

Relationship between composition and lattice parameters of some sedimentary dolomite varieties

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Abstract: A representative collection of iron-poor non-stoichiometric sedimentary dolomite samples of various composition, location, and age was studied by X-ray qualitative and quantitative phase analysis as well as by coupled plasma-atomic emission (ICP-AES) and X-ray fluorescence (XRF) spectroscopy. The main task is to determine relationships between the lattice parameters and Ca content in non-stoichiometric dolomite.

It is found that the unit cell parameters as well as the lattice *hkl* spacings of the studied dolomite samples are related by the following linear equations with strong linear correlation coefficients:

$$\begin{array}{ll} c = 7.3097a - 19.135 & R = 0.9988 \\ a = 1.0306d(104) + 1.8337 & R = 0.9991 \\ c = 7.6284d(104) - 6.0059 & R = 0.9984 \\ c_{\text{eff}} = 7.4038a_{\text{eff}} - 19.59 & R = 0.9991 \\ a_{\text{eff}} = 1.0251d(104) + 1.8499 & R = 0.9989 \\ a_{\text{eff}} = 1.8215d(113) + 0.8157 & R = 0.9990 \\ c_{\text{eff}} = 7.5244d(104) - 5.7065 & R = 0.9983 \end{array}$$

where $a_{\text{eff}} = d(110) + \sqrt{3}d(030)$ and $c_{\text{eff}} = 6d(006)$.

These almost perfect interdependences exist because in the studied dolomite structures not only unit cell parameters (as expected by Vergard's Law), but also corresponding *hkl* spacings co-vary in a linear manner with Ca content as follows:

$$\begin{array}{ll} c = 0.8632n_{\text{Ca}} + 15.14 & R = 0.9971 \\ a = 0.1168n_{\text{Ca}} + 4.6903 & R = 0.9967 \\ d(104) = 0.119n_{\text{Ca}} + 2.7658 & R = 0.9981 \\ a_{\text{eff}} = 0.11967n_{\text{Ca}} + 4.6872 & R = 0.9975 \\ c_{\text{eff}} = 6d(006) = 0.8852n_{\text{Ca}} + 15.1146 & R = 0.9958. \end{array}$$

The validity of these equations is confirmed by a comparison of Ca contents determined by the regressions and chemical analysis for monophase dolomite samples for which $1.00 < n_{\text{Ca}} < 1.07$ where n_{Ca} is the average amount of Ca per structural unit.

The difference between the compared Ca contents determined for each monophase sample by the two independent techniques in average is equal to 0.005 atoms of Ca per structural unit. The standard deviation determined for the 47 studied samples is equal to 0.004 atoms of Ca or 0.002 mol % CaCO₃.

Excess-Ca dolomite samples for which $n_{\text{Ca}} > 1.09$ consist of two dolomite phases with different amounts of excess Ca. Quantitative determination of proportions of each of these phases in the two-phase dolomite samples was carried out using the Rietveld software program Autoquan[®]. The lattice parameters and *hkl* spacings are used to determine Ca content in each of these phases using the regressions obtained for the monophase samples. Comparison of the calculated average Ca content with that determined from the chemical analysis shows that in average the difference between the compared values are equal to ± 0.012 atoms of Ca per formula or ± 0.06 mol % CaCO₃.

The results are in accordance with a structural model where only the B sites have a mixed occupancy confirming the results of a previous work.

Key-words: excess-Ca dolomite, lattice parameters, dolomite phase composition, X-ray diffraction, unit cell refinement.

1. Introduction

Dolomite, CaMg(CO₃)₂, consists of corner-linked Ca- and Mg-bearing octahedra in which the corners are oxygen atoms of CO₃ groups. In a dolomite structure there are two

nonequivalent cation sites, A and B, and in dolomite of ideal composition these sites are occupied by Ca and Mg, respectively, and as a result layers of Ca octahedra are regularly interstratified along the *c* axis with layers of Mg octahedra.

In sedimentary rocks dolomite is often non-stoichiometric containing Ca in excess of the ideal 1:1 Ca:Mg ratio. The Ca:Mg ratios may be 1.25:0.75 or 10:12 mol % excess CaCO₃ (Goldsmith & Graf, 1958; Füchtbauer & Goldsmith, 1965; Lumsden, 1979; Lumsden & Chimahusky, 1980; Reeder & Sheppard, 1984; Searl, 1994; Jones *et al.*, 2001). Although wide variations of excess-Ca dolomite varieties are well known, the role of Ca/Mg variations in dolomite formation remains poorly understood.

Determination of Ca-Mg ratios may be important because they may reflect environmental factors that controlled conditions of dolomite formation and transformation in sedimentary basins. Some authors assume that excess-Ca dolomite initially formed for kinetic reasons and is less stable and more soluble than the stoichiometric dolomite. Therefore, a continuous metastable solid solution series from high excess-Ca dolomite to stoichiometric dolomite is postulated to form in response to dissolution-precipitation reactions during diagenesis (Lippman, 1973; Land, 1980; Sperber *et al.*, 1984; Mazzullo, 1992). Evolution of Ca-Mg ratios through time may provide some evidence to support or reject this hypothesis. Finally, variation in Ca:Mg ratios may contain unique information about the crystal growth mechanism.

Determination of Ca:Mg ratio in dolomite samples can be carried out by different techniques including X-ray fluorescence (XRF) and/or atomic absorption spectroscopy, X-ray diffraction (XRD) and electron microprobe analysis. Each of these techniques has its own advantages and limitations related with accuracy, reproducibility, analysis time, cost, *etc.* Among these techniques XRD analysis looks like an ideal tool for determination of the Ca excess in dolomite samples because as was shown for the first time by Goldsmith & Graf (1958) Ca-enrichment of dolomite is accompanied by a significant expansion of the unit cell parameters. Goldsmith & Graf (1958) and later Lumsden (1979), assuming that there is a linear relationships between $d(104)$ values of dolomite and its composition, suggested simple techniques for determination of Ca content in Fe-poor dolomite samples. Therefore, XRD methods were widely used to estimate the composition of natural dolomites.

However, there was not a systematic investigation of well-characterized dolomite samples to corroborate the validity of these methods. Such investigation was carried out by Reeder & Sheppard (1984) for the first time. Lattice parameters and composition of low-iron non-stoichiometric dolomite samples taken from Eocene and Ordovician rocks were determined by XRD and electron microprobe analysis, respectively. These dolomite samples exhibited a variety of cation compositions from 1.06 to 1.12 CaCO₃ per formula. They showed a bimodal distribution with two different trends of lattice parameter variation. In particular, in the range of Ca-content from 1.0 to 1.04 the a and c parameters of the dolomite unit cell show very poor correlation with the Ca content and a relatively large variation in Ca content was not accompanied by noticeable change in the lattice parameters. A better correlation was observed in the range of Ca content from 1.07 to 1.12 atoms per formula. Reeder & Sheppard (1984) concluded that the distinct trends in the different regions indicate a non-linear variation of cell parameters with dolomite composition. In addition these au-

thors noted that there is no benefit to use variations in the $d(104)$ values for determination of Ca content in dolomite samples. It is more preferable to determine dolomite unit cell parameters because in this case better precision is obtained and errors are minimized by the least-squares procedure. Moreover, any error associated with the determination of peak position would further increase the overall error.

For a long time it was commonly accepted that each dolomite sample consists of crystals of the same composition. However, occurrence of non-stoichiometric dolomite samples consisting of two or even three dolomite varieties which differ from each other by the Ca excess was recently described by Jones *et al.* (2001), Jones & Luth (2002, 2003) and Drits *et al.* (2005). Using a pseudo-Voigt function Jones *et al.* (2001) decomposed a complex profile of 104 reflections into two maxima each of which corresponds to one of the coexistent excess-Ca populations. The positions of the individual 104 maxima were used to determine Ca content in each phase using the linear relationship between $d(104)$ values and the composition of a dolomite variety suggested by Lumsden (1979). Normalized areas of the decomposed maxima are used for estimation of the coexistent phase contents. Jones *et al.* (2001) concluded that for unimodal dolomite samples this technique determines the Ca content with an accuracy of ± 0.005 atoms per formula and can derive the proportion of each population with an accuracy ± 10 %.

It is clear that the results obtained by Reeder & Sheppard (1984) and Jones *et al.* (2001) are not consistent with each other. The former authors discovered a non-linear relationship between the unit cell parameters and composition in sedimentary dolomites whereas the latter authors declared an excellent linear dependence between $d(104)$ values and Ca-content in Fe-poor non-stoichiometric dolomites. Although Jones *et al.* (2001) took into account the effect of the bimodal Ca distribution in the same sample they confined their XRD study to only looking at the positions and profiles of 104 reflections. In addition, Jones *et al.* (2001) studied rather young (Miocene, Pliocene) sedimentary rocks in comparison with those (Eocene and Ordovician) studied by Reeder & Sheppard.

In the present study we have determined independently lattice parameters and cation composition of some sedimentary Fe-poor dolomite samples using XRD techniques, X-ray fluorescence and electron microprobe analysis in combination with programs providing refinement of the lattice parameters and determination of the phase contents in case of multiphase dolomite samples. Our purpose was to carry out a careful systematic investigation of well-characterized dolomite samples to confirm or reject the validity of linear relationships between the lattice parameters and composition of non-stoichiometric dolomite samples.

2. Materials and methods

2.1. Samples

Samples were obtained from cores and outcrops of different locations and age. The M236, M325, M327 and M335 groups of samples were obtained from cores taken in four oil

wells in Lea County, New Mexico. The rocks belong to the lower part of the Permian (Leonardian, ~263–268 Ma) Drinkard Formation, deposited near the western shelf margin of the Central Basin platform. Depositional facies of the original limestone includes inner-ramp mudstones or wackestones and tidal-flat deposits. Samples designated M214 and 821–511 through 821–516 are of Lower Mississippian age from the Lodgepole Formation in Uinta County, Wyoming.

Note that samples designated M214, M236, and 821 were studied previously by Drits *et al.* (2005) in their detailed study of the structure of excess-Ca dolomites. The former study did not analyze relationships between the lattice parameters and composition of non-stoichiometric dolomite samples. Additional dolomite samples are used in this study to prove that the particular structural and compositional variability of non-stoichiometric dolomite samples described and explained by Drits *et al.* (2005) is common for excess-Ca dolomites.

2.2. Sample preparation and X-ray diffraction

To prepare samples for XRD with an internal calibration standard, the bulk rock was first hand ground in a ceramic mortar and pestle to pass a 425 μm sieve and for each sample 3.0 g of hand ground material was then ground in a McCrone[®] micronizing mill in 4 ml of hexane for 5 minutes. The ground material was then dried at 85 °C in an air oven. Then 0.9 g of the McCrone ground powder was combined with 0.1 g of silicon powder (NIST SRM 640b). The McCrone ground powder and silicon standard were placed in a polystyrene vial with 3 polystyrene mixing balls and mixed in a Retch[™] mixing mill for 15 minutes at a frequency of 15.0 cycles. The mixture was then passed through a 425 μm Sieve before side loading it into an aluminum sample holder 20 x 450 x 3 mm under a frosted glass as a cover (McCarty & Reynolds, 1995). Diffraction data were collected with a Thermo XTRA[®] diffractometer with θ/θ geometry and a 260 mm goniometer radius equipped with a solid-state Si Peltier detector. Scans were made at various angular ranges, mainly from 20 to 76°2 θ (Cu K α). The step increment was 0.02°2 θ and counting rate was 30–40 s per step or longer. The slit configuration consisted of a 2.0 mm divergence slit, 0.02 mm Soller slits and a 4 mm anti scatter slit for the incident beam. The diffracted beam slit set up was a 0.5 mm anti scatter slit, 0.02 mm Soller slits, and a 0.2 mm receiving slit. The peak decomposition method of Jones *et al.* (2001) was tested using a step increment of 0.004°2 θ for selected samples.

2.3. Data processing and unit cell refinement

In order to refine the unit cell parameters using the least squares technique each XRD scan was first calibrated to the *hkl* reflections of Si internal standard. The non-linear error in calibration never exceeded half measurement step for any Si peak and was usually much lower. After calibration a linear background was removed along with mathematically removing the contribution of K α_2 from each *hkl* reflection

using the Jade[®] computer program (MDI, Inc.) that employed the Rachinger algorithm and a constant K α_1 /K α_2 ratio of 0.5. Jones *et al.* (2001) tested many functions to model dolomite 104 reflections and found that a pseudo-Voigt function provided the best peak shape. In addition to following the recommendation of Jones *et al.* (2001) to use a pseudo-Voigt function, we tested a number of other functions that included asymmetry corrections and split functions. A pseudo-Voigt function provided a fit with the lowest Rwp factor.

For mono-phase dolomite samples for which Ca-excess does not exceed 0.06–0.07 atoms of Ca per formula unit the *d(hkl)* values of Bragg reflections were calculated from the positions of diffraction maxima obtained by fitting a pseudo-Voigt function to each profile after applying the 2 θ correction based on Si-standard measurement.

2.4. Elemental analysis

Major and trace element data on bulk samples were obtained at SGS Laboratories, Toronto, Canada by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and X-ray fluorescence (XRF) spectroscopy.

2.5. Autoquan[®] analysis

The Rietveld software program Autoquan[®] (Kleeberg & Bergmann, 1998, 2002) was used to (1) determine the relative proportions of coexisting low excess-Ca and high excess-Ca dolomite phases, (2) to refine unit cell parameters of the coexisting dolomite phases, and (3), to quantify bulk sample mineral composition in order to correct dolomite Ca content in the presence of additional Ca-containing minerals.

3. Results

3.1. Qualitative analysis of XRD patterns

The diffraction features of a new set of dolomite samples turned out to be quite similar to those described by Drits *et al.* (2005), and are therefore presented here in a concise form.

The mono-phase dolomite samples form two groups. One of them includes varieties for which the measured and calculated *d(hkl)* values coincide within the expected experimental error (Table 1). For these samples standard deviations for the refined unit cell parameters are equal to 0.0001–0.0006 Å for *a* and 0.0003–0.0008 Å for the *c* parameters. This group consists mostly of dolomite samples containing relatively low excess-Ca which varies from 0 to 0.03 atoms per formula unit (samples M327-001, -002, -008, -011, -013; M325-008, -009, -014, -016, -037).

The characteristic feature of the second group of mono-phase dolomite samples is that the refined unit cell parameters provide a good agreement between the compared *d(hkl)* values only for some of the *hkl* reflections. Typically, the experimental and calculated reflection positions coincide only

for hkl reflections with low l . The higher l the greater the disagreement between the measured and predicted $d(hkl)$ values. In fact these reflections do not obey to Bragg's law. To

illustrate the degree of deviation from Bragg's law for reflections having different hkl , Table 2 compares the experimental 2θ (hkl) and $d(hkl)$ with those calculated using unit

Table 1. The refined unit cell parameters, experimental positions ($2\theta_{\text{exp}}$), experimental (d_{exp}) and calculated (d_{cal}) spacings, the differences between the experimental and calculated positions ($\Delta 2\theta$), and spacings (Δd) of hkl reflections for samples M327-011 and M325-037.

sample	M327-011					M325-037				
unit cell parameters	$a = 4.809174(9) \text{ \AA}; c = 16.0176 (3) \text{ \AA}$					$a = 4.8089(1)\text{\AA}; c = 16.0150 (9) \text{ \AA}$				
hkl	$2\theta_{\text{exp}}$	$\Delta(2\theta)$	$d_{\text{exp}} \text{ \AA}$	$d_{\text{cal}} \text{ \AA}$	$\Delta d \text{ \AA}$	$2\theta_{\text{exp}}$	$\Delta(2\theta)$	$d_{\text{exp}} \text{ \AA}$	$d_{\text{cal}} \text{ \AA}$	$\Delta d \text{ \AA}$
104	30.953	0.002	2.8867	2.8866	-0.0001	30.956	0.001	2.8864	2.8863	-0.0001
006	33.542	0.000	2.6696	2.6696	0.0000	33.553	-0.006	2.6687	2.6692	0.0004
015	35.319	-0.010	2.5392	2.5393	0.0001	35.330	-0.007	2.5385	2.5389	0.0005
110	37.367	0.000	2.4046	2.4046	0.0000	37.373	-0.003	2.4043	2.4045	0.0002
113	41.138	-0.001	2.1924	2.1925	0.0001	41.142	-0.001	2.1923	2.1923	0.0000
021	43.801	0.002	2.0651	2.0651	-0.0001	43.813	-0.007	2.0646	2.0649	0.0003
202	44.939	0.001	2.0155	2.0154	-0.0001	44.938	0.005	2.0155	2.0153	-0.0002
024	49.281	0.001	1.8476	1.8475	-0.0001	49.291	-0.005	1.8472	1.8474	0.0002
018	50.538	0.000	1.8045	1.8045	0.0000	50.555	-0.009	1.8040	1.8043	0.0003
116	51.078	0.001	1.7867	1.7867	0.0000	51.082	0.003	1.7866	1.7865	-0.0001
009	51.295	-0.003	1.7796	1.7797	0.0001					
211	58.903	0.000	1.5666	1.5666	0.0000	58.903	0.004	1.5666	1.5666	-0.0001
122	59.829	-0.002	1.5446	1.5446	0.0000	59.833	-0.002	1.5445	1.5445	0.0000
0110	62.030	-0.002	1.4950	1.4950	0.0000					
214	63.445	-0.003	1.4650	1.4650	0.0000	63.448	-0.001	1.4649	1.4649	0.0000
208	64.513	-0.001	1.4433	1.4433	0.0000	64.523	-0.003	1.4431	1.4431	0.0000
119	65.165	-0.006	1.4304	1.4305	0.0001	65.176	-0.008	1.4302	1.4304	0.0002
125	66.074	0.006	1.4129	1.4128	-0.0001	66.086	-0.001	1.4127	1.4127	0.0000
300	67.402	-0.001	1.3883	1.3883	0.0000	67.408	-0.003	1.3882	1.3882	0.0000
0012	70.499	-0.007	1.3347	1.3348	0.0001	70.519	-0.014	1.3343	1.3346	0.0003
217	72.876	-0.001	1.2969	1.2969	0.0000	72.880	0.002	1.2968	1.2968	0.0000
0210	74.707	-0.003	1.2696	1.2696	0.0000					

Table 2. The refined unit cell parameters, experimental positions ($2\theta_{\text{exp}}$), experimental (d_{exp}) and calculated (d_{cal}) spacings, the differences between the experimental and calculated positions ($\Delta 2\theta$) and spacings (Δd) of hkl reflections for samples M335-093 and M335-074.

sample	M335-093					M335-074				
unit cell parameters	$a = 4.8132 (6) \text{ \AA}; c = 16.049(3) \text{ \AA}$					$a = 4.8138(6) \text{ \AA}; c = 16.050(3) \text{ \AA}$				
hkl	$2\theta_{\text{exp}}$	$\Delta(2\theta)$	$d_{\text{exp}} \text{ \AA}$	$d_{\text{cal}} \text{ \AA}$	$\Delta d \text{ \AA}$	$2\theta_{\text{exp}}$	$\Delta(2\theta)$	$d_{\text{exp}} \text{ \AA}$	$d_{\text{cal}} \text{ \AA}$	$\Delta d \text{ \AA}$
104	30.903	0.006	2.8913	2.8907	-0.0006	30.897	0.009	2.8918	2.8910	-0.0008
006	33.484	-0.010	2.6741	2.6749	0.0008	33.481	-0.009	2.6743	2.6750	0.0007
015	35.272	-0.010	2.5425	2.5432	0.0007	35.270	-0.011	2.5426	2.5434	0.0007
110	37.330	0.004	2.4069	2.4066	-0.0003	37.327	0.003	2.4071	2.4069	-0.0002
113	41.094	-0.001	2.1947	2.1948	0.0000	41.089	-0.001	2.1950	2.1950	0.0000
021	43.766	-0.002	2.0667	2.0668	0.0001	43.762	-0.003	2.0669	2.0671	0.0001
202	44.894	0.003	2.0174	2.0173	-0.0001	44.888	0.003	2.0176	2.0175	-0.0001
024	49.232	-0.007	1.8493	1.8496	0.0002	49.225	-0.005	1.8495	1.8497	0.0002
018	50.489	-0.046	1.8062	1.8077	0.0015	50.482	-0.041	1.8064	1.8078	0.0014
116	51.032	-0.027	1.7882	1.7891	0.0009	51.024	-0.023	1.7885	1.7892	0.0007
211	58.848	0.000	1.5680	1.5680	0.0000	58.841	-0.001	1.5681	1.5681	0.0000
122	59.776	-0.007	1.5458	1.5460	0.0002	59.767	-0.006	1.5460	1.5462	0.0001
214	63.381	-0.009	1.4663	1.4665	0.0002	63.373	-0.009	1.4665	1.4667	0.0002
208	64.456	-0.047	1.4444	1.4454	0.0009	64.447	-0.044	1.4446	1.4455	0.0009
119	65.107	-0.063	1.4315	1.4328	0.0012	65.102	-0.063	1.4316	1.4329	0.0012
125	66.012	-0.013	1.4141	1.4143	0.0002	66.006	-0.013	1.4142	1.4145	0.0003
300	67.344	-0.008	1.3893	1.3895	0.0001	67.335	-0.007	1.3895	1.3896	0.0001
0012	70.428	-0.096	1.3359	1.3374	0.0016	70.430	-0.100	1.3358	1.3375	0.0017
217	72.810	-0.038	1.2979	1.2985	0.0006	72.804	-0.039	1.2980	1.2986	0.0006
0210	74.636	-0.068	1.2706	1.2716	0.0010	74.634	-0.072	1.2706	1.2717	0.0010

Table 3. Monophase samples, Ca content and unit cell parameters from least squares compared with regression values and chemical analysis.

Sample	a	c	$d_{(104)}$	$a_{(\text{eff})}$	$c_{(\text{eff})}$	$n\text{Ca-}a$	$n\text{Ca-}c$	$n\text{Ca-}d_{(104)}$	$n\text{Ca-}a_{(\text{eff})}$	$n\text{Ca-}c_{(\text{eff})}$	Average	$n\text{Ca}$ (XRF)	Difference Average- XRF
821–235	4.8085	16.0113	2.8861	4.8085	16.0140	1.011	1.010	1.010	1.012	1.040	1.017	1.016	0.000
821–511	4.8115	16.0311	2.8887	4.8120	16.0290	1.037	1.033	1.032	1.041	1.057	1.040	1.041	0.000
Eugui	4.8086	16.0129	2.8860	4.8088	16.0140	1.013	1.012	1.009	1.015	1.040	1.018	1.017	0.001
M236–022	4.8127	16.0476	2.8906	4.8130	16.0446	1.047	1.052	1.048	1.050	1.074	1.054	1.046	0.008
M236–056	4.8126	16.0455	2.8905	4.8130	16.0410	1.047	1.050	1.047	1.050	1.070	1.053	1.048	0.005
M236–083	4.8137	16.0536	2.8923	4.8148	16.0536	1.056	1.059	1.063	1.065	1.085	1.065	1.063	0.002
M236–089	4.8130	16.0368	2.8907	4.8134	16.0410	1.050	1.040	1.049	1.053	1.070	1.052	1.047	0.006
M236–093	4.8135	16.0517	2.8922	4.8140	16.0578	1.054	1.057	1.062	1.058	1.089	1.064	1.050	0.014
M236–104	4.8129	16.0575	2.8915	4.8134	16.0535	1.049	1.064	1.056	1.053	1.084	1.061	1.053	0.008
M325–009	4.8082	16.0101	2.8852	4.8082	16.0100	1.009	1.009	1.002	1.010	1.035	1.013	1.006	0.007
M325–014	4.8083	16.0105	2.8860	4.8082	16.0074	1.009	1.009	1.009	1.010	1.032	1.014	1.008	0.006
M325–016	4.8082	16.0077	2.8857	4.8080	16.0062	1.008	1.006	1.006	1.008	1.031	1.012	1.002	0.010
M325–037	4.8089	16.0150	2.8864	4.8086	16.0122	1.015	1.014	1.012	1.013	1.038	1.018	1.012	0.006
M325–087	4.8123	16.0295	2.8899	4.8122	16.0368	1.044	1.031	1.042	1.043	1.066	1.045	1.057	–0.011
M325–100	4.8128	16.0364	2.8906	4.8129	16.0386	1.048	1.039	1.048	1.049	1.068	1.050	1.057	–0.006
M327–064	4.8144	16.0597	2.8925	4.8150	16.0524	1.062	1.066	1.064	1.067	1.083	1.068	1.068	0.000
M327–065	4.8123	16.0391	2.8902	4.8123	16.0374	1.044	1.042	1.045	1.044	1.066	1.044	1.048	–0.005
M327–075	4.8126	16.0403	2.8907	4.8127	16.0416	1.047	1.044	1.049	1.047	1.071	1.046	1.059	–0.012
M327–079	4.8129	16.0459	2.8908	4.8134	16.0398	1.049	1.050	1.050	1.053	1.069	1.054	1.057	–0.002
M335–008	4.8122	16.0422	2.8901	4.8122	16.0368	1.043	1.046	1.044	1.043	1.066	1.048	1.044	0.004
M335–015	4.8130	16.0496	2.8910	4.8132	16.0452	1.050	1.054	1.052	1.051	1.075	1.057	1.058	–0.001
M335–022	4.8140	16.0569	2.8920	4.8142	16.0548	1.058	1.063	1.060	1.060	1.086	1.065	1.058	0.007
M335–028	4.8142	16.0595	2.8922	4.8142	16.0536	1.060	1.066	1.062	1.060	1.085	1.066	1.068	–0.001
M335–046	4.8138	16.0502	2.8919	4.8142	16.0488	1.057	1.055	1.059	1.060	1.079	1.062	1.056	0.006
M335–047	4.8128	16.0458	2.8915	4.8138	16.0458	1.048	1.050	1.056	1.056	1.076	1.057	1.058	0.000
M335–054	4.8157	16.0581	2.8929	4.8147	16.0567	1.073	1.064	1.068	1.064	1.088	1.071	1.071	0.000
M335–061	4.8151	16.0506	2.8925	4.8147	16.0506	1.068	1.056	1.064	1.064	1.081	1.067	1.063	0.004
M335–073	4.8136	16.0526	2.8921	4.8137	16.0482	1.055	1.058	1.061	1.056	1.078	1.062	1.055	0.007
M335–074	4.8138	16.0498	2.8918	4.8142	16.0458	1.057	1.055	1.058	1.060	1.076	1.061	1.060	0.001
M335–078	4.8150	16.0586	2.8932	4.8156	16.0530	1.067	1.065	1.070	1.072	1.084	1.072	1.068	0.003
M335–083	4.8122	16.0600	2.8923	4.8134	16.0410	1.043	1.067	1.063	1.053	1.070	1.059	1.050	0.010
M335–092	4.8134	16.0533	2.8916	4.8133	16.0482	1.054	1.059	1.057	1.053	1.078	1.060	1.052	0.008
M335–093	4.8132	16.0480	2.8913	4.8138	16.0458	1.052	1.053	1.054	1.056	1.076	1.058	1.057	0.001
M214–057	4.8116	16.0251	2.8888	4.8112	16.0140	1.038	1.026	1.033	1.034	1.040	1.034	1.027	0.007
M214–046	4.8119	16.0278	2.8890	4.8116	16.0326	1.041	1.029	1.035	1.038	1.061	1.041	1.027	0.014
M214–015	4.8123	16.0238	2.8892	4.8118	16.0302	1.044	1.025	1.036	1.040	1.058	1.041	1.040	0.001
821–514	4.8104	16.0248	2.8876	4.8104	16.0248	1.028	1.026	1.023	1.028	1.052	1.031	1.029	0.003
821–515	4.8095	16.0211	2.8870	4.8092	16.0218	1.020	1.021	1.017	1.018	1.049	1.025	1.029	–0.004
821–516	4.8090	16.0139	2.8835	4.8094	16.0158	1.016	1.013	0.987	1.020	1.042	1.016	1.014	0.001
821–235	4.8085	16.0113	2.8861	4.8086	16.0134	1.011	1.010	1.010	1.013	1.039	1.017	1.016	0.000
821–512	4.8096	16.0213	2.8872	4.8096	16.0212	1.021	1.022	1.019	1.021	1.048	1.026	1.033	–0.007
821–513	4.8090	16.0191	2.8867	4.8090	16.0188	1.015	1.019	1.015	1.016	1.045	1.022	1.019	0.004
M283–004	4.8111	16.0245	2.8880	4.8110	16.0296	1.034	1.025	1.026	1.033	1.057	1.035	1.025	0.010
M283–005	4.8115	16.0266	2.8886	4.8110	16.0302	1.037	1.028	1.031	1.033	1.058	1.037	1.031	0.006
m283–036	4.8119	16.0217	2.8884	4.8106	16.0236	1.041	1.022	1.029	1.030	1.051	1.034	1.028	0.007
M283–052	4.8125	16.0312	2.8900	4.8122	16.0362	1.046	1.033	1.043	1.043	1.065	1.046	1.040	0.006
M286–032	4.8122	16.0249	2.8888	4.8122	16.0320	1.043	1.026	1.033	1.043	1.060	1.041	1.028	0.013

cell parameters refined for samples M335-074 and M335-093. Modeling of the experimental XRD patterns shows that samples with the described diffraction features have a mixed-layer structure in which different proportions of non-stoichiometric and stoichiometric dolomite layers are interstratified with 2–4 % of 17 Å calcite-like layers (Drits *et al.*, 2005). Table 3 contains the refined unit cell parameters for the studied mono-phase samples of both groups. In samples of the second group Ca-excess varies from 0.03 to 0.07.

In the two-phase samples the coexistent phases differ from each other by the amount of excess-Ca and, therefore, for each given pair of hkl reflections the higher spacing value corresponds to the phase with higher content of Ca. Note, that the difference between the unit cell parameters of these phases is so small that the presence of these phases is not always evident from the qualitative analysis of the experimental XRD pattern. To provide better discrimination of the co-existing phases the $K\alpha_2$ contribution to the experimental

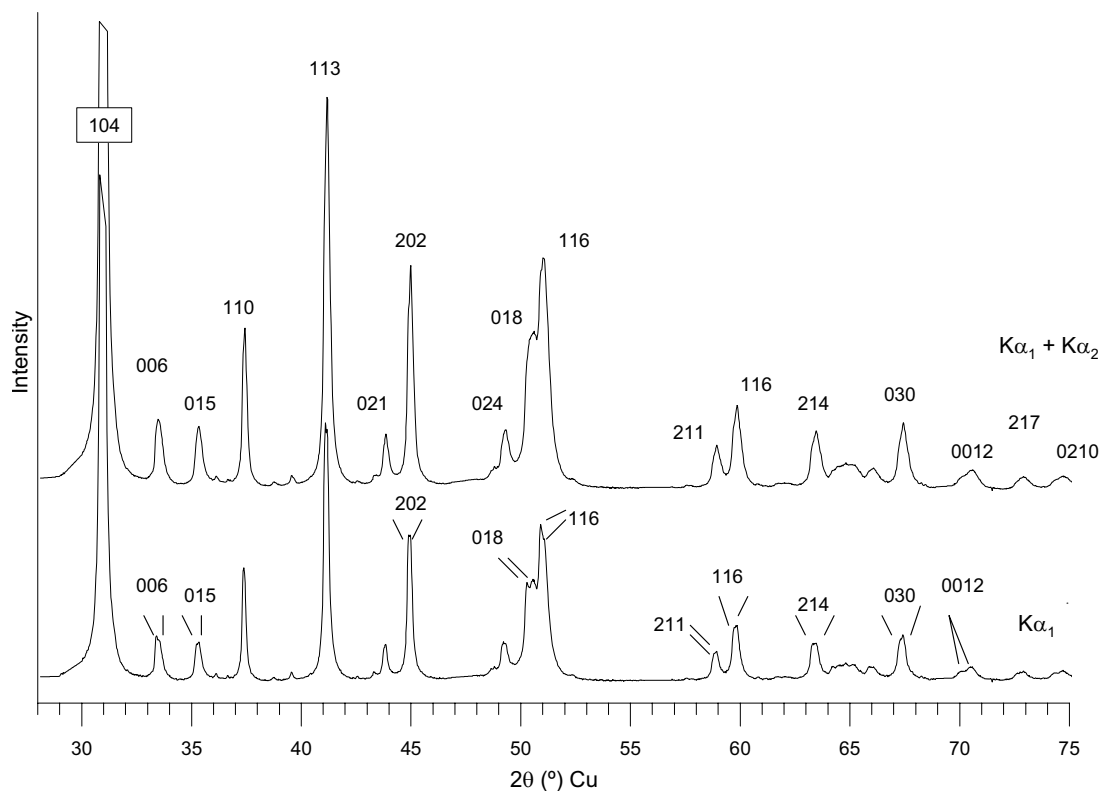


Fig. 1. XRD patterns from sample M325-043 with (a) and without (b) $K\alpha_2$ contribution.

XRD patterns should be subtracted. For example, XRD patterns from sample M325-043 (Fig. 1) illustrate the efficiency of this approach. To determine the unit cell parameters the profile of each pair of hkl reflections is decomposed for individual maxima corresponding to each of the coexistent phases. In most cases a pseudo-Voigt function provides a perfect approximation of the observed profiles of the over-

lapping hkl maxima. This procedure allows us to determine positions of these maxima and then with the least-square technique to determine the unit cell parameters of both phases. As in the case of monophase samples, hkl reflections of both low excess-Ca (phase I) and high excess-Ca (phase II) dolomite varieties deviate from Bragg positions with high l (Table 4).

Table 4. The refined unit cell parameters, experimental positions ($2\theta_{\text{exp}}$), experimental (d_{exp}) and calculated (d_{cal}) spacings, the differences between the experimental and calculated positions ($\Delta 2\theta$), and spacings (Δd) of hkl reflections for sample M327-036.

unit cell parameters	$a = 4.8245(3) \text{ \AA}; c = 16.128(1) \text{ \AA}$ phase II					$a = 4.8141(9) \text{ \AA}; c = 16.042(4) \text{ \AA}$ phase I				
	hkl	$2\theta_{\text{exp}}$	$\Delta(2\theta^\circ)$	$d_{\text{exp}} \text{ \AA}$	$d_{\text{cal}} \text{ \AA}$	$\Delta d \text{ \AA}$	$2\theta_{\text{exp}}$	$\Delta(2\theta^\circ)$	$d_{\text{exp}} \text{ \AA}$	$d_{\text{cal}} \text{ \AA}$
104	30.792	0.001	2.9015	2.9014	0.0001	30.899	0.015	2.8917	2.8903	0.0014
006	33.314	-0.009	2.6873	2.6880	0.0007	33.494	-0.004	2.6733	2.6737	0.0003
015	35.135	-0.017	2.5521	2.5533	0.0012	35.284	-0.014	2.5417	2.5426	0.0010
110	37.242	0.003	2.4124	2.4123	0.0002	37.326	0.002	2.4072	2.4070	0.0001
113	40.976	-0.002	2.2008	2.2009	0.0001	41.089	0.002	2.1950	2.1949	0.0001
021	43.657	-0.003	2.0716	2.0718	0.0001	43.763	-0.007	2.0669	2.0672	0.0003
202	44.775	0.003	2.0225	2.0223	0.0001	44.887	0.004	2.0177	2.0175	0.0002
024	49.103	-0.029	1.8539	1.8549	0.0010	49.240	-0.018	1.8490	1.8496	0.0006
018	50.202	0.004	1.8158	1.8157	0.0001	50.478	-0.017	1.8065	1.8071	0.0006
116	50.813	0.002	1.7954	1.7953	0.0001	51.022	-0.011	1.7885	1.7889	0.0003
211	58.705	-0.009	1.5715	1.5717	0.0002	58.856	-0.018	1.5678	1.5682	0.0004
122	59.607	0.002	1.5498	1.5498	0.0000	59.768	-0.009	1.5460	1.5462	0.0002
214	63.207	-0.024	1.4699	1.4704	0.0005	63.389	-0.024	1.4661	1.4666	0.0005
208	64.155	-0.011	1.4505	1.4507	0.0002	64.461	-0.042	1.4443	1.4451	0.0008
119	64.770	-0.017	1.4382	1.4385	0.0003	65.129	-0.068	1.4311	1.4325	0.0013
125	65.767	0.023	1.4188	1.4183	0.0004	66.025	-0.029	1.4138	1.4144	0.0006
300	67.174	-0.015	1.3924	1.3927	0.0003	67.343	-0.020	1.3893	1.3897	0.0004
0012	69.981	-0.043	1.3433	1.3440	0.0007	70.448	-0.079	1.3355	1.3368	0.0013

Table 5. The refined unit cell parameters, experimental positions ($2\theta_{\text{exp}}$), experimental (d_{exp}) and calculated (d_{cal}) spacings, the differences between the experimental and calculated positions ($\Delta 2\theta$) and spacings (Δd) of hkl reflections for sample M325-039.

unit cell parameters	$a = 4.8267(2) \text{ \AA}; c = 16.1449(7) \text{ \AA}$ phase II					$a = 4.8127(2) \text{ \AA}; c = 16.0469(8) \text{ \AA}$ phase I				
	hkl	$2\theta_{\text{exp}}$	$\Delta(2\theta^\circ)$	$d_{\text{exp}} \text{ \AA}$	$d_{\text{cal}} \text{ \AA}$	$\Delta d \text{ \AA}$	$2\theta_{\text{exp}}$	$\Delta(2\theta^\circ)$	$d_{\text{exp}} \text{ \AA}$	$d_{\text{cal}} \text{ \AA}$
104	30.768	0.000	2.9036	2.9036	0.0000	30.912	0.001	2.8904	2.8904	0.0000
006	33.271	-0.002	2.6907	2.6908	0.0001	33.485	-0.007	2.6739	2.6745	0.0006
015	35.097	-0.008	2.5548	2.5554	0.0006	35.264	0.003	2.5431	2.5429	-0.0002
110	37.228	-0.002	2.4133	2.4134	0.0001	37.338	0.001	2.4064	2.4063	-0.0001
113	40.954	-0.003	2.2019	2.2021	0.0002	41.103	-0.005	2.1943	2.1945	0.0002
202	44.754	0.001	2.0234	2.0233	-0.0001	44.906	-0.004	2.0169	2.0170	0.0001
024	49.046	-0.003	1.8559	1.8560	0.0001	49.217	0.014	1.8498	1.8493	-0.0005
018	50.146	0.009	1.8177	1.8174	-0.0003	50.483	-0.033	1.8063	1.8074	0.0011
116	50.779	-0.003	1.7965	1.7966	0.0001	51.007	0.005	1.7890	1.7889	-0.0001
211	58.663	0.002	1.5725	1.5724	-0.0001	58.850	0.006	1.5679	1.5678	-0.0001
122	59.574	0.003	1.5506	1.5505	-0.0001	59.776	0.000	1.5458	1.5458	0.0000
214	63.152	-0.008	1.4711	1.4712	0.0001	63.376	0.004	1.4664	1.4663	-0.0001
208	64.055	0.035	1.4525	1.4518	-0.0007	64.431	-0.013	1.4449	1.4452	0.0003
119	64.697	-0.004	1.4396	1.4397	0.0001	65.093	-0.039	1.4318	1.4326	0.0008
125	65.760	-0.013	1.4189	1.4192	0.0003	66.016	-0.007	1.4140	1.4142	0.0002
300	67.122	0.001	1.3934	1.3934	-0.0000	67.345	0.001	1.3893	1.3893	0.0000
0012	69.871	-0.017	1.3451	1.3454	0.0003	70.403	-0.059	1.3363	1.3372	0.0009
217	72.452	0.000	1.3034	1.3034	0.0000	72.794	-0.011	1.2982	1.2983	0.0001
0210	74.178	-0.025	1.2773	1.2777	0.0004	74.633	-0.053	1.2707	1.2714	0.0007

However, it is remarkable that the unit cell parameters of the high excess-Ca phases of the studied samples usually provide better agreement between the observed and calculated peak positions (2θ) and $d(hkl)$ than those of the low excess-Ca dolomite phases. To illustrate this Table 5 shows deviations between the experimental and calculated positions ($\Delta 2\theta$) and spacings ($\Delta d(hkl)$) obtained for the phase I and the phase II dolomite varieties of sample M325-039. For the phase II the mean $\Delta 2\theta$ is less than $0.01^\circ 2\theta$ and the mean $\Delta d = 0.0002 \text{ \AA}$. This means that the average lattice of this phase has 3D periodicity and it contains a few (if any) structural imperfections. In contrast, for phase I a significant disagreement between the experimental and calculated $\Delta 2\theta$ and $\Delta d(hkl)$ is observed for hkl reflections with $l > 8$. Similar features of the phase I and phase II are observed for samples M325-074, M335-057, and others.

It should be stressed that the distortion of the lattice periodicity of the phase I varies from sample to sample. In fact, the values of the unit cell parameters of phases I as well as the degree of deviation of their lattices from 3D periodicity are quite similar to those observed for mono-phase dolomite samples having defective structure. However, in some two-phase samples both high and low excess-Ca dolomite varieties have periodic (M236-098, M236-116) or almost 3D periodic (M327-036) lattices. Rietveld refinements of samples with two 3D periodic phases showed that only the B sites have a mixed occupancy of Ca and Mg (Drits *et al.*, 2005).

Finally, XRD patterns of some studied samples consist of sharp and rather symmetrical hkl reflections (samples *e.g.* M335-097, M236-124, and M236-127) located in the 2θ range from 25 to 66° . Therefore, they might be identified as mono-phase dolomite varieties. Moreover, for these reflections $d_{\text{exp}}(hkl)$ and $d_{\text{cal}}(hkl)$ almost coincide within the experimental errors. However, above $66^\circ 2\theta$ the profiles of the

hkl reflections clearly indicate that these samples consist of two phases. Indeed, the 0012, 217, 0210 and other reflections show a bimodal distribution of intensity. The decomposition of 0012 profiles shows that they consist of two reflections; one is a rather intense and narrow, while the other is less intense and much broader. We suppose that these samples are in fact two phases in which high and low excess-Ca dolomite phases coexist.

3.2. Quantitative phase analysis

Quartz, feldspar, calcite, anhydrite and pyrite are often associated with sedimentary dolomite. Even in almost monomineral dolomite small amounts of these minerals usually exist. The program Autoquan[®] was used to estimate quantities of accessory minerals in the studied samples. For most samples the content of calcite varies from 0.5 to 3 % although in some it is up to 8 %. Anhydrite in most samples usually varies from 0 to 0.5 % and does not exceed 1.5 % in the samples selected for detailed study. The total amount of Ca corresponding to the anhydrite and calcite found in each sample was subtracted from the CaO content determined for the bulk sample by chemical analysis and then a mean structural formulae of dolomite phases were calculated (Table 3).

Along with quantitative analysis of these impurities Autoquan[®] was also used for determination of proportions of phase I and phase II. To do this certain limits for variation of the a and c parameters for each of these phases were introduced in accordance with the values of these parameters determined by the least squares refinement of the data obtained by profile decomposition. The estimation of each phase is carried out independently of the content of the other phases in the sample by accounting for the 10 % Si internal

standard added to each sample. The contents of each of the coexistent phases in the studied samples are shown in Table 7.

3.3. Relationship between unit cell parameters

Unit cell data for 95 dolomite varieties studied are given in Tables 3 and 7. They contain a and c parameters for the mono-phase samples (Table 3) as well as for the phase I and phase II in the two-phase samples (Table 7). The relationship between the a and c values is shown in Fig. 2a. These values show a consistent linear dependence throughout the wide composition range.

$$c = 7.3097a - 19.135; R = 0.9988 \quad (1)$$

For the almost pure stoichiometric Eugi dolomite standard the composition $\text{Ca}_{1.001}\text{Mg}_{0.987}\text{Fe}_{0.010}\text{Mn}_{0.002}(\text{CO}_3)$ (Reeder & Wenk, 1983), is close to the ideal formula, and the a and c parameters determined by the Rietveld technique are equal to 4.8072 Å and 16.0048 Å, respectively (Antao *et al.*, 2004). If we assume that $c = 16.0048$ Å, then according to equation (1) the a parameter should be equal to 4.8073 Å. This value coincides with the expected one within a standard deviation.

In the dolomite varieties analysed, there appears to be a bimodal distribution in terms of the a and c values (Fig. 2a). In one population the a and c values vary from 4.807 Å to 4.817 Å and from 16.004 Å to 16.070 Å, respectively. For the other population the a and c values vary from 4.823 Å to 4.830 Å and from 16.12 Å to 16.17 Å, respectively. The a

and c parameters of monophase dolomites and of phase I of the two-phase samples fall into the former range, whereas a and c parameters of phase II of the two-phase samples form the latter range.

3.4. Relationships between the unit cell parameters and $d(104)$ values

The 104 reflection has the strongest intensity and beginning with Lumsden (1979) many mineralogists used $d(104)$ values for a determination of Ca-content in dolomite samples. Therefore, it is interesting to determine relationships between $d(104)$ and the a and c parameters of the monophase dolomites as well as of phase I and phase II of two-phase samples. The relationships between a vs. $d(104)$ and c vs. $d(104)$ are shown in Fig. 2b and 2c. Both relationships show a strong linear correlation. Two populations with different unit cell parameters can again be distinguished in Fig. 2b, 2c. It is significant that in both populations a and $d(104)$, as well as c and $d(104)$ obey to the same linear dependences:

$$a = 1.0306d(104) + 1.8337; R = 0.9991 \quad (2)$$

$$c = 7.6284d(104) - 6.0059; R = 0.9984 \quad (3)$$

If we assume that a stoichiometric dolomite has $a = 4.8072$ Å and $c = 16.0048$ Å then $d(104)$ values calculated from equations (2) and (3) are equal to 2.8852 Å and 2.8853 Å, respectively. These values coincide with that expected for the $d(104)$ value of stoichiometric dolomite (Antao *et al.*, 2004).

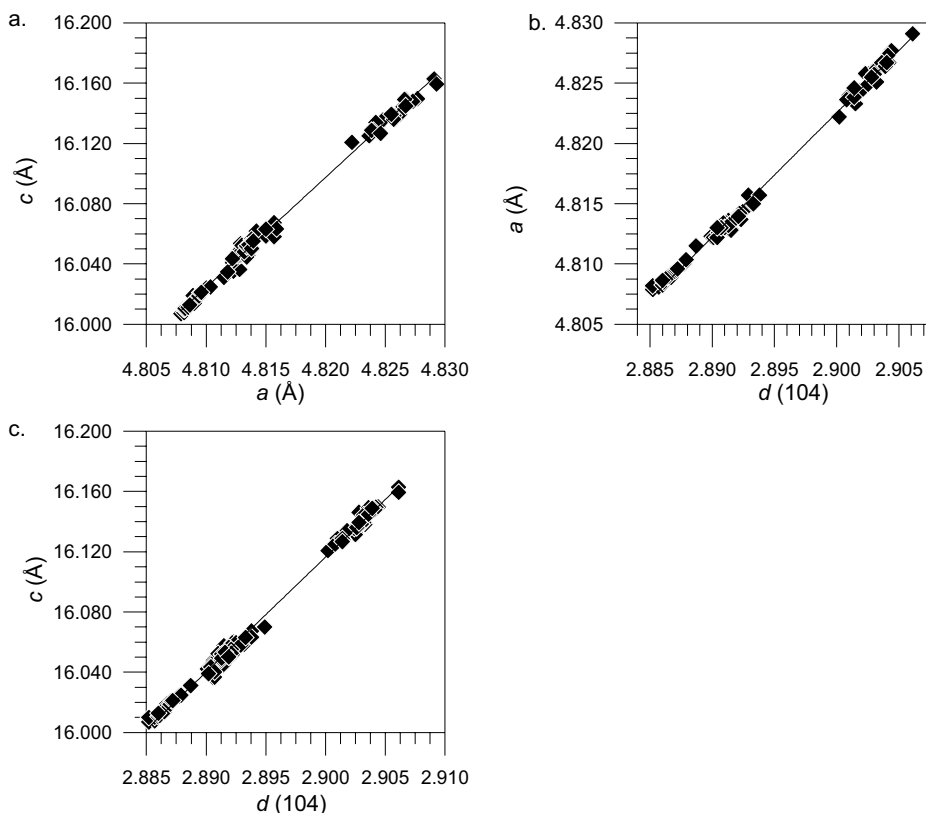


Fig. 2. Relationships between (a) the a and c unit cell parameters, (b) the a parameter and $d(104)$, and (c) the c parameter and $d(104)$.

3.5. Relationships between $d(006)$, $d(104)$, $d(113)$ and $(d(110) + \sqrt{3} d(030))$

As mentioned above, most monophase samples of the second sub-group and phase I of the two-phase dolomite samples are characterized by a defective structure. Their characteristic feature is that the disagreement between the measured and calculated $d(hkl)$ values increases with l . Because these deviations are related to layer interstratification the effects should be minimal for the positions of the 110 and 030 reflections. The most noticeable deviations between experimental and calculated $d(hkl)$ reflections are observed for $l > 7$ (Table 3). Therefore, the 104 and 006 reflections may not be too sensitive to the interstratification effects. To check these considerations we analysed correlations between $c_{\text{eff}} = 6d(006)$ and $a_{\text{eff}} = (d(110) + \sqrt{3} d(030))$, between c_{eff} and $d(104)$, between a_{eff} and $d(104)$, and a_{eff} and $d(113)$ values. Because $d(110) = a/2$ and $\sqrt{3} d(030) = a/2$ their sum is equal to the a parameter of the unit cell and is named as a_{eff} to distinguish these values from those obtained by the least-squares refinement. Fig. 3a–c show that these relationships are linear and interdependent:

$$\begin{aligned} d(006) &= 1.234a_{\text{eff}} - 3.265 \text{ or} \\ c_{\text{eff}} &= 7.4038a_{\text{eff}} - 19.59; \quad (R = 0.9991) \end{aligned} \quad (4)$$

$$a_{\text{eff}} = 1.0251d(104) + 1.8499; \quad (R = 0.9989) \quad (5)$$

$$a_{\text{eff}} = 1.8215d(113) + 0.8157; \quad (R = 0.9990) \quad (6)$$

$$\begin{aligned} d(006) &= 1.2540d(104) - 0.951 \text{ or} \\ c_{\text{eff}} &= 7.5244d(104) - 5.7065; \quad (R = 0.9983) \end{aligned} \quad (7)$$

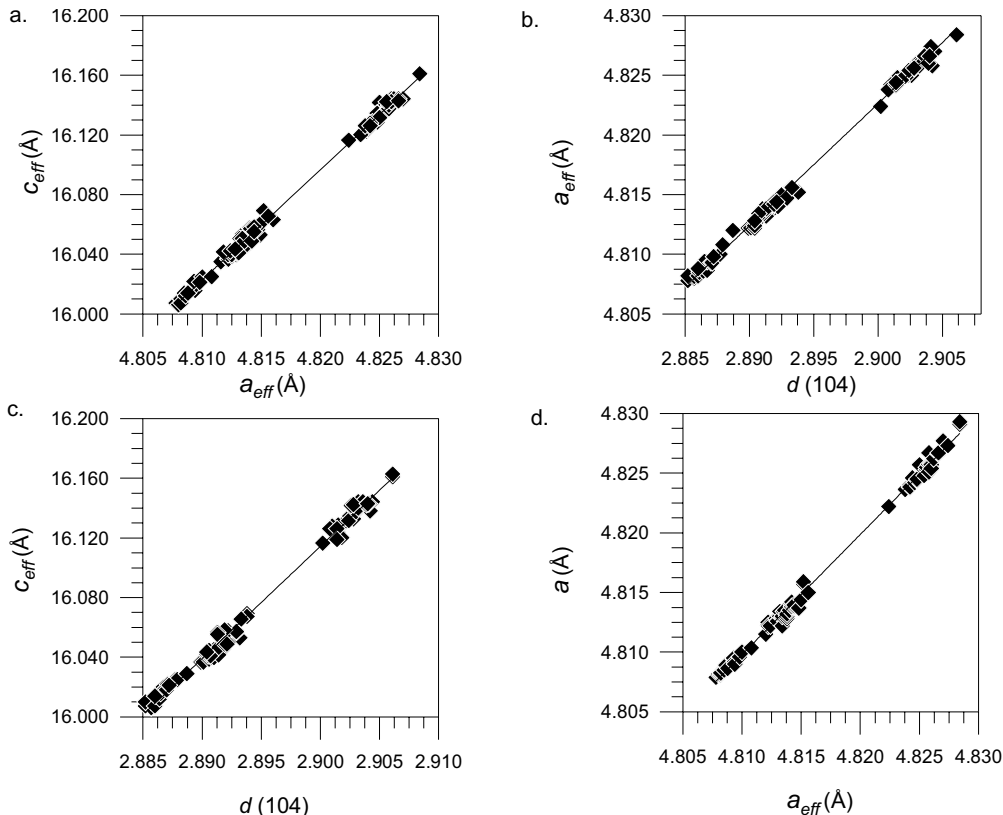


Fig. 3. Relationships between (a) the a_{eff} and c_{eff} unit cell parameters (b), the a_{eff} parameter and $d(104)$, (c), the c_{eff} parameter and $d(104)$, and (d) the a and a_{eff} unit cell parameters.

It is remarkable that equations (1) and (4), (2) and (5), (3) and (7) are very similar although not completely identical. The reason is that $6d(006)$ and $(d(110) + \sqrt{3} d(030))$ are slightly different from the corresponding c and a parameters. In particular, as can be seen in Fig. 3d the a values determined for dolomite varieties by the least squares method in average are slightly smaller than the a_{eff} calculated from the measured $d(110)$ and $d(030)$ values, that is $a = 1.0076a_{\text{eff}} - 0.0368$ ($R = 0.9990$).

3.6. Relationships between the cell parameters and amount of Ca for mono-phase samples

Results of the quantitative phase analysis allowed us to select 26 mono-phase dolomite samples in which total amount of calcite and anhydrite does not exceed 1.5 %. Therefore, errors in amount of the Ca content in each of these samples are related mostly with those of the chemical analysis itself. Note that all the studied dolomite samples usually contain less than 0.5 mol % FeCO_3 . Therefore, the presence of small amounts of Fe in structural formulae is even lower than the experimental errors in determination of CaO by the analytical chemistry methods. In other words, variations in the Fe contents do not noticeably influence the Ca content values in the samples. Compositions of the studied samples are given in Table 3 and the relationships between amounts of Ca, n_{Ca} , and the a , c and $d(104)$ values for the selected 26 samples are shown in Fig. 4a–c. Note that we were not able to directly determine the Ca content of each coexisting phase

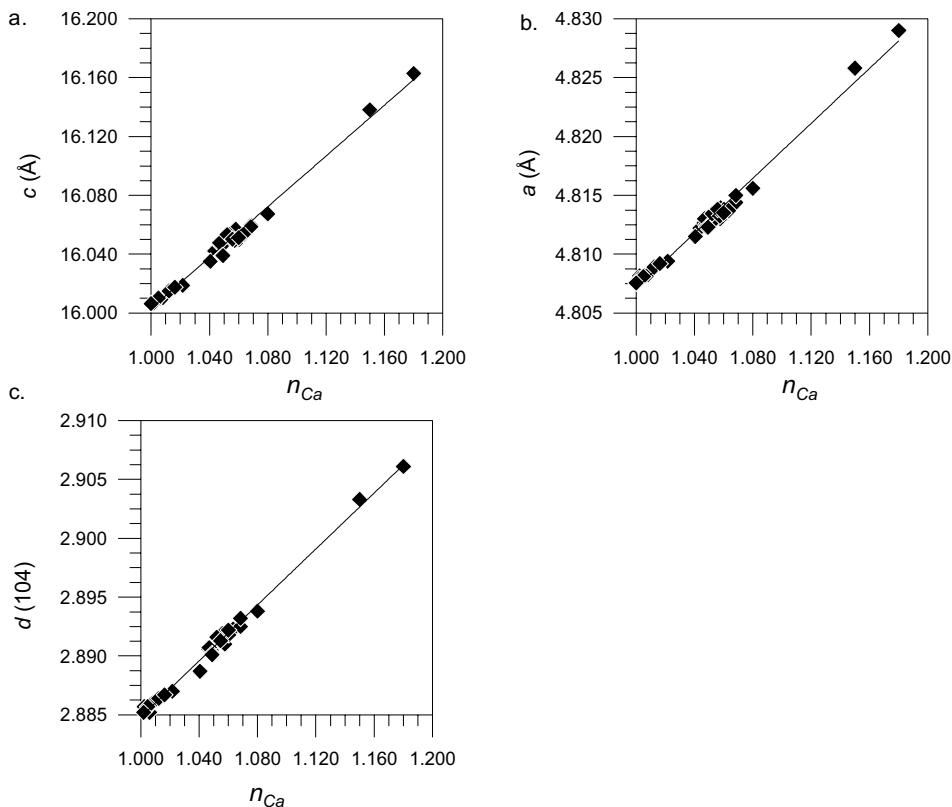


Fig. 4. Relationships between the (a) c unit cell parameter and n_{Ca} , (b) the a parameter and n_{Ca} , and (c), $d(104)$ and n_{Ca} .

in the two-phase samples. However, we used the results of the Rietveld refinements of these phases from samples M236-116 and M236-098 (Drits *et al.*, 2005). The occupancy of the B sites refined for phase I and phase II of these samples are included in the regressions shown in Fig. 4a–c. The regression equations are:

$$c = 0.8632n_{Ca} + 15.14; R = 0.9971 \quad (8)$$

$$a = 0.1168n_{Ca} + 4.6903; R = 0.9967 \quad (9)$$

$$d(104) = 0.119n_{Ca} + 2.7658; R = 0.9981 \quad (10)$$

As was mentioned by Reeder & Sheppard (1984) the maximum variation in the a parameter over the compositions interval is rather small (0.02 Å) compared to that for the c parameter (0.16 Å). Therefore increased substitution of Ca affects the c parameter considerably more than the a parameter. The axial ratio c/a also increases linearly with n_{Ca} according to the equation:

$$c/a = 0.0981n_{Ca} + 3.2309; R = 0.9978$$

All these relationships show that not only unit cell parameters, but also the intraplanar spacings linearly increase with an increase of n_{Ca} in the dolomite structures.

Fig. 5a and 5b shows that a_{eff} and c_{eff} are also related with the n_{Ca} by nearly perfect linear dependences:

$$a_{eff} = 0.11967n_{Ca} + 4.6872; R = 0.9975 \quad (11)$$

$$c_{eff} = 6d(006) = 0.8852n_{Ca} + 15.1146; R = 0.9958 \quad (12)$$

Table 3 compares amounts of Ca atoms obtained from the structural formulae calculated using the corrected chemical

analyses and calculated from equations 8–12 using the lattice parameter values a , c , $d(104)$, a_{eff} , and c_{eff} . Recall that equations 8–12 were obtained for the most pure dolomite samples. For the rest of the samples corrections were made in their chemical analysis by taking into account the concentrations of calcite and anhydrite in each sample.

4. Discussion

4.1. Validity of the relationships between the lattice parameters and Ca-content for mono-phase low Ca-excess dolomite

Lattice parameters including a , c , $d(104)$, c_{eff} and a_{eff} and Ca-contents in iron-poor mono-phase samples were independently determined and they are interrelated by linear equations (8–12). As can be seen in Table 3 the average Ca content determined for each sample from equations (8–12) is very close to the Ca content calculated from the corrected chemical analysis. The difference between the compared values varies from sample to sample from 0 to 0.014 atoms of Ca and in average is equal to 0.005 atoms of Ca per structural unit. The standard deviation determined for the 47 studied samples is equal to 0.004 atoms of Ca or 0.002 mol % $CaCO_3$. This value is comparable with the errors in determination of CaO and MgO by chemical analysis. Table 3 also shows that Ca-contents determined for each individual sample using different lattice parameters are quite similar to each other. Exceptions are n_{Ca} values determined by equation 12 using $d(006)$. They are systematically higher than

the others by 0.01–0.02 atoms (Table 3). The most probable reason is that dolomite structures corresponding to low Ca excess samples contain 2–4 % of calcite-like layers. Their interstratification with non-stoichiometric dolomite layers results in a slight displacement of the 006 reflections to lower 2θ angles increasing of the $d(006)$ values (Drits *et al.*, 2005). The reliability of Equations 8–12 is confirmed by R values that vary from 0.9950 to 0.9990.

One of the remarkable features of Equations 8–10 is that at $n_{\text{Ca}} = 1$ the calculated a , c , $d(104)$, and c/a values are equal to the lattice parameters of a stoichiometric dolomite ($a_{\text{cal}} = 4.8071 \text{ \AA}$, $c = 16.0032 \text{ \AA}$, $d(104) = 2.8849 \text{ \AA}$, $c/a = 3.3290 \text{ \AA}$) within experimental error. For example, these values coincide with the unit cells parameters of a stoichiometric dolomite sample (LA) of Reeder & Sheppard (1984) ($a = 4.807 \text{ \AA}$ and $c = 16.003 \text{ \AA}$) and the Eugi sample of Antao *et al.* (2004) ($a = 4.8072 \text{ \AA}$, $c = 16.0048 \text{ \AA}$, $d(104) = 2.8848 \text{ \AA}$, $c/a = 3.3295$). The a and c values given by Antao *et al.* (2004) are slightly higher than those calculated from equations 8–12 at $n_{\text{Ca}} = 1.0$. The possible reason is that Eugi dolomite contains small but noticeable amount of Fe and Mn (Antao *et al.*, 2004). Therefore, the equations 8–12 can be rewritten in the following form:

$$\begin{aligned} a &= a_0 + 0.1168 \Delta n_{\text{Ca}} \\ c &= c_0 + 0.8632 \Delta n_{\text{Ca}} \\ d(104) &= d_0(104) + 0.119 \Delta n_{\text{Ca}} \end{aligned}$$

where Δn is the excess Ca content and a_0 , c_0 and $d_0(104)$ are the lattice parameters of a stoichiometric dolomite. It is interesting to note that the gradients of increasing a and $d(104)$ with Δn_{Ca} , that is $\Delta a/\Delta n$ and $\Delta d(104)/\Delta n_{\text{Ca}}$, are almost equal to each other.

4.2. Meaning of the linear relationships between lattice parameters of non-stoichiometric dolomite varieties

As shown above, a linear relationship exists between a and c lattice parameters and the content of Ca, which shows that the Vegard's law is obeyed for Ca-excess dolomites investigated in this work. However, linear interdependences between $d(hkl)$ values and the lattice constants observed for the studied dolomite are not predicted by Vegard's law because in general $d(hkl)$ for a periodic lattice are related to

each other and the lattice parameters by non-linear functions even when the unit cell parameters do follow Vegard's law. The reason is that $d(hkl)$ values of the studied samples co-vary in an almost linear manner with the lattice constants and Ca contents because the c/a ratio and Ca content also has a linear relationship.

Unfortunately, we have no direct independent determinations of Ca contents in each coexistent dolomite variety in the polymodal samples. Therefore, to confirm validity of equations 8–12 for both high and low Ca excess dolomite varieties the following procedure is carried out. The a , c , $d(104)$, a_{eff} and c_{eff} values determined for the coexistent dolomite varieties are used to estimate Ca content in each of these phases using equations 8–12. The proportion of each phase is determined by the Autoquan[®] refinement of the experimental XRD patterns. Then the average Ca content in each sample is determined as a sum of products of the proportion and Ca content in each of the coexistent phases.

The results obtained for 25 two-phase samples are given in Table 7. Comparison of the mean Ca content calculated for each sample consisting of two-phases with that determined from the chemical analysis shows that in average difference between the compared values are equal to ± 0.012 atoms of Ca per formula or ± 0.006 mol % CaCO_3 . Table 7 shows that the high Ca-excess phases of the samples have $n_{\text{Ca}} > 1.15$. In contrast to the monophase dolomite samples the range of Ca content variation in the low Ca-excess phases is significantly different ($1.05 \leq n_{\text{Ca}} \leq 1.10$). Thus among the studied samples two populations of dolomite varieties may be distinguished: a low excess-Ca population in which $1.00 \leq n_{\text{Ca}} \leq 1.10$, and a high excess-Ca one with $n_{\text{Ca}} \geq 1.15$.

Among two-phase samples, six of them (M335-097, M236-120, M236-124, M236-125, M236-126 and M236-127) given in the end of Table 7 deserve special discussion. As was mentioned the most characteristic features of their XRD patterns are that they look like monophase with a high Ca excess. The average Ca content in these samples varies from 1.077 to 1.114 atoms per formula unit (Table 6). It was not possible to use the decomposition procedure to determine a and c parameters for the low excess-Ca phases. Therefore, the c parameters of these phases were estimated using the $d(0012)$ value and their a parameters from equation 1. For the low excess-Ca varieties the $d(0012)$ values

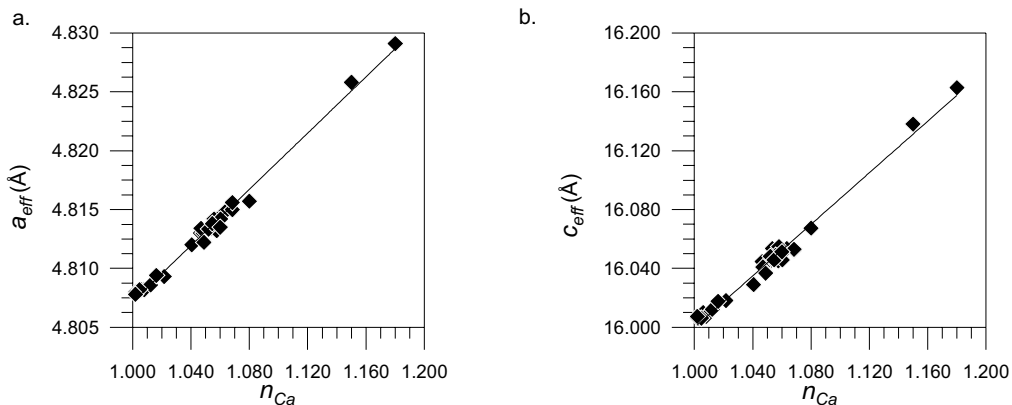


Fig. 5. Relationships between the (a) a_{eff} unit cell parameter and n_{Ca} , and (b) the c_{eff} parameter and n_{Ca} .

Table 6. Average chemical composition and cation proportions for two-phase dolomite samples.

Sample	CaO (%)	MgO (%)	Fe ₂ O ₃ (%)	Ca	Mg	Fe
M325-039	30.52	18.08	0.12	1.0943	0.9020	0.0037
M325-043	30.71	19.35	0.20	1.0785	0.9457	0.0058
M325-044	30.76	18.78	0.13	1.0885	0.8735	0.0038
M325-047	31.75	18.65	0.18	1.0913	0.9035	0.0052
M325-060	30.72	17.85	0.12	1.1030	0.8934	0.0036
M325-074	31.86	19.88	0.27	1.0664	0.9259	0.0077
M327-019	29.56	17.01	0.21	1.1069	0.8862	0.0068
M327-022	30.22	17.27	0.16	1.1096	0.8822	0.0082
M327-023	31.16	18.00	0.29	1.1036	0.8875	0.0089
M327-027	24.72	14.37	0.16	1.1025	0.8913	0.0062
M327-036	30.70	18.77	0.16	1.0781	0.9170	0.0049
M327-050	29.42	16.77	0.13	1.1089	0.8833	0.0039
M327-052	29.87	15.90	0.31	1.1431	0.8476	0.0093
M335-013	32.12	18.95	0.19	1.0953	0.8991	0.0056
M335-019	31.87	19.02	0.21	1.0891	0.9046	0.0062
M335-043	32.03	18.55	0.29	1.1028	0.8886	0.0086
M335-057	31.24	18.67	0.13	1.0898	0.9062	0.0040
M335-097	32.18	18.11	0.44	1.1143	0.8720	0.0137
M236-118	31.95	18.55	0.13	1.1038	0.8922	0.0040
M236-122	32.98	18.87	0.14	1.1113	0.8846	0.0041
M236-125	29.17	17.62	0.12	1.0856	0.9115	0.0039
M236-128	28.94	17.61	0.14	1.0806	0.9249	0.0045
M236-081	30.64	18.78	0.15	1.0770	0.9184	0.0046
M236-096	31.70	19.08	0.09	1.0870	0.9103	0.0027
M236-098	31.462	19.37	0.02	1.0900	0.9089	0.0011
M236-108	30.93	17.90	0.23	1.1048	0.8881	0.0071
M236-116	29.52	16.50	0.04	1.1035	0.8948	0.0017
M236-120	31.58	18.18	0.09	1.1090	0.8883	0.0027
M236-124	31.20	18.30	0.19	1.0981	0.8996	0.0058
M236-127	30.36	17.63	0.30	1.1010	0.8895	0.0095
M236-126	32.03	17.70	0.36	1.1207	0.6817	0.0176
M335-013	32.03	19.04	0.13	1.0912	0.9026	0.0062

were 1.337 ± 0.001 Å. The proportion of each phase was determined using Autoquan[®] program with fixed a and c parameters for the low excess-Ca phase. Despite the low accuracy of the determined a and c parameters for the low excess-Ca phases, the average Ca content in each these particular samples determined by the XRD methods is close to the Ca content determined by chemical analysis (Table 7). Nevertheless the actual structure of the coexisting phases in such samples requires future study.

Two conclusions can be made from these data. First, the equations 8–12 are valid for determination of Ca content in high excess-Ca dolomite varieties with $a > 4.820$ and $c > 16.095$ Å. Second, the combination of these equations with the proportions of the coexistent phases determined by the Autoquan[®] program provides a tool for estimation of average amount of Ca per structural formula in multi-phase dolomite samples.

4.3. Compositional heterogeneity of non-stoichiometric dolomite and precautions in application of the Autoquan[®] program

Jones *et al.* (2001) and Drits *et al.* (2005) in describing compositional heterogeneity of non-stoichiometric dolomite by

electron microprobe analysis and XRD techniques showed that, in fact, there are two levels of this heterogeneity. One of them is related with compositional zonation responsible for a population having a statistically weighted mean Ca content, and producing diffraction effects as those from a mono-phase sample. A second more fine level of compositional heterogeneity exists within the population. It may be characterized by a nearly normal unimodal Ca distribution. This heterogeneity is associated with a similar variation of lattice parameters which in turn leads to the hkl reflection broadening. At the same time the profile of the hkl reflections, and their width in particular, depend on the distribution of coherent scattering domains within the population, on microstrains, and other structural imperfections. Therefore, the actual FWHH's of the hkl reflections of non-stoichiometric unimodal dolomite are significantly wider in comparison with those of stoichiometric dolomite such as the Eugi standard for example.

In such cases precautions are required using the Autoquan[®] program for determination of the phase proportions. To illustrate this let us consider the results from Autoquan[®] for the mono-phase sample M327-064. Quantitative phase analysis was carried out for two different models: a mono-phase, and a two-phase dolomite, respectively. In the mono-phase approach unit cell parameters may vary around a and

Table 7. Unit cell parameters, $d(hkl)$ values and amount of Ca cations per formula calculated from the regressions for each of the coexistent phases, and average total content of Ca cations obtained from the structural formulae.

Sample	a	c	$d(104)$	a_{eff}	$6(d006)$	$d(113)$	$n\text{Ca-}a$	$n\text{Ca-}c$	$n\text{Ca-}d(104)$	$n\text{Ca-}a_{\text{eff}}$	$n\text{Ca-}(6(d006))$	average Amt %	total	$n\text{Ca}$ (XRF)	T-chem	
M325-039																
H-excess	4.8267	16.1449	2.9036	4.8266	16.1442	2.2019	1.17	1.16	1.16	1.16	1.19	1.17	32.1	1.09	1.094	-0.004
L-excess	4.8127	16.0469	2.8904	4.8128	16.0434	2.1943	1.05	1.05	1.05	1.05	1.07	1.05	67.9			
M325-043																
H-excess	4.8254	16.1489	2.9039	4.8260	16.1424	2.2011	1.16	1.17	1.16	1.16	1.18	1.17	32.5	1.11	1.079	0.031
L-excess	4.8147	16.0700	2.8949	4.8160	16.0632	2.1952	1.06	1.08	1.08	1.07	1.10	1.08	67.5			
M325-044																
H-excess	4.8255	16.1394	2.9028	4.8256	16.1424	2.2014	1.16	1.16	1.15	1.16	1.18	1.16	32.7	1.10	1.084	0.016
L-excess	4.8150	16.0631	2.8933	4.8156	16.0656	2.1956	1.07	1.07	1.07	1.07	1.10	1.08	67.3			
M325-047																
H-excess	4.8267	16.144	2.9040	4.8266	16.1430	2.2020	1.17	1.16	1.16	1.16	1.19	1.17	35.7	1.12	1.091	0.029
L-excess	4.8177	16.079	2.8973	4.818	16.0800	2.1972	1.09	1.09	1.11	1.09	1.11	1.10	64.3			
M325-060																
H-excess	4.8236	16.1332	2.9018	4.8232	16.1220	2.2008	1.14	1.15	1.14	1/14	1.16	1.15	43.8	1.11	1.104	0.006
L-excess	4.8180	16.0832			~16.0830							1.07	56.2			
M325-074																
H-excess	4.8246	16.1267	2.9014	4.8244	16.1190	2.2008	1.15	1.14	1.14	1.15	1.16	1.15	35.6	1.09	1.066	0.024
L-excess	4.8140	16.0552	2.8921	4.8144	16.0488	2.1952	1.06	1.06	1.06	1.06	1.08	1.06	64.4			
M327-019																
H-excess	4.8267	16.1494	2.9042	4.8258	16.1382	2.2021	1.17	1.17	1.16	1.16	1.18	1.17	42.3	1.10	1.107	0.003
L-excess	4.8120	16.0347	2.8910	4.8122	16.0398	2.1947	1.05	1.04	1.05	1.04	1.07	1.05	57.7			
M327-023																
H-excess	4.8253	16.1462	2.9028	4.8256	16.1328	2.2013	1.16	1.17	1.15	1.16	1.17	1.16	36.7	1.09	1.104	-0.014
L-excess	4.8130	16.0524	2.8910	4.8125	16.0400	2.1947	1.05	1.06	1.05	1.05	1.07	1.05	63.3			
M327-027																
H-excess	4.8253	16.1462	2.9028	4.8256	16.1328	2.2013	1.16	1.17	1.15	1.16	1.17	1.16	50.6	1.11	1.103	0.007
L-excess	4.8130	16.0524	2.8910	4.8125	16.0400	2.1947	1.05	1.06	1.05	1.05	1.07	1.05	49.4			
M327-036																
H-excess	4.8245	16.1282	2.9015	4.8248	16.1238	2.2008	1.15	1.15	1.14	1.15	1.16	1.15	35.2	1.09	1.078	0.012
L-excess	4.8141	16.0154	2.8917	4.8134	16.0400	2.1950	1.06	1.01	1.06	1.05	1.07	1.05	64.8			
M327-050																
H-excess	4.8273	16.1479	2.9041	4.8274	16.1430	2.2022	1.17	1.17	1.16	1.17	1.19	1.17	38.0	1.11	1.102	0.008
L-excess	4.8181	16.0450	2.8949	4.8156	16.0330	2.1960	1.09	1.05	1.08	1.07	1.06	1.07	62.0			
M335-011																
H-excess	4.8251	16.1444	2.9032	4.8258	16.1400	2.2011	1.15	1.16	1.16	1.16	1.18	1.16	37.6	1.09	1.055	0.035
L-excess	4.8122	16.0434	2.8904	4.8124	16.0422	2.1942	1.04	1.05	1.05	1.04	1.07	1.05	62.4			
M335-013																
H-excess	4.8248	16.1357	2.9024	4.8254	16.1316	2.2011	1.15	1.15	1.15	1.15	1.17	1.16	44.2	1.10	1.095	0.005
L-excess	4.8134	16.0446	2.8914	4.8118	16.0416	2.1948	1.05	1.05	1.06	1.04	1.07	1.05	55.8			
M335-019																
H-excess	4.8242	16.1339	2.9018	4.8246	16.1202	2.2007	1.15	1.15	1.14	1.15	1.16	1.15	47.3	1.10	1.089	0.011
L-excess	4.8146	16.0521	2.8920	4.8138	16.0338	2.1952	1.06	1.06	1.06	1.06	1.06	1.06	52.7			
M335-043																
H-excess	4.8262	16.1395	2.9032	4.8262	16.1442	2.2016	1.16	1.16	1.16	1.16	1.19	1.16	39.7	1.11	1.103	0.007
L-excess	4.8138	16.0564	2.8919	4.8144	16.0584	2.1951	1.06	1.06	1.06	1.06	1.09	1.07	60.3			
M335-057																
H-excess	4.8240	16.1287	2.9010	4.8242	16.1280	2.2004	1.14	1.15	1.14	1.14	1.17	1.15	34.9	1.10	1.090	-0.010
L-excess	4.8128	16.0323	2.8906	4.8126	16.0374	2.1945	1.05	1.03	1.05	1.05	1.07	1.05	65.1			
M335-097																
H-excess	4.8244	16.1316	2.9018	4.8248	16.1286	2.2008	1.15	1.15	1.14	1.15	1.17	1.15	55.3	1.104	1.114	-0.01
L-excess	4.8130				~16.0430							1.05	44.7			
M236-124																
H-excess	4.8239	16.1287	2.9014	4.8242	16.1262	2.2005	1.14	1.15	1.14	1.14	1.17	1.15	53.1	1.10	1.096	-0.004
L-excess	4.8130				~16.0430		1.05				1.05	1.05	46.9			
M236-125																
H-excess	4.8238	16.1268	2.9013	4.8242	16.1226	2.2005	1.14	1.14	1.14	1.14	1.16	1.15	48.9	1.096	1.085	-0.011
L-excess	~4.8130				~16.0430		1.05				1.05	1.05	51.1			
M236-126																
H-excess	4.8257	16.1392	2.9030	4.8260	16.1370	2.2015	1.16	1.16	1.15	1.16	1.18	1.16	42.1	1.097	1.120	-0.023
L-excess	~4.8130				~16.043		1.05				1.05	1.05	57.9			
M236-127																
H-excess	4.8277	16.1497	2.9044	4.8270	16.1442	2.2027	1.18	1.17	1.17	1.17	1.19	1.17	45.9	1.107	1.100	-0.007
L-excess	~4.8130				~16.043		1.05				1.05	1.05	54.1			
M236-120																
H-excess	4.82573	16.1386	2.9030	4.8258	16.1376		1.16	1.16	1.15	1.16	1.18	1.16	42.1	1.099	1.109	-0.010
L-excess	~4.8130				~16.0430		1.05				1.05	1.05	57.9			
M236-081																
H-excess	4.8266	16.1492					1.17	1.17				1.17	36.8	1.10	1.077	0.023
L-excess	4.8134	16.0520					1.05	1.06				1.06	63.2			

c values typical for the low excess-Ca dolomite, and in the two-phase approach the second range includes a and c variations around parameters close to those of stoichiometric dolomite. Refinement in the mono-phase approximation leads to $R_{wp} = 10.9\%$ and $a = 4.813 \text{ \AA}$, $c = 16.049 \text{ \AA}$ for the dolomite lattice. Refinement in the two-phase approach leads to $R_{wp} = 8.86\%$ and 64 % of the low Ca excess dolomite with $a = 4.814 \text{ \AA}$ and $c = 16.070 \text{ \AA}$ and 36 % of an almost stoichiometric dolomite with $a = 4.809 \text{ \AA}$ and $c = 16.002 \text{ \AA}$. It is interesting that statistically weighted values of the a and c parameters of these two phases are equal to 4.812 \AA and 16.045 \AA which are close to those determined for the mono-phase.

Microprobe data (Fig. 6) show a rather broad, but nearly Gaussian distribution of compositions in the sample. This can either represent a broad unimodal variation of the composition, or an overlap of the two very close populations. However, as shown by the results of the XRD analysis based on the two-phase model, the results do not match the distribution observed by microprobe, which suggests that the first model is more realistic.

Sometimes an unambiguous solution can be obtained when a combination of the regressions, Autoquan[®] refinement and electron microprobe analysis is used. The results obtained for sample M335-097 are remarkable in this respect. According to electron microprobe analysis sample M335-097 is characterized by a very homogeneous composition with the mean Ca content equal to (1.102 ± 0.006) atoms per formula. In contrast the Autoquan[®] refinement shows that the sample consists of 55.3 % high and 44.7 % low excess-Ca varieties leading to the mean Ca content equal to 1.11 atoms per formula (Table 7). This value within error coincides with that determined by electron microprobe analysis. It means that sample M335-097 does consist of high and low excess-Ca dolomite finely intergrown having contrasting amounts of Ca cations of 1.15 and 1.05 per formula.

4.4. Potential problems with utilization of the 104 reflection for determination of the coexistent phase contents

As was mentioned, to estimate the proportion and composition of the coexistent dolomite phases Jones *et al.* (2001) decomposed the 104 reflection profile of a two-phase dolomite sample. They found that a scan speed of $0.2^\circ 2\theta/\text{min}$ and a sampling interval of $0.004^\circ 2\theta/\text{step}$ for the reflection profile recording and a pseudo-Voigt function for decomposition provided the optimal solution of the problem. According to Jones *et al.* (2001) under these conditions the peak-fitting technique allows determination of the proportion of each phase with an accuracy of $\pm 10\%$.

We have used the same experimental conditions and the peak fitting technique for recording and treatment of the 104 reflection profiles of the studied two-phase dolomite samples. In addition, we have recorded 104 reflections when the step increment is $0.02^\circ 2\theta$ and counting rate is 40 s per step.

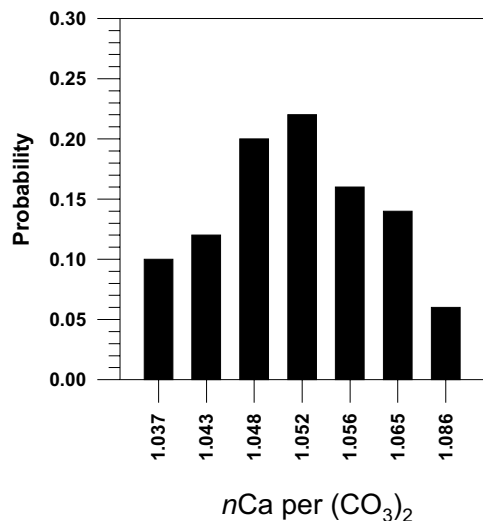


Fig. 6. Occurrence probability and amount of Ca per structural formulae for dolomite domains in sample M327-064.

In both cases for the decomposition procedure a pseudo-Voigt function was used. Comparison of the results shows, first, that an agreement between the experimental profile and profile obtained as a sum of the decomposed functions corresponding to each of the coexistent phases is much better in the second case when significantly higher statistics are obtained for the recorded intensity even if the step increment is an order larger. Second, the contents of the coexistent phases determined for the same sample from the areas under the decomposed functions may be significantly different when the different experimental conditions for recording of the 104 reflection are used. In particular, the results are not reproducible for samples in which the overlapped 104 reflections belonging to the coexistent phases are poorly resolved or these phases have quite different proportions. For example Fig. 7a–b shows the results of decomposition of the 104 reflection recorded for sample M325-043 according to two techniques described above. In both cases the fitting factors R are very small (2.55 % and 2.37 %) but ratios of the areas corresponding to high-excess and low excess dolomite phases differ substantially. These ratios are equal to 56:44 and 67:33, for data collected with step sizes of 0.004 and $0.02^\circ 2\theta$, respectively. Therefore, in accordance with Reeder & Sheppard (1984) we conclude that it is preferable to analyze the profiles of all hkl reflections in the whole 2θ range in order to obtain reliable results.

To estimate amount of Ca in non-stoichiometric dolomite Jones *et al.* (2001) used the linear relationship between $d(104)$ and the mol % excess CaCO_3 of Lumsden (1979). To get this equation this author assumed that $d(104)$ values are equal to 2.886 \AA for a stoichiometric dolomite and to 2.901 \AA for a dolomite of $\text{Ca}_{0.55}\text{Mg}_{0.45}(\text{CO}_3)_2$ composition. In fact, for a stoichiometric dolomite the $d(104) = (2.885 \pm 0.0002) \text{ \AA}$ (Reeder & Sheppard, 1984; Antao *et al.*, 2004; present work) and $d(104)$ should be 2.8967 \AA for the non-stoichiometric sample with $n_{\text{Ca}} = 1.10$. This means that the Lumsden equation underestimates n_{Ca} .

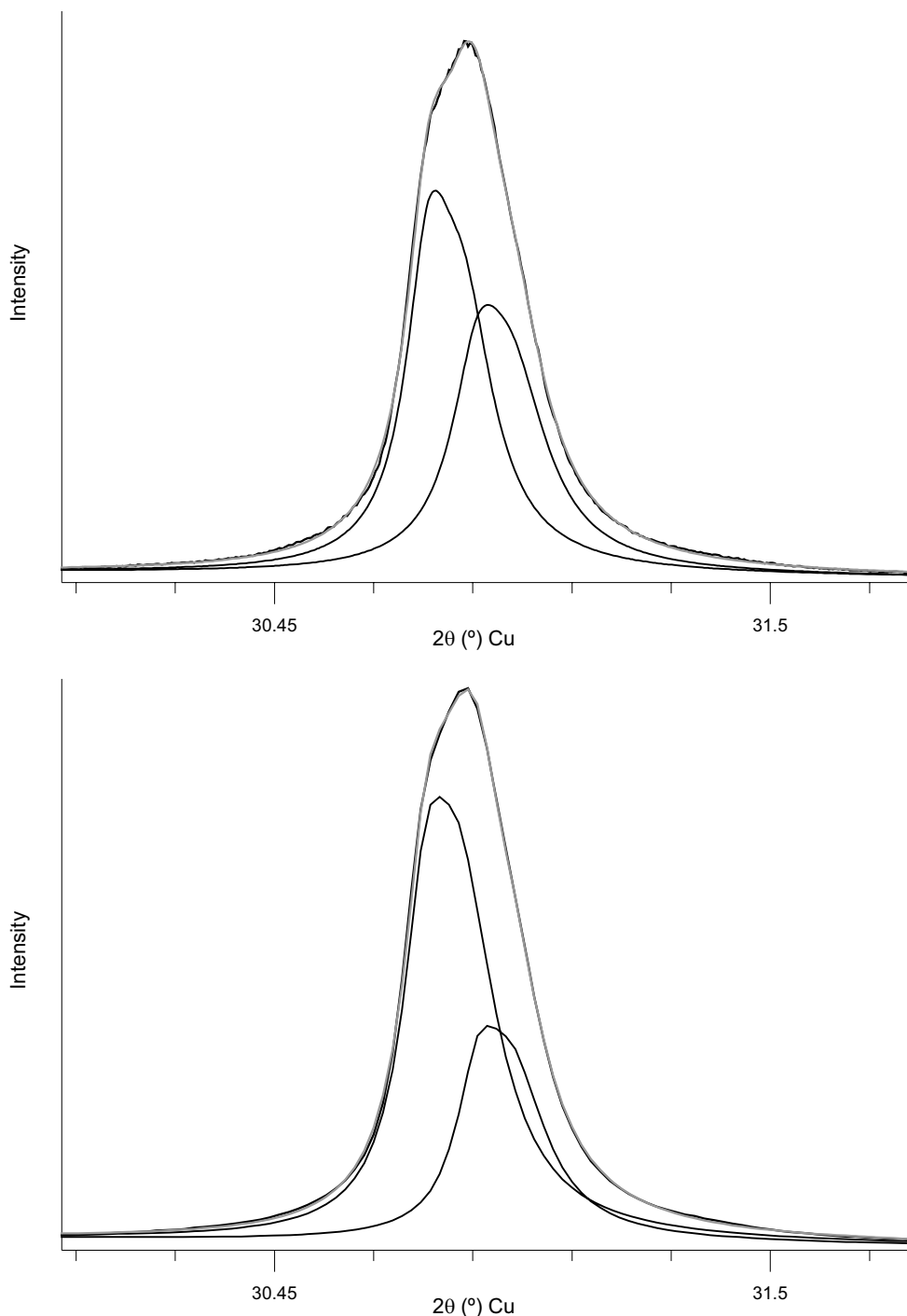


Fig. 7. XRD decomposition of 104 reflection of high and low-excess Ca phases in sample M325-043, (a) data was collected with a step size of $0.004^{\circ}2\theta$, and (b) with a step size of $0.02^{\circ}2\theta$ (shaded line = fit sum).

4.5. Possible sources of inconsistency in previous work

As was mentioned, Reeder & Sheppard (1984) concluded that the use of either unit cell parameters or individual hkl reflections to infer the composition of dolomite was not reliable. This conclusion contradicts the results obtained in this work. In general, in both studies the procedure of recording and treatment of the experimental XRD patterns were similar but not identical. In both cases internal standards were

used, the positions of hkl reflections and the unit cell parameters were determined by least-squares refinement programs. However, Reeder & Sheppard (1984) excluded some hkl reflections from the unit cell parameters refinement. In particular, the 030 dolomite reflection was often excluded because its shape was asymmetrical. It is surprising that these authors ignored positions and profiles of 0012 reflections which are most sensitive to the phase heterogeneity of dolomite samples. Therefore, one can assume that one of the

possible reasons for their non-linear variation of the unit cell parameters with composition is that most samples with $n_{\text{Ca}} > 1.08$ studied by Reeder & Sheppard (1984) consist of two dolomite populations with different Ca contents. According to our experience the asymmetrical profile of the 030 reflection is good evidence for the phase heterogeneity of a dolomite sample.

Another possible reason for the observed deviation from linear relationships between the unit cell parameters and Ca content is that the composition of the studied samples was determined only by electron microprobe analysis. Our example of sample M335-097 is remarkable in this respect. According to microprobe analysis its composition is very homogeneous and the amount of Ca varies within a very small range from 1.096 to 1.108 atoms per structural unit, although the sample does contain two different intimately intergrown populations. Therefore, a small standard deviation of the population of analyses for each sample is not a guarantee of the sample homogeneity as Reeder & Sheppard assumed.

On the other hand, quantitative XRD phase analysis provides direct determination of calcite and anhydrite content. The presence of even small amount of these minerals significantly disturbs the relationship between the unit cell parameters and composition, especially in a range $1.00 \leq n_{\text{Ca}} \leq 1.05$ where Reeder & Sheppard observed the strongest discrepancy between the compared cell parameters and Ca contents.

Reeder & Sheppard (1984) considered cation disorder, structural defects and cation substitution according to the Newton & Wood (1980) equivalent site and non-equivalent site models as possible reasons for the observed non-linear variations of the cell parameters with composition. Among these reasons different cation occupancy of the A and B sites in the studied samples looks most plausible. As was mentioned some samples studied in this work consist of two dolomite phases each of which is characterized by a 3D periodic lattice. In particular, Rietveld refinement of the coexistent phases in samples M236-116 and M236-098 shows that the phases differ from each other by Ca excess in the B sites (Drits *et al.*, 2005). It should be noted that the lattice para-

eters and Ca content in each of the coexistent phases in both samples fit the linear relationship shown in Fig. 4a, c.

In contrast, refinement of two non-stoichiometric dolomite single crystals from Eocene carbonates has shown that in their structure both A and B sites have a mixed cation composition (Reeder, 2000). Because these single crystals and samples studied by Reeder & Sheppard (1984) have the same origin one may assume that the observed non-linear relationships between the unit cell parameters and composition are related with different distribution of Ca and Mg in each particular sample studied by these authors.

Drits *et al.* (2005) have shown that different cation occupancy of the A and B layers in non-stoichiometric dolomite exerts different influence on expansion of the a and c parameters. In particular, for dolomite structures an increase in excess Ca uptake in the B site is accompanied by a parallel increase of the a and c parameters because an increase of Ca content in the B sites increases the mean size of (MgCa)-octahedra and leads to the homogeneous unit cell expansion. In this work we have shown that this lattice expansion is proportional to the Ca content in the B sites.

In contrast, according to Reeder (2000) a mixed cation composition of both A and B octahedra disturbs this regularity. In particular, his sample 124-23B having a higher excess of Ca ($\text{Ca}_{1.12}\text{Mg}_{0.88}$) has a smaller a (4.8122 Å) and higher c (16.12 Å) parameters in comparison with those (4.820 Å and 16.0721 Å) in sample 124-9B with a lower total content of Ca ($\text{Ca}_{1.09}\text{Mg}_{0.91}$). Comparison of the relationship between the unit cell parameters of samples studied by Reeder & Sheppard (1984) and in the present work (Fig. 2 and 8) is consistent with the assumption that different cation distribution over the A and B sites exerts different influence on lattice parameters of dolomite structures. In particular, Fig. 8 shows that for some dolomite samples studied by Reeder & Sheppard (1984) a significant variation of the c parameter values is observed for almost the same value of the a parameter. Similar regularity was observed by Reeder & Wenk (1983) for thermally disordered stoichiometric dolomite. Cation disorder caused by the thermal treatment leads to mixed cation compositions in both A and B sites. This process is accompanied by a significant increase only of the c parameter whereas the a value has low sensitivity to such cation disorder. Because determination of cation composition in the A and B layer even in an average unit cell of non-stoichiometric dolomites may provide important information about energetic state of these mineral varieties further investigations in this direction involving dolomite of different age and origin are needed.

5. Conclusion

Permian and Lower Mississippian dolomites taken from cores and outcrops of Lea County in New Mexico and the Lodgepole Formation in Uinta County, Wyoming form two groups of samples differing from each other by average amounts of Ca cations per formula, n_{Ca} . Samples for which $1.00 < n_{\text{Ca}} < 1.07$ consist of a single dolomite phase whereas each sample with $n_{\text{Ca}} \geq 1.07$ contain two coexistent phases which differ from each other by content of Ca, their relative

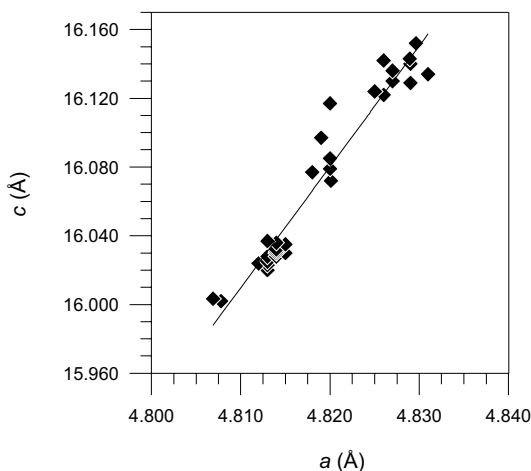


Fig. 8. Relationship between a and c unit cell parameters for samples studied by Reeder & Sheppard (1984).

proportions, degree of structural order and unit cell parameters. There are two populations of low and high excess-Ca phases with $1.00 \leq n_{Ca} \leq 1.10$ and $n_{Ca} > 1.15$, respectively. In contrast to Reeder & Sheppard (1984) it is found that the refined lattice parameters and *hkl* spacings are interrelated with each other by linear equations with strong linear correlation coefficients ($R > 0.99$). These linear relationships demonstrate that the lattice parameters and *hkl* spacings covary linearly with Ca content. This conclusion is in agreement with linear relationships determined between the amounts of Ca in structural formula and the lattice parameters determined by two independent techniques. It is probable that the linear relationships between unit cell parameters and Ca content occur in non-stoichiometric dolomites in which excess-Ca is located only in B structural sites. It is shown that these linear equations can be used for estimation of Ca content in a dolomite phase independent of excess of Ca in this phase.

To distinguish mono and two-phase dolomite samples the following diffraction criteria may be used. The XRD patterns of monophase samples should contain symmetrical *hkl* reflections especially above $66^\circ 2\theta$ (Cu $K\alpha$). Two-phase dolomite samples should show either visually resolved peaks with the same *hkl* indices or the peaks should show a pronounced shoulder indicating the presence of a second phase. Removal of the $K\alpha_2$ contribution is necessary to reveal such features. However, XRD patterns of some excess-Ca dolomite samples may contain so strongly asymmetrical reflections on the high 2θ angle side that the techniques described can not be applied. In such samples computer simulation of the diffraction effects may be required to describe the structure of each coexisting phase.

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