to be an intra-layer type disordering. Since *in situ* XRPD crystal structure refinements find intra-layering

disordered dolomite structures at HT conditions (Antao *et al.*, 2004; Hammouda *et al.*, 2011), they are considered a reliable analysis of the *in situ* thermally induced cation distribution in dolomite structure.

2. The evidences of twinning domains coming out from *ex situ* SC-XRD imply reordering processes during the quench. Therefore, twin domains are hereby proposed as a witness to thermally induced intra-layer-type cation disordering. The fraction of twinning increases with T and the two twinned components result in almost the same fraction at 1200 °C when a complete disordering is expected. Moreover, twinning structures have already been observed in samples annealed at 1100 °C, so that the order/disorder transition is inferred to start below 1100 °C.

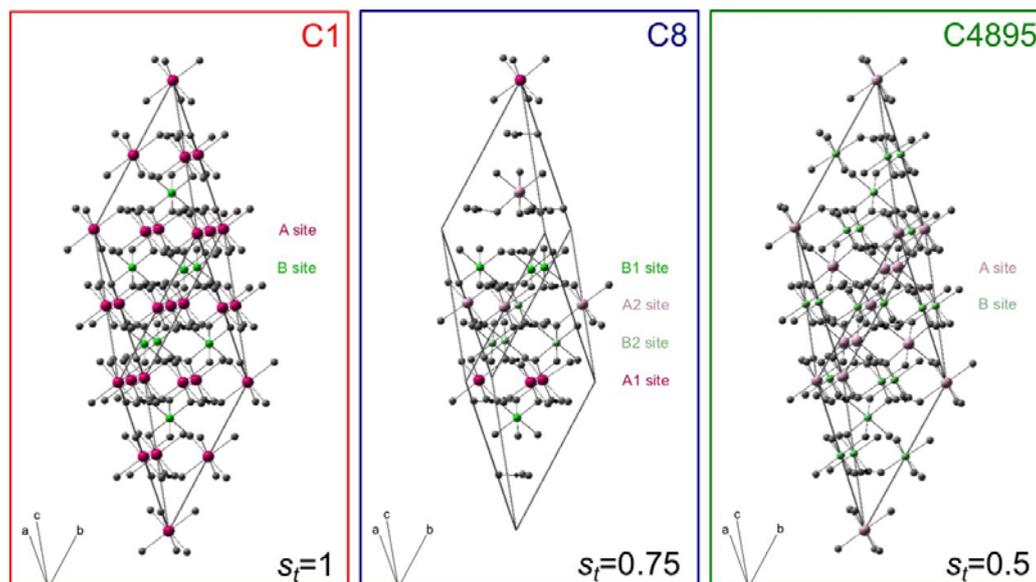


Fig. 2 - SC1, SC8 and SC4895 cation configurations in dolomite structures. Dark and light pink refer to respectively a fully calcium occupied and a disordered Ca sites. Dark and light green refer to respectively fully magnesium occupied and disordered Mg sites. Gray and black colours are about to O and C. Dark and light coloured labels are respectively related to fully either Ca or Mg occupied sites and intra-layered disordered sites.  $s_i$  parameters related to each configuration are also shown.

## DOLOMITE STABILITY IN NATURAL SYSTEMS - HIGH P/T SYSTEM

The effect of the cation distribution on dolomite stability under high pressure conditions was again analysed by both experimental and theoretical approaches.

### *Experimental approach*

Natural and thermally treated samples coming from the Eugui complex (Spain) were used for a study of dolomite behaviour under HP-HT conditions. Three single crystal XRD experiments were performed at the ID09A beamline at the European Synchrotron Radiation Facility (ESRF) (Grenoble, France) by using a diamond anvil cell (DAC) apparatus. Pressure was varied in the range 0-16 GPa and temperature was fixed at 25 °C (room temperature experiments) and 300 °C (HT conditions). The first two experiments were carried out on fully-stoichiometric and ordered dolomite samples from Eugui (Spain) at HP (EU-HP) and HP-HT (EU-HP-HT) conditions. The third experiment was carried out under HP conditions on a sample thermally treated at 1200 °C and previously characterized (EU1200-HP) (*cf.* Cation distribution over dolomite crystallographic sites study - experimental study).

Variation of normalised unit cell parameters to the room pressure values with respect to  $P$  showed that, as  $P$  increases, the compressibility of  $c$  axes is higher as compared to  $a$ . As regards the influence of  $P$  on the cell volume variation, the Equation of States (EoS) of natural and *ex situ* annealed samples were determined by fitting the  $P$ - $V$  data with a second order Birch-Murnaghan (B-M) equation of state (Birch, 1952). Fig. 3 shows the variation of cell volumes, normalised to the room pressure value, with  $P$ . Volume compressibility was found to increase as a consequence of both high temperature conditions (*in situ* annealing) and *ex situ* thermal treatment.  $K_0$  changes from 94.3(7) GPa for fully-ordered dolomite at room temperature to 91(1) GPa and 85(2) GPa as *ex situ* and *in situ* thermal treatments are respectively applied. Therefore, it is possible to state that HT conditions (*in situ* annealing) increase dolomite compressibility showing a similar but enhanced effect as compared to *ex situ* thermal treatment (Fig. 3).

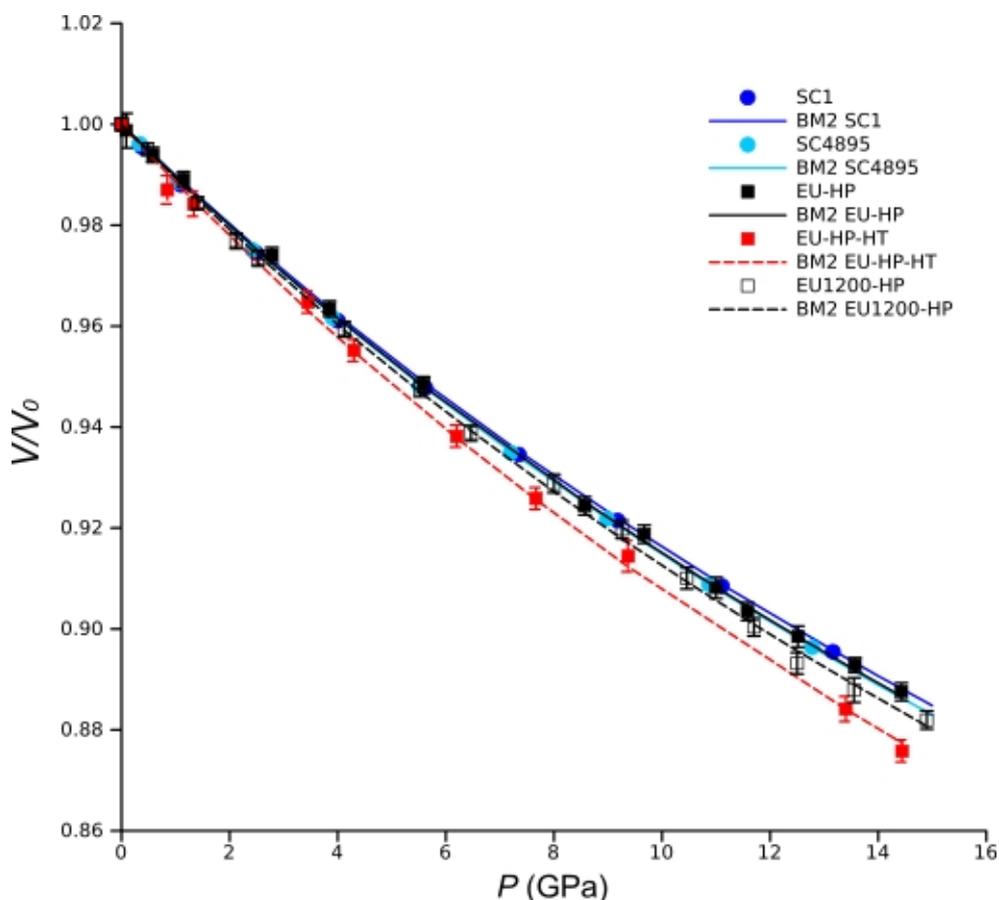


Fig. 3 -  $V/V_0$  -  $P$  plot of theoretical (dark and light blue) and experimental (black and red) data. Symbols and lines are observed data and second order B-M EoS fitting (BM2) respectively.

#### Theoretical approach

Since the *ex situ* annealed samples were found to be formed by twinned structures (*cfr.* Cation distribution over dolomite crystallographic sites study - experimental study), the fully-intra-layer type disordering influence on high pressure behaviour of dolomite was studied by means of *ab initio* calculations. Total static energy calculations were performed by using the above mentioned computational strategy. The study was carried out on both a fully ordered dolomite crystal structure and an intra-layering disordered configuration previously modelled (*cfr.* Cation distribution over dolomite crystallographic sites study – experimental study). Volume cell variations were operated and energy optimization was performed at each optimized geometry. The

correspondent P range lies from 0 to 13 GPa. Pressure-Volume data were fitted by a 2<sup>nd</sup>-order Birch-Murnaghan Equation of State (Birch, 1952) (Fig. 3). Bulk moduli were calculated and they count 95.9(4) GPa and 93.9(3) GPa for the fully ordered and the inter-layering disordered configurations respectively. So that, a higher volume compressibility for the disordered configuration was observed with respect to the ordered one.

A strong anisotropy on the compressibility of *a* and *c* axes was also observed and *c/a* compressibility ratio approaches again 3:1.

Three main results arise from the dolomite stability study under HP-HT conditions:

1. The *c/a* axial compressibility ratio is approximately 3:1 for fully-ordered as well as disordered and twinned dolomites;
2. A bulk modulus of 94.3(7) GPa was experimentally found for fully-ordered dolomite at room temperature as in agreement with data from Ross & Reeder (1992);
3. T and non-ordered cation distributions in dolomite structure were found to increase the volume compressibility of the mineral. However, temperature is shown to have the strongest effect on dolomite compressibility with respect to cation disordering.

#### DOLOMITE STABILITY IN NATURAL SYSTEMS - LOW P/T SYSTEM

In the present work, the influence of cation disorder on the solubility of dolomite was studied with respect to T, *p*CO<sub>2</sub> and rock composition (hereafter *external parameters*). A water/rock interaction laboratory study at equilibrium conditions was carried out. The analytical study was divided into two steps: *external parameters* influenced experiments and cation distribution influenced experiments.

##### *External parameters influenced experiments*

A set of dissolution experiments over a *p*CO<sub>2</sub> range from atmospheric conditions up to 30 bar and a T range between 50 and 250 °C was carried out using a compact lab reactor in collaboration with the IGG-CNR of Florence in order to investigate the influence of those parameters on the dissolution reaction of dolomite. Starting material was a powdered mixture (calcite, dolomite, gypsum, fluorite, quartz) simulating a commonly known geothermal reservoir. The cationic and anionic composition of the output solutions was analysed by using flame atomic absorption spectroscopy and ionic chromatography respectively. Results showed that [Ca]/[Mg] ratio in solution decreases as temperature increases. Regarding the CO<sub>2</sub> partial pressure, the greater the temperature the more *p*CO<sub>2</sub> acts in increasing the [Ca]/[Mg] ratio. By those observations we can speculate that, at high T conditions, the enhancement of the sulphate dissolution reaction (confirmed by the increment of SO<sub>4</sub>/HCO<sub>3</sub> ratio with T) and the consequent precipitation of calcite cause an enhancement in dolomite dissolution progress, *i.e.* decrease of [Ca]/[Mg] values with T increase.

##### *Cation distribution influenced experiments*

Two dissolution experiments were performed at the University of Perugia at room conditions on a natural and an *ex situ* thermally treated dolomite samples (1200 °C and 2.5 GPa) in order to clarify the effect of the cation distribution over crystallographic sites on the dolomite dissolution reaction. Solution analysis results show that *ex situ* thermal treatment, namely the twinning occurrence in dolomite structure, enhances dolomite solubility in aqueous solution. However, in the presence of a multiphase host rock system, temperature and CO<sub>2</sub> partial pressure have the highest influence on the dolomite dissolution reaction progress.

Summarizing results from the study of dolomite solubility:

1. At low T conditions, *p*CO<sub>2</sub> takes a leading role which reflects on an enhancement of the dolomite dissolution progress, *i.e.* [Mg] increases as *p*CO<sub>2</sub> increases;
2. At increasing T conditions, the enhancement of both gypsum dissolution and calcite back-reaction precipitation allow further dolomite dissolution which reflects on increasing [Mg] in solution;

3. The thermally treated sample is more soluble than the fully-ordered one.

## CONCLUSIONS

Two main conclusions can be made referring to the study of cation distribution over dolomite crystallographic sites:

1. Single crystal and powder data gave contrasting results. A twinned domain structure was observed by SC-XRD for the annealed samples whereas it was not detectable by XRPD analysis which systematically underrated  $s$  parameter. Thus, X-ray powder diffraction analysis does not seem to be the best way to study the cation distribution over crystallographic sites in the dolomite structure, at least concerning *ex situ* experiments.

2. Theoretical calculations showed that the intra-layered type disordering is the driving process for the thermally induced non-ideal Ca-Mg distribution over dolomite crystallographic sites. Therefore, the twinned structures refined in the *ex situ* single crystal X-ray diffraction study were found to arise from a reordering process which took place during the quench. The un-quenchability of thermally induced disordering in dolomite, as proposed by Reeder & Wenk (1983), can be confirmed.

As regards the study of dolomite stability in natural systems:

1. The dolomite behaviour under HP conditions is influenced by cation distribution over crystallographic sites. In fact, the twinned structure as well as the intra-layered-type disordered structure analysed by means of theoretical calculations become more compressible than the ordered one with increasing pressure. However, increasing temperature conditions showed the strongest effect in increasing the dolomite compressibility with  $P$ . Additionally, a strong compressional anisotropy was found in the direction of  $a$  and  $c$  axes, *i.e.*  $c/a$  axial compressibility ratio was found to be approximately 3:1.

2. The *ex situ* thermally treated dolomite showed a higher dissolution progress than the ordered one. However, in the presence of a multiphase host rock system, temperature and  $p\text{CO}_2$  were shown to have the highest influence on the dolomite dissolution reaction progress.

Further experiences on theoretical study of cation ordering in minerals were provided by studying the effect of clustering/ordering on the ferropericlase [(Mg,Fe)O] thermodynamic stability under high pressure conditions in the frame of LLP Erasmus Placement program at Bayerisches Geoinstitut (University of Bayreuth, Germany).

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