

Synchrotron High-Resolution XRD and thermal expansion of synthetic Mg Calcites

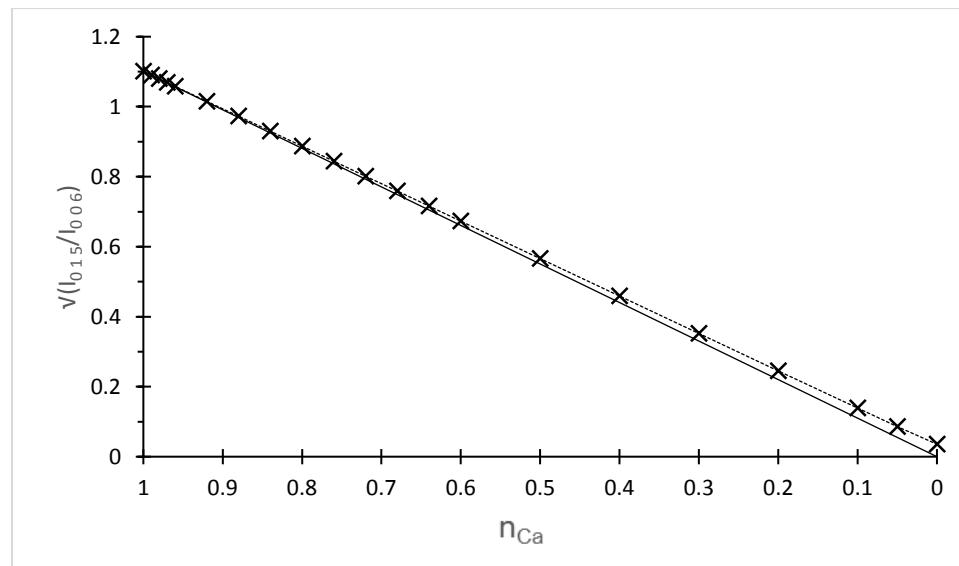
Nicole Floquet,^{*,a} Daniel Vielzeuf,^a Vasile Heresanu,^a Didier Laporte^b and Jonathan Perrin.^c

^a Aix-Marseille University, CNRS, CINaM UMR7325, 13288 Marseille, France

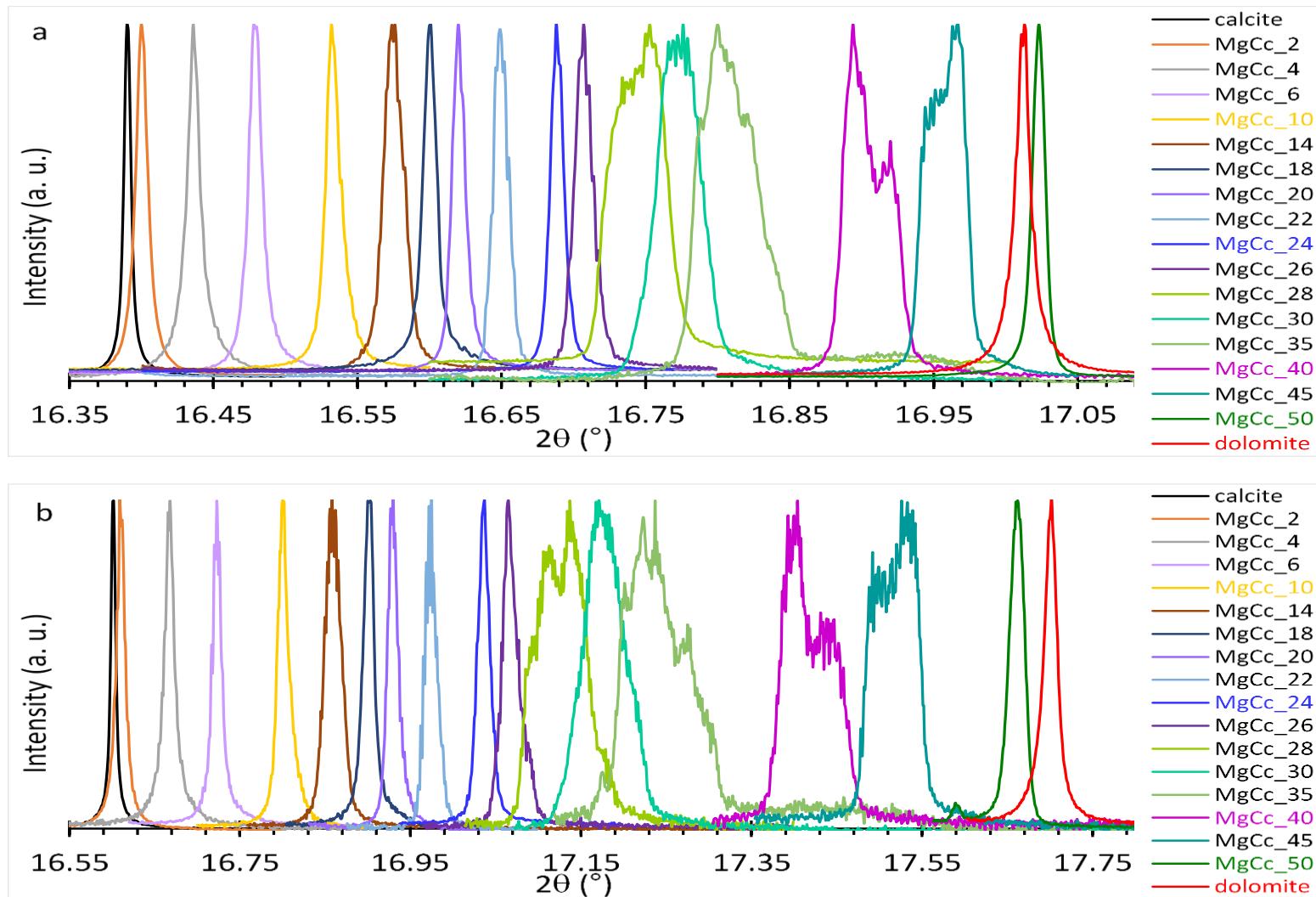
^b Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, 63000 Clermont-Ferrand, France

^c Synchrotron SOLEIL, BP 38, Saint-Aubin, Gif-sur-Yvette, France

*Corresponding author N. Floquet.: floquet@cinam.univ-mrs.fr



Supp. Mat. Fig. S1. Long range order parameter $\sqrt{(I_{015}/I_{006})}$ calculated for dolomite as a function of Ca occupancy (n_{Ca}) at its normal site in the dolomite structure. The order parameter varies as $\sqrt{(I_{015}/I_{006})} = 0.0058 \times n_{Ca}^2 + 1.0621 \times n_{Ca} + 0.0335$. Black line is linear line $\sqrt{(I_{015}/I_{006})} = 1.1x$ from fully ordered dolomite ($n_{Ca} = 1$) to calcite ($n_{Ca} = 0$)



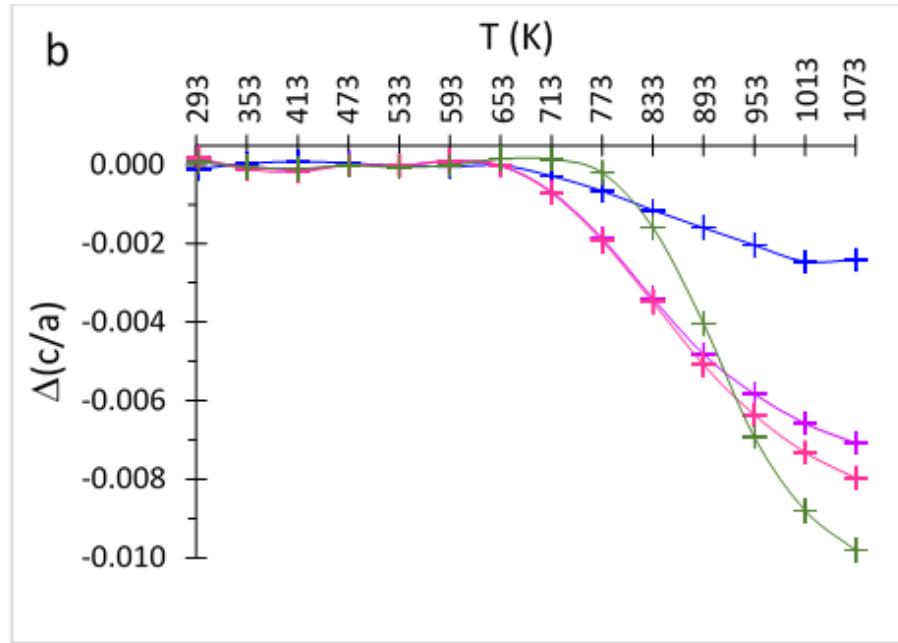
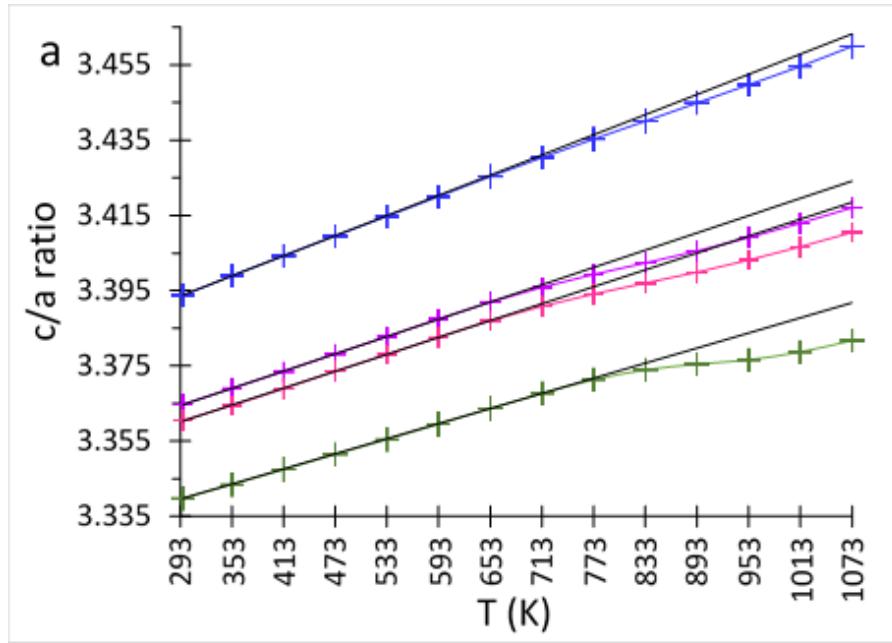
Supp. Mat. Fig. S2 a) (3 0 0) and **b)** (0 0 12) Bragg diffraction peaks of OCN calcite (black), synthetic magnesian calcites (MgCc₂ to MgCc₅₀) and OCN dolomite (red) [wavelength of $\lambda = 0.41068(1)$ Å (30 keV)].

Supp. Mat. Table S1 Refined unit cell parameters and FWHM of the (1 0 4) peak of MgCc24 and MgCc40 from SXRPD patterns recorded at increasing temperature under self-controlled CO₂ [wavelength of 0.41068(1) Å (30 keV)]

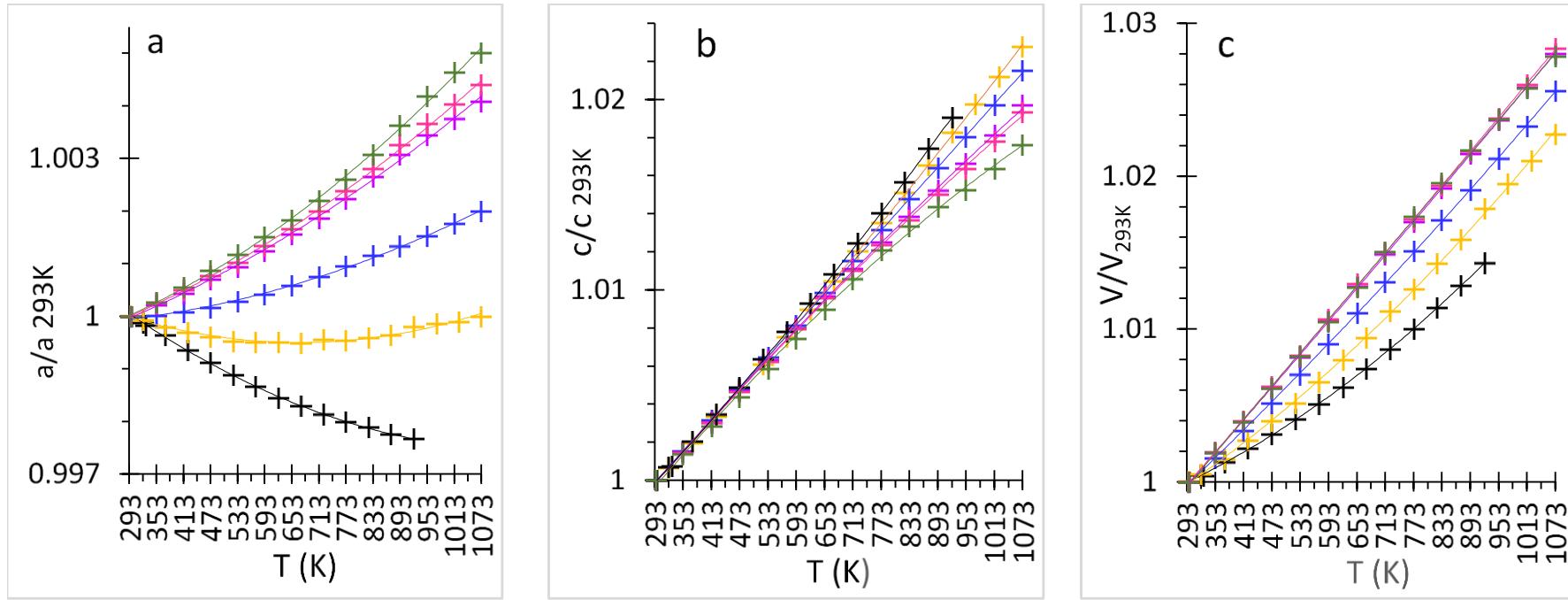
Structural parameters	Annealing temperature (K)														
	RT	353	413	473	533	593	653	713	773	833	893	953	1013	1073	RT after heat
<i>MgCc24</i>															
<i>a</i> (Å)	4.90156(5)	4.90161(4)	4.90191(1)	4.90236(1)	4.90292(1)	4.90364(1)	4.90443(3)	4.90527(6)	4.90619(7)	4.90722(8)	4.90810(2)	4.90906(5)	4.91014(6)	4.91135(3)	4.90154(7)
<i>c</i> (Å)	16.63502(5)	16.66049(4)	16.68759(9)	16.71485(7)	16.74227(3)	16.77056(3)	16.79932(4)	16.82680(7)	16.85399(8)	16.88102(5)	16.90777(2)	16.93483(9)	16.96244(2)	16.99277(5)	16.63447(8)
<i>FWHM(104) °2θ</i>	0.0077	0.0076	0.0077	0.0076	0.0076	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0075	0.0077	0.0077	0.0077
<i>MgCc40 phase 1</i>															
<i>Weight%</i>	60.2(2)	60.2	60.2(2)	60.4(2)	60.3(2)	60.1(2)	60.2(2)	60.2(2)	60.2(2)	60.4(2)	60.5(3)	60.7(5)	61.3(7)	62.6(1.4)	64.0(1)
<i>a</i> (Å)	4.84162(3)	4.8426(3)	4.84375(3)	4.84500(3)	4.84613(3)	4.84760(3)	4.84913(4)	4.85064(4)	4.85240(4)	4.85443(4)	4.85646(7)	4.85823(1)	4.8598(2)	4.8614(2)	4.84346(3)
<i>c</i> (Å)	16.2909(1)	16.3149(1)	16.3404(1)	16.3675(1)	16.3934(1)	16.4212(1)	16.4481(1)	16.4722(2)	16.4947(2)	16.5165(2)	16.5388(3)	16.5622(5)	16.5862(1)	16.611(1)	16.2870(1)
<i>FWHM(104) °2θ</i>	0.0125	0.0126	0.0127	0.0125	0.0126	0.0122	0.0122	0.0124	0.0123	0.0125	0.0128	0.0126	0.0125	0.0123	0.0136
<i>MgCc40 phase 2</i>															
<i>Weight%</i>	39.8(2)	39.8	39.8(2)	39.6(2)	39.7(2)	39.9(2)	39.8(2)	39.8(2)	39.8(2)	39.6(2)	39.5(2)	39.3(4)	38.7(6)	37.4(1)	36.0(1)
<i>a</i> (Å)	4.83551(2)	4.83674(3)	4.83792(3)	4.83925(4)	4.84043(4)	4.84196(4)	4.84355(4)	4.84515(4)	4.84700(4)	4.84906(5)	4.85123(8)	4.85318(1)	4.8549(2)	4.8567(2)	4.83823(2)
<i>c</i> (Å)	16.2499(1)	16.2732(1)	16.2986(1)	16.3256(1)	16.3512(1)	16.3788(1)	16.4053(1)	16.4291(2)	16.4511(2)	16.4723(2)	16.4937(3)	16.5160(5)	16.5391(1)	16.564(1)	16.24349(1)
<i>FWHM(104) °2θ</i>	0.0148	0.0148	0.0145	0.0146	0.0146	0.0148	0.0149	0.0146	0.0146	0.0142	0.0142	0.0145	0.0148	0.0152	0.0197

Supp. Mat. Table S2 - Refined unit cell parameters, FWHM of the (1 0 4) peak and $\sqrt{I_{015}/I_{006}}$ order parameter of synthetic MgCc50 (dolomite) from HRXRPD patterns recorded at increasing temperature under self-controlled CO₂ [wavelength of 0.41068(1) Å (30 keV)]

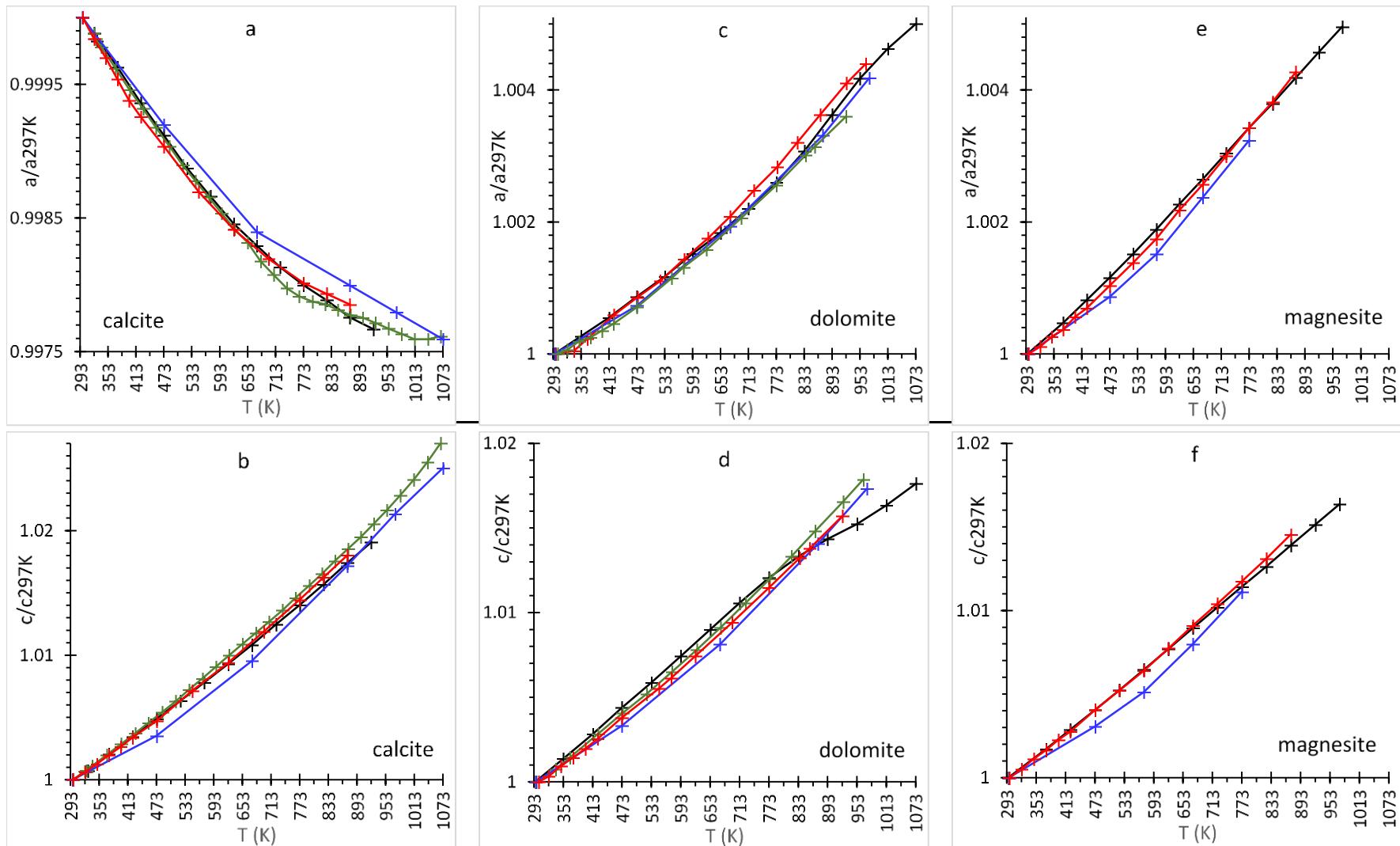
Structural parameters	Annealing temperature (K)													
	RT	353	413	473	533	593	653	713	773	833	893	953	1013	1073
<i>MgCc50</i>														
a (Å)	4.80585(4)	4.80713(7)	4.80847(6)	4.81002(4)	4.81149(2)	4.81313(7)	4.81467(1)	4.81643(5)	4.81833(3)	4.82061(4)	4.82326(8)	4.82591(3)	4.82810(1)	4.82989(4)
c (Å)	16.05064(8)	16.07256(5)	16.09605(8)	16.12090(1)	16.14480(5)	16.16984(9)	16.19503(8)	16.22018(1)	16.24418(3)	16.26439(9)	16.28083	16.29514(3)	16.31278(5)	16.33330(9)
FWHM(1 0 4) 2θ (°)	0.0083(2)	0.0083 (0)	0.0082(6)	0.0083(1)	0.0084(1)	0.0084(2)	0.0084(8)	0.0084(6)	0.0083(1)	0.0083(3)	0.0084(1)	0.0088(1)	0.0091(5)	0.0110(1)
$\sqrt{I_{015}/I_{006}}$	0.634	0.630	0.628	0.640	0.645	0.640	0.647	0.650	0.670	0.721	0.805	0.882	0.908	0.908



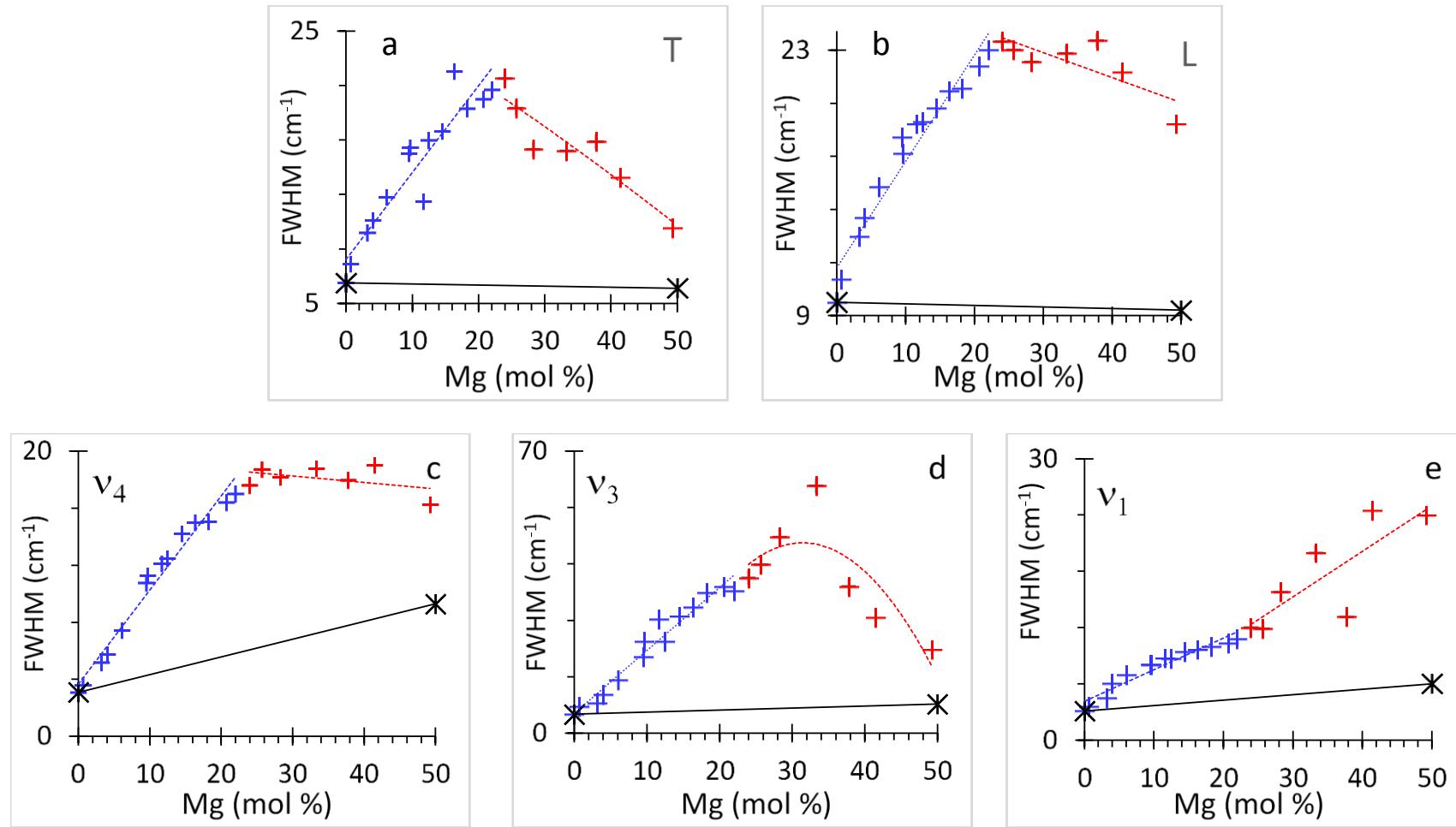
Supp. Mat. Fig. S3 **a)** Thermal expansion of the c/a ratio between 293 K and 653 K; **b)** c/a ratio excess from linearity as a function of T for MgCc24 (blue), MgCc40-1 and 2 (purple and pink) and MgCc50 (green), respectively



Supp. Mat. Fig. S4 Relative thermal expansion of the cell parameters **a)** a/a_{293K} , **b)** c/c_{293K} and **c)** V/V_{293K} ratio as function of T for OCN calcite (black), synthetic MgCc10 (yellow), MgCc24(blue), MgCc40 (purple and pink), MgCc50 (green)



Supp. Mat. Fig. S5 a) and b) Relative thermal expansion of the cell parameters $a/a_{293\text{K}}$ and $c/c_{293\text{K}}$ as function of T for OCN calcite (black) Markgraf and Reeder, 1985 (blue) – Merlini et al., 2016 (red), Antao et al., 2009 (green), **c) and d)** – idem for dolomite : OCN dolomite Reeder and Markgraf, 1986 (blue) De Aza 2002 (green) Merlini et al., 2016 (red) and MgCc50 (black), **e) and f)** – idem for magnesite: OCN magnesite(black) Markgraf and Reeder, 1985 (blue) Merlini et al., 2016 (red). No thermal measurements on OCN dolomite was realized by ourselves



Supp. Mat. Fig. S6 Full-width at half maximum of the Raman modes of synthetic Mg calcites as a function of composition in the range 0–50 mol% MgCO_3 . Blue plus: low-Mg synthetic calcites, Red plus: high-Mg synthetic calcites, OCN calcite and OCN dolomite are also shown (dark crosses) (after Perrin et al. 2016)