

Article

The Effect of Stoichiometry, Mg-Ca Distribution, and Iron, Manganese, and Zinc Impurities on the Dolomite Order Degree: A Theoretical Study

Yuliya Zvir ¹, Carlos Pimentel ^{2,*} and Carlos M. Pina ^{1,3,*}

¹ Departamento de Mineralogía y Petrología, Universidad Complutense de Madrid, E-28040 Madrid, Spain; yzvir@ucm.es

² Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), E-18100 Armilla, Granada, Spain

³ Instituto de Geociencias (UCM-CSIC), E-28040 Madrid, Spain

* Correspondence: c.pimentel@csic.es (C.P.); cmpina@geo.ucm.es (C.M.P.)

Abstract: The determination of the degree of Mg-Ca order in the dolomite structure is crucial to better understand the process or processes leading to the formation of this mineral in nature. $I_{01.5}/I_{11.0}$ intensity ratios in the X-ray powder diffractograms are frequently measured to quantify dolomite cation order in dolomites. However, the intensity of diffraction peaks can be affected by factors other than the Mg-Ca distribution in the dolomite structure. The most relevant among these factors are (i) deviations from the ideal dolomite stoichiometry, and (ii) the partial substitution of Mg and Ca atoms by Fe, Mn, and Zn impurities. Using the VESTA software, we have constructed crystal structures and calculated $I_{01.5}/I_{11.0}$ ratios for dolomites with Mg:Ca ratios ranging from 0.5 to 1.5, and with Fe, Mn, and Zn contents up to 30%. Our results show that both deviations from dolomite ideal stoichiometry and the presence of impurities in its structure lead to a significant decrease in $I_{01.5}/I_{11.0}$ intensity ratios, an effect which must be considered when cation orders of natural dolomites from different origins are compared.

Keywords: dolomite; carbonate minerals; cation ordering; intensity ratios; cation impurities

Citation: Zvir, Y.; Pimentel, C.; Pina, C.M. The Effect of Stoichiometry, Mg-Ca Distribution, and Iron, Manganese and Zinc Impurities on the Dolomite Order Degree: A Theoretical Study. *Minerals* **2021**, *11*, 702. <https://doi.org/10.3390/min11070702>

Academic Editor: Natale Perchiazzi

Received: 14 May 2021

Accepted: 24 June 2021

Published: 29 June 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Dolomite, $\text{CaMg}(\text{CO}_3)_2$, is an abundant carbonate mineral with a structure characterized by a highly ordered alternation of magnesium and calcium layers along the *c* axis. However, at temperatures below ~ 100 °C, the formation of dolomites with such a high cation order cannot occur by direct precipitation from aqueous solutions, but it requires a Mg-Ca ordering process or processes after first crystallisation [1–3]. The investigation of both the mechanisms and kinetics of dolomite ordering process in nature first requires to accurately quantify the degree of Mg-Ca order within the dolomite structure. Since the dolomite structural order depends on the distribution of Mg and Ca cations in their corresponding crystallographic positions, the following order parameter can be defined:

$$s = 2X_{Mg} - 1, \quad (1)$$

where X_{Mg} is the occupancy factor of Mg atoms in the magnesium sublattice in the dolomite structure [4–7].

Although the s order parameter is suitable to describe cation order in dolomite, its direct experimental determination is not possible. However, given that changes in the X_{Mg} in the dolomite structure have a clear effect on diffraction patterns [8], the degree of the cationic order of dolomites can be conveniently evaluated from X-ray powder diffractograms. One method to proceed is to calculate the ratio of the intensities of a selected ordering peak (i.e., a Bragg reflection which only appears in the dolomite diffractograms when Mg-rich and Ca-rich alternate along the dolomite c -axis) and the nearest non-ordering peak to the selected ordering peak (i.e., a dolomite Bragg reflection not related to the Mg-Ca order) [8–11]. Ordering peaks, also known as superstructure peaks or superstructure reflections, must fulfill the following condition: $h0.l$ and $0k.l$ with l odd (e.g., 00.3, 10.1, and 01.5 peaks) [12].

By far, the $I_{01.5}/I_{11.0}$ ratio is the most frequently intensity ratio used to quantify dolomite cation order (e.g., [9,10,13,14] and references therein). Using the $I_{01.5}/I_{11.0}$ ratio, researchers have not only characterized some natural dolomites, but also monitored crystallisation processes of dolomites under controlled experimental conditions [1,2,15]. Nevertheless, it is important to take into account that two main factors can affect $I_{01.5}/I_{11.0}$ ratios other than Ca-Mg distribution in dolomite structure: (i) the dolomite stoichiometry, i.e., deviations from Mg:Ca = 1 ratio, and (ii) the presence of impurities, which can partially substitute Mg atoms. Therefore, an adequate use of the $I_{01.5}/I_{11.0}$ ratio as dolomite order index requires to precisely quantify the effects of these factors on the intensities of dolomite diffraction peaks. Otherwise, the degree of cation order in the dolomite structure might be underestimated.

The aim of this paper is to provide a first insight into the effects of Mg-Ca distribution, slight deviations from ideal dolomite stoichiometry and chemical composition (i.e., dolomites with Mg or Ca excess, and with Fe, Mn, and Zn impurities) on the index most commonly used to quantify the degree of cation order in the structure of dolomite. Our results can be useful for future crystallochemical characterizations of natural and synthetic dolomites.

2. Calculation Procedure

Dolomite structures with different Mg-Ca distributions and Mg:Ca stoichiometries have been constructed and depicted using the VESTA software 3.5 [16]. In a number of cases, dolomite structures also included small amounts of iron, manganese, and zinc atoms as impurities. In these dolomites, these cation impurities were only added in the Mg-sites of stoichiometric dolomites, i.e., with $(Mg + M):Ca = 1$, where $M = Fe, Mn, \text{ or } Zn$. It is important to note here that the VESTA software does not use atomistic simulations or quantum-mechanical methods. Therefore, no optimization of the geometry of dolomite structures prior to the calculation of diffractograms was performed. Accordingly, the shifting of diffraction peaks was not calculated, and only changes in the intensities of these peaks were considered in this work.

Both dolomite and calcite structures were used as starting structures for calculations. Dolomite and calcite crystallographic data were taken from Miser et al. [17] and Maslen et al. [18], respectively (see Table 1). In the case of calcite, after generating all fractional coordinates of the atoms corresponding to the space group $R\bar{3}c$, the s.g. $P1$ was assigned while keeping all fractional coordinates unvaried. By doing that, magnesium atoms can be added in alternating layers to create a “dolomite structure” in which the cation disorder can be subsequently modified.

Table 1. Dolomite and calcite unit cell parameters and fractional coordinates from Miser et al. [17] and Maslen et al. [18], respectively.

	Dolomite	Calcite
$a = b$ (nm)	0.4811	0.4988
c (nm)	1.6047	1.7068
$\alpha = \beta$ ($^{\circ}$)	90	90
γ ($^{\circ}$)	120	120
s.g.	$R\bar{3}$	$R\bar{3}c$
Ca (x, y, z)	0, 0, 0	0, 0, 0
Mg (x, y, z)	0, 0, 0.5	-
C (x, y, z)	0, 0, 0.2430	0, 0, 0.25
O (x, y, z)	0.2476, 0.9650, 0.2441	0.257, 0, 0.25

Once dolomite structures with different Mg-Ca arrangements and impurity contents were constructed, diffractograms were calculated with the RIETAN-FP code [19] included in VESTA software [16]. Then, $I_{01.5}/I_{11.0}$ ratios were measured in the calculated diffractograms using a standard protocol that can be found elsewhere (e.g., [9,10,13,14,20,21]). This method consists in calculating the intensity $I_{01.5}/I_{11.0}$ ratios by measuring peak intensities in counts, and without conducting any previous treatment of the diffractograms (e.g., Rietveld method).

3. Results and Discussion

3.1. Stoichiometric Dolomites

Stoichiometric dolomites have a Mg:Ca ratio equal to unity. Therefore, the relative amount of Ca and Mg cations must be changed in the Mg and Ca crystallographic sites to generate variations in cation order within these stoichiometric dolomites (Figure 1). Thus, a maximum order is reached when both calcium and magnesium sites are fully occupied by the corresponding cation, i.e., magnesium in the Mg-site and calcium in the Ca-site, and, therefore, $X_{Mg} = 1$. In turn, the order degree reaches a minimum when both sites are occupied by 50% of magnesium cations and 50% of calcium cations, i.e., $X_{Mg} = 0.5$. Other occupancy factors of the Mg- and Ca-sites result in intermediate order degrees.

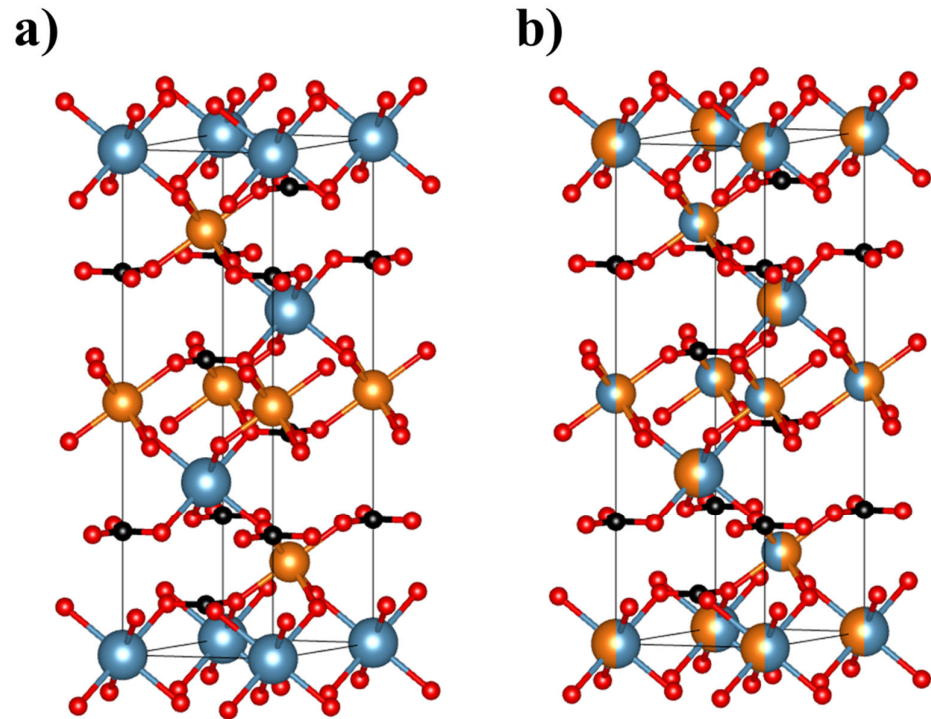


Figure 1. Structures of stoichiometric dolomite: (a) completely ordered: $X_{Mg} = 1$; (b) completely disordered: $X_{Mg} = 0.5$. The Ca^{2+} cations are depicted in blue, the Mg^{2+} in orange, and the CO_3^{2-} anionic groups in black (carbon atoms) and red (oxygen atoms). The Mg:Ca ratio in each site is represented by spherical sectors with radii proportional to occupancy factors.

Figure 2 shows the calculated diffractograms for both a fully ordered and a fully disordered stoichiometric dolomite structure. As can be seen in this figure, the intensities of superstructure peaks (i.e., diffraction peaks which result from cation order) are different. In principle, superstructure peaks in the diffractogram of a fully disordered dolomite should be absent. Nevertheless, in Figure 2b, superstructure peaks are still visible. This is because calculations shown in Figure 2 were performed using crystallographic data for a dolomite structure [17]. In the dolomite $R\bar{3}$ structure, the Ca- and Mg-sites are crystallographically distinct sites. As a consequence, diffraction peaks for superstructure planes remain even when the Mg-Ca distribution within them is random (i.e., $X_{Mg} = 0.5$). In a different way, when the calcite $R\bar{3}c$ structure is used for the calculations [18], both crystallographic sites are identical, and superstructure peaks vanish for $X_{Mg} = 0.5$ (see Figure S1 in the Supporting Information).

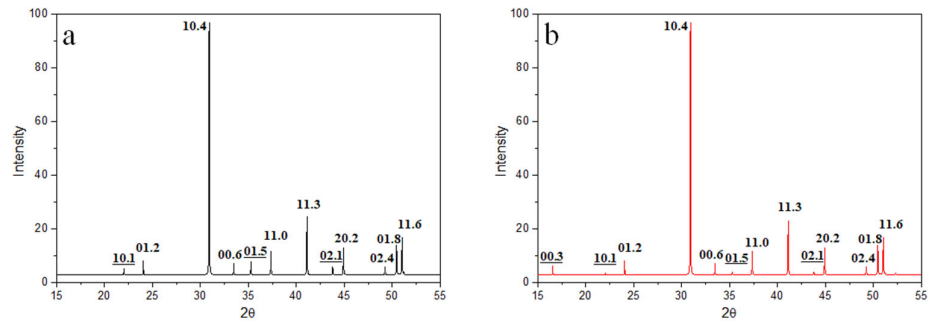


Figure 2. Diffraction patterns calculated with the RIETAN-FP code [19] for a stoichiometric dolomite structure [17]: (a) fully ordered: $x_{Mg} = 1$; (b) fully disordered: $x_{Mg} = 0.5$. In both diffraction patterns superstructure indexes appear underlined.

The results presented here were obtained by considering the structure of dolomite only. As explained in the introductory section, diffraction patterns of dolomites can show very low $I_{01.5}/I_{11.0}$ ratios, indicating a very low cation order [14,20]. However, the minimum order to distinguish between a dolomite and a VHMC, i.e., when its structure changes from an $R\bar{3}$ to an $R\bar{3}c$, has not yet been clearly defined. Taking this into account, we consider that a significant overestimation of the order indexes observed for a completely disordered dolomite will only occur for dolomites with an Mg mole fraction close to 0.5. Above that value, all dolomites will present a structure with $R\bar{3}$ space group and, therefore, superstructure peaks will be present in the diffraction patterns.

From diffraction patterns like those shown in Figure 2 and calculated for X_{Mg} ranging from 0.5 to 1.0, $I_{01.5}/I_{11.0}$ ratios were systematically measured. These intensity ratios were found to increase nonlinearly from 0.13 to 0.53 as the X_{Mg} increases (Figure 3a). Since intensity ratios were measured from diffraction patterns simulated using a dolomite structure [17], an $I_{01.5}/I_{11.0}$ value of 0.13 was obtained for a completely disordered dolomite (i.e., for $x_{Mg} = 0.5$). As explained above, this “residual order” for a fully disordered dolomite structure results from the symmetry constraints of the $R\bar{3}$ space group.

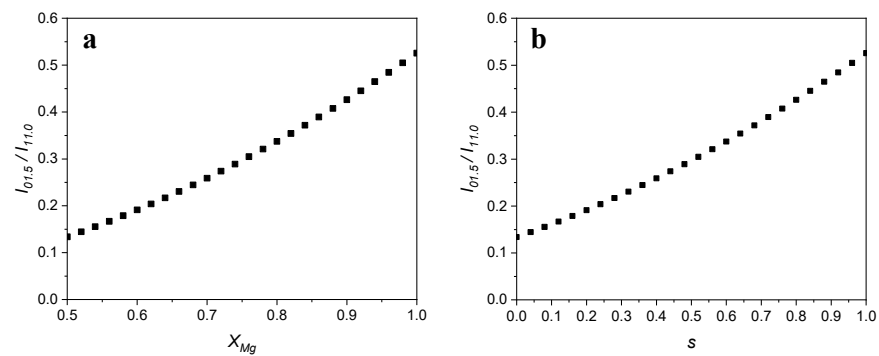


Figure 3. (a) $I_{01.5}/I_{11.0}$ ratio versus the molar fraction of Mg in the Mg-site, X_{Mg} , for a stoichiometric dolomite. (b) $I_{01.5}/I_{11.0}$ ratio versus order parameter, s .

When the distribution of Mg and Ca is varied in the structure of a stoichiometric dolomite, the changes in $I_{01.5}/I_{11.0}$ ratios can be also related to the order parameter, s , using Equation (1). Figure 3b shows the non-linear increase of $I_{01.5}/I_{11.0}$ ratio as the s parameter increases from $s = 0$ to $s = 1$. Noticeably, for the maximum value of the order parameter ($s = 1$), a superstructure/non-superstructure intensity ratio is not equal to one, as previously assumed in the analysis by Luth [5] of the Schultz-Güttler [11] method for quantifying the

cation degree of order in dolomites. From this assumption, Luth [5] concluded that measurements of dolomite superstructure/non-superstructure intensity ratios might lead to a systematic underestimation of the s parameter. Our calculations do not support this conclusion, but they instead indicate that a precise correlation between intensity ratios and s requires a previous calibration with the experimental dolomite diffractograms.

3.2. Non-Stoichiometric Dolomites

For the non-stoichiometric dolomites considered in this work, Mg:Ca ratios were varied from 0.5 to 1.5, i.e., their compositions were gradually changed from $\text{Ca}_{0.5}\text{Mg}_{1.5}(\text{CO}_3)_2$ to $\text{Ca}_{1.5}\text{Mg}_{0.5}(\text{CO}_3)_2$. Structurally, the cation in excess can fill its corresponding sites and a fraction of the sites of the minority cation (see Figure 4a), or alternatively, Mg:Ca ratios can vary in both cation sites, while keeping the same Mg:Ca ratio of the given stoichiometry (see Figure 4b). Dolomites of both types have been found in nature, i.e., dolomites with excess of Ca atoms which fill completely its own site and a fraction of the magnesium sites [22], and dolomites with an excess of Ca atoms which occupy both magnesium and calcium sites [23].

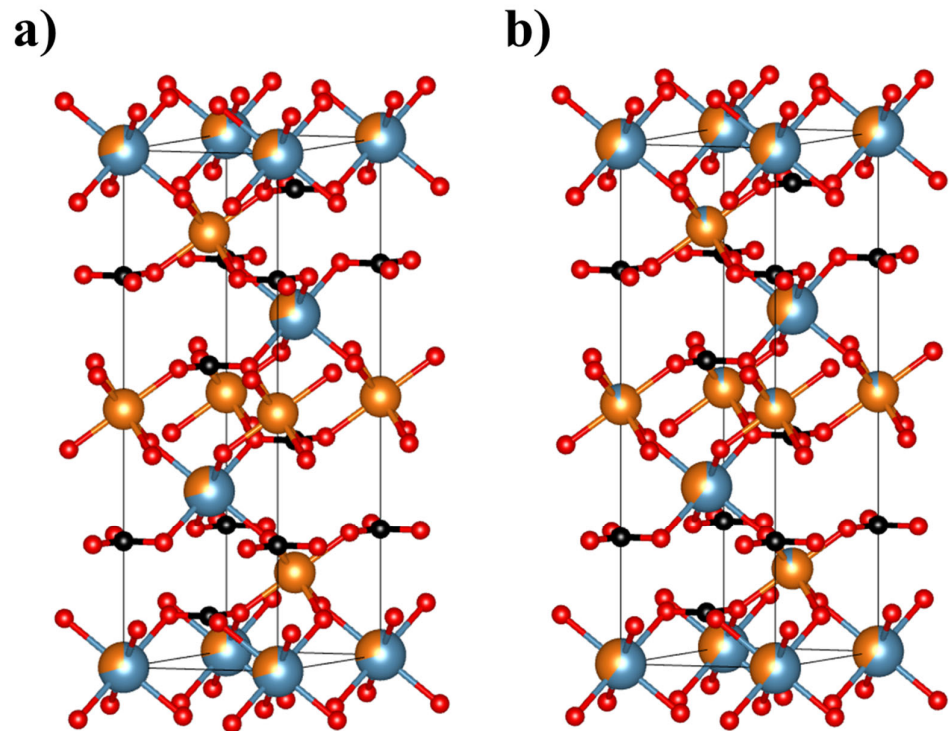


Figure 4. Non-stoichiometric dolomite structures: (a) a dolomite structure in which 100% of Mg-sites and 30% of Ca-sites are occupied by magnesium atoms, while only 70% of Ca-sites are occupied by calcium atoms; (b) a dolomite structure in which 90% of magnesium sites and 40% of calcium sites are occupied by magnesium atoms, while 60% of calcium sites and 10% of magnesium sites are occupied by calcium atoms. The Mg:Ca ratio in each site is represented by spherical sectors with radii proportional to occupancy factors. In both structures, the total Mg:Ca ratio is 1.3:0.7.

Figure 5a shows the variation of $I_{01.5}/I_{11.0}$ ratios in the diffractograms calculated for non-stoichiometric dolomites with x ranging from 0.5 to 1.5 in the $\text{Ca}_{2-x}\text{Mg}_x(\text{CO}_3)_2$ formula, and for which one of both cation sites is always fully occupied by the corresponding cation. As can be seen in this figure, deviations from the dolomite stoichiometry towards an

excess of calcium have a more pronounced effect on the $I_{01.5}/I_{11.0}$ ratios than in the case of an excess of magnesium in the dolomite structure. The reason for this asymmetry lies in the larger atomic scattering factor of calcium compared to that of magnesium. Thus, the intensity of the $I_{01.5}$ peak is more effectively reduced when calcium atoms increasingly occupy Mg-sites than in the case of magnesium atoms occupying Ca-sites. In other words, dolomite order quantified by $I_{01.5}/I_{11.0}$ ratios will be more underestimated for Ca-rich dolomites than for Mg-rich dolomites.

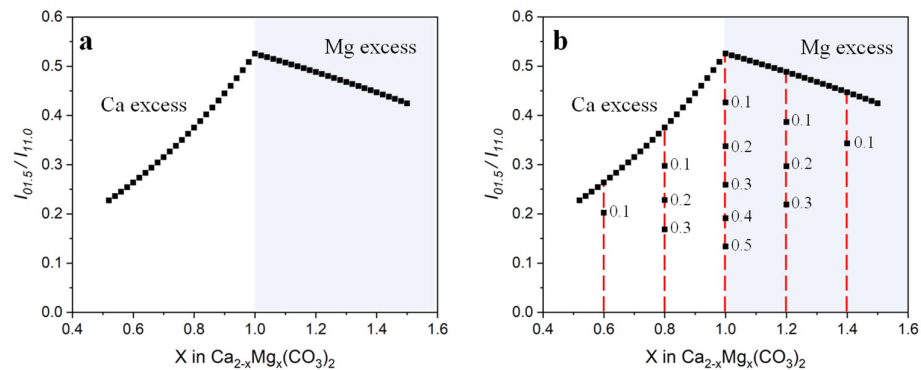


Figure 5. $I_{01.5}/I_{11.0}$ versus x in the range from $x = 0.5$ to $x = 1.5$ for non-stoichiometric dolomites with formula $\text{Ca}_{2-x}\text{Mg}_x(\text{CO}_3)_2$: (a) variation of $I_{01.5}/I_{11.0}$ by changing x in the dolomite formula while always maintaining Mg- or Ca-sites filled with the corresponding cation, as shown in Figure 5a; (b) variation of $I_{01.5}/I_{11.0}$ by changing Mg:Ca ratios in both Ca- and Mg-sites for a given x , as shown in Figure 5b. Numbers along the dashed vertical red lines indicate the molar fraction of the cation in excess in the site of the other cation.

For a given dolomite stoichiometry, $I_{01.5}/I_{11.0}$ ratios can be further reduced by allowing Mg and Ca atoms to occupy both sites in different ratios, i.e., by removing the previous constraint of filling first the layer corresponding to the atom in excess. Figure 5b illustrates the effect on the $I_{01.5}/I_{11.0}$ ratios when both the molar ratio of Mg atoms in Ca-sites (Mg excess region in the plot) and the molar ratio of Ca atoms in Mg-sites (Ca excess region in the plot) increase. As in the case shown in Figure 5a, the decrease in $I_{01.5}/I_{11.0}$ ratios is more pronounced in the Ca-excess region of the plot.

The results shown in Figure 5a,b demonstrate that, in the case of non-stoichiometric dolomites, the degree of order directly derived from in $I_{01.5}/I_{11.0}$ ratios will be always underestimated, i.e., the experimental value of $I_{01.5}/I_{11.0}$ of a non-stoichiometric dolomite is always lower than that of a stoichiometric dolomite. Therefore, in order to precisely quantify the order of a dolomite crystal it is necessary to know first the maximum theoretical $I_{01.5}/I_{11.0}$ ratio for its particular stoichiometry and Ca-Mg distribution in the two cation sites.

3.3. Dolomites With Iron, Manganese, and Zinc Impurities

Frequently, natural dolomites contain variable amounts of Fe, Mn, and Zn impurities in their structures. It is obvious that the presence of these impurities will have an effect on dolomite cation order and, therefore, on $I_{01.5}/I_{11.0}$ ratios. Although cation impurities can be accommodated in both Ca- and Mg-sites, in this work, we will only analyse this effect in the case of the partial substitution of Mg^{2+} by Fe^{2+} , Mn^{2+} , or Zn^{2+} cations in the Mg-site of dolomites. Moreover, we have assumed that these dolomites fulfill the condition: $(\text{Mg}+\text{M}):\text{Ca} = 1$ (where $\text{M} = \text{Fe}, \text{Mn}, \text{or Zn}$ atoms). Therefore, the general formula of the dolomites considered is $\text{Ca}(\text{Mg}_{1-x}\text{M}_x)(\text{CO}_3)_2$. As an example, Figure 6 shows a dolomite structure in which a 20% of the Mg-sites are occupied by Fe^{2+} .

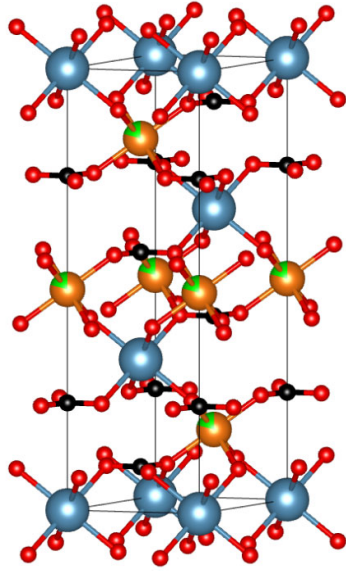


Figure 6. Dolomite structure with 20% of iron impurities in the magnesium sites. Ca^{2+} cations are shown in blue, Mg^{2+} in orange, Fe^{2+} in green, and the CO_3^{2-} anionic groups in black (carbon atoms) and red (oxygen atoms). The Fe:Mg ratio of 0.2 in the Mg-sites is represented by spherical sectors with radii proportional to the occupancy factors.

Measurements conducted on diffractograms of dolomites in which the Mg-site was progressively occupied by Fe, Mn, and Zn show that dolomite cation order decreases as the impurity content increases. Figure 7 shows the variation of $I_{01.5}/I_{11.0}$ when Fe was progressively substituted in the Mg-site up to 30%. In this compositional range, $I_{01.5}/I_{11.0}$ ratios decrease from 0.53 (dolomite without iron impurities) to 0.21 (dolomite with $X_{\text{Fe}} = 0.3$ in the Mg-site). A similar decrease in the dolomite cation order also occurs when Mg atoms are partially substituted by Mn and Zn impurities in the Mg-site (see Figure S2 in the Supporting Information). However, the significantly larger atomic scattering factor of the Zn atoms compare to those of Fe and Mn atoms results in a more pronounced decrease of $I_{01.5}/I_{11.0}$ ratios when magnesium is gradually substituted by Zn. Thus, for $X_{\text{Zn}} = 0.3$ in the Mg-site, $I_{01.5}/I_{11.0}$ is only 0.14.

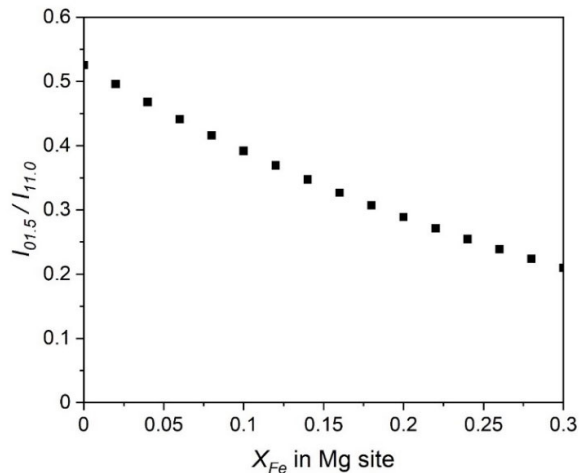


Figure 7. $I_{01.5}/I_{11.0}$ versus X_{Fe} for dolomites with iron impurities in the Mg-site.

4. Conclusion

Our calculations using the VESTA software [16] allowed us to quantify the decrease in $I_{01.5}/I_{11.0}$ intensity ratios when the amount of calcium and magnesium was varied in the Mg- and Ca-sites of a dolomite structure with Mg:Ca = 1 (i.e., an ideally stoichiometric dolomite). Similarly, when non-stoichiometric dolomites were considered (i.e., dolomites with Mg:Ca \neq 1), $I_{01.5}/I_{11.0}$ values decreased significantly when x was varied in the $\text{Ca}_{2-x}\text{Mg}_x(\text{CO}_3)_2$ dolomite formula. We found that such a decrease is more pronounced for dolomites with an excess of calcium than for dolomites with an excess of magnesium. Finally, we calculate the decrease in $I_{01.5}/I_{11.0}$ intensity ratios as the Mg-site was progressively occupied by Fe, Mn, or Zn impurities up to 30%. Since both the deviations from stoichiometry and the presence of impurities result in a significant decrease in the $I_{01.5}/I_{11.0}$ intensity ratios, these factors should be considered to quantify the degree of cation order of natural and experimentally produced dolomites.

Supplementary Materials: The following are available online at www.mdpi.com/article/10.3390/min11070702/s1, Figure S1: dolomite diffractograms simulated using the calcite structure as starting structure, Figure S2: $I_{01.5}/I_{11.0}$ versus X_M (M = Mn or Zn) for dolomites with Mn and Zn impurities in the Mg-site.

Author Contributions: Conceptualization, C.P. and C.M.P.; data curation, Y.Z., C.P., and C.M.P.; formal analysis, Y.Z., C.P., and C.M.P.; funding acquisition, C.P.; investigation, Y.Z., C.P., and C.M.P.; methodology, C.P. and C.M.P.; supervision, C.P. and C.M.P.; validation, Y.Z., C.P., and C.M.P.; writing—original draft, C.P. and C.M.P.; writing—review & editing, Y.Z., C.P., and C.M.P. All authors have read and agreed to the published version of the manuscript.

Funding: Carlos Pimentel is supported by the Spanish Ministry of Science and the Spanish State Research Agency with a Juan de la Cierva - Formación postdoctoral contract (ref. FJC2018-035820-I).

Acknowledgments: Carlos Pimentel is grateful to the Spanish Ministry of Science and the Spanish State Research Agency for a Juan de la Cierva - Formación postdoctoral contract (ref. FJC2018-035820-I).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kaczmarek, S.E.; Sibley, D.F. On the evolution of dolomite stoichiometry and cation order during high-temperature synthesis experiments: An alternative model for the geochemical evolution of natural dolomites. *Sediment. Geol.* **2011**, *240*, 30–40, doi:10.1016/j.sedgeo.2011.07.003.
2. Kell-Duivesteyn, I.J.; Baldermann, A.; Mavromatis, V.; Dietzel, M. Controls of temperature, alkalinity and calcium carbonate reactant on the evolution of dolomite and magnesite stoichiometry and dolomite cation ordering degree—An experimental approach. *Chem. Geol.* **2019**, *529*, 119292, doi:10.1016/j.chemgeo.2019.119292.
3. Montes-Hernandez, G.; Findling, N.; Renard, F. Dissolution-precipitation reactions controlling fast formation of dolomite under hydrothermal conditions. *Appl. Geochem.* **2016**, *73*, 169–177, doi:10.1016/j.apgeochem.2016.08.011.
4. Hammouda, T.; Andrault, D.; Koga, K.T.; Katsura, T.; Martin, A.M. Ordering in double carbonates and implications for processes at subduction zones. *Contrib. Miner. Pet.* **2010**, *161*, 439–450, doi:10.1007/s00410-010-0541-z.
5. Luth, R.W. Experimental determination of the reaction aragonite + magnesite = dolomite at 5 to 9 GPa. *Contrib. Miner. Pet.* **2001**, *141*, 222–232, doi:10.1007/s004100100238.
6. Putnis, A. *Introduction to Mineral Sciences*; Cambridge University Press: Cambridge, UK, 1992.
7. Zucchini, A.; Prencipe, M.; Comodi, P.; Frondini, F. Ab initio study of cation disorder in dolomite. *Calphad* **2012**, *38*, 177–184, doi:10.1016/j.calphad.2012.07.001.
8. Graf, D.L.; Goldsmith, J.R. Some Hydrothermal Syntheses of Dolomite and Protodolomite. *J. Geol.* **1956**, *64*, 173–186, doi:10.1086/626332.
9. Hird, K. Petrography and Geochemistry of Some Carboniferous and Precambrian Dolomites. Ph.D. Thesis, Durham University, Durham, UK, 1985.
10. McKenzie, J.A. Holocene Dolomitization of Calcium Carbonate Sediments from the Coastal Sabkhas of Abu Dhabi, U.A.E.: A Stable Isotope Study. *J. Geol.* **1981**, *89*, 185–198, doi:10.1086/628579.
11. Schultz-Güttler, R. The influence of disordered, non-equilibrium dolomites on the Mg-solubility in calcite in the system $\text{CaCO}_3\text{-MgCO}_3$. *Contrib. Miner. Pet.* **1986**, *93*, 395–398, doi:10.1007/bf00389397.

12. Lippmann, F. *Sedimentary Carbonate Minerals*; Springer: Berlin/Heidelberg, Germany, 1973.
13. Alonso-Zarza, A.M.; Martín-Pérez, A. Dolomite in caves: Recent dolomite formation in oxic, non-sulfate environments. Castañar Cave, Spain. *Sediment. Geol.* **2008**, *205*, 160–164, doi:10.1016/j.sedgeo.2008.02.006.
14. Pina, C.M.; Pimentel, C.; Crespo, Ángel Dolomite cation order in the geological record. *Chem. Geol.* **2020**, *547*, 119667, doi:10.1016/j.chemgeo.2020.119667.
15. Rodríguez-Blanco, J.D.; Shaw, S.; Benning, L.G. A route for the direct crystallization of dolomite. *Am. Miner.* **2015**, *100*, 1172–1181, doi:10.2138/am-2015-4963.
16. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, *44*, 1272–1276, doi:10.1107/s0021889811038970.
17. Miser, D.E.; Swinnea, J.S.; Steinfink, H. TEM Observations and X-Ray Crystal-Structure Refinement of a Twinned Dolomite with a Modulated Microstructure. *Am. Mineral.* **1987**, *72*, 188–193.
18. Maslen, E.N.; Streltsov, V.A.; Streltsova, N.R.; Ishizawa, N. Electron density and optical anisotropy in rhombohedral carbonates. III. Synchrotron X-ray studies of CaCO₃, MgCO₃ and MnCO₃. *Acta Crystallogr. Sect. B Struct. Sci.* **1995**, *51*, 929–939, doi:10.1107/s0108768195006434.
19. Izumi, F.; Momma, K. Three-Dimensional Visualization in Powder Diffraction. *Solid State Phenom.* **2007**, *130*, 15–20, doi:10.4028/www.scientific.net/ssp.130.15.
20. Manche, C.J.; Kaczmarek, S.E. A global study of dolomite stoichiometry and cation ordering through the Phanerozoic. *J. Sediment. Res.* **2021**, *91*, 520–546, doi:10.2110/jsr.2020.204.
21. Mayayo, M.; Bauluz, B.; Galindo, A.L.; González-López, J. Mineralogy and geochemistry of the carbonates in the Calatayud Basin (Zaragoza, Spain). *Chem. Geol.* **1996**, *130*, 123–136, doi:10.1016/0009-2541(95)00185-9.
22. Drits, V.A.; McCarty, D.K.; Sakharov, B.; Milliken, K.L. New Insight into Structural and Compositional Variability in Some Ancient Excess-Ca Dolomite. *Can. Miner.* **2005**, *43*, 1255–1290, doi:10.2113/gscanmin.43.4.1255.
23. Reeder, R.J. Constraints on Cation Order in Calcium-rich Sedimentary Dolomite. *Aquat. Geochem.* **2000**, *6*, 213–226, doi:10.1023/a:1009659122772.