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1 **High-resolution solid-state ⁷Li NMR study of lithium incorporation in**
2 **calcite and aragonite**

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21 **Abstract:**

22 The concentration of Li and its isotope compositions in CaCO₃ minerals have been
23 proposed as emerging paleo-environmental tools. Yet the bonding environment of Li in these
24 phases, a prerequisite for interpreting mechanisms controlling Li incorporation and isotope
25 fractionation, is not known. In this study, for the first time ever the atomic-scale environment
26 of lithium in two synthetic calcite and aragonite samples is determined using ⁷Li Magic Angle
27 Spinning Nuclear Magnetic Resonance (MAS NMR). The spectra display several overlapping
28 signals with ⁷Li chemical shift ranging between -2 and +1 ppm in the calcite sample, and
29 spanning a narrower range, from -1 to 0 ppm, in the aragonite sample. This attests to a
30 diversity of Li atomic-scale environments, which are interpreted in the light of a theoretical
31 study of Li-bearing calcite and aragonite models using the Density Functional Theory (DFT).
32 In the aragonite sample, Li is dominantly located at neighbouring substitutional and interstitial
33 sites, the interstitial Li atom ensuring the charge balance of the Li for Ca substitution. In the
34 calcite sample, Li ions occur at substitutional and interstitial sites but additional mechanisms
35 could ensure the charge balance, notably involving the incorporation of H⁺ ions at nearby
36 carbonate sites. This variability of Li solid-state environment could explain why it is
37 challenging to identify the dominating factors controlling the Li incorporation in inorganic
38 calcium carbonates from aqueous solutions.

39 **Keywords:**

40 Calcite, Aragonite, lithium, NMR, DFT calculations, GIPAW

41

42 1. Introduction

43 The trace element composition of CaCO₃ minerals calcite and aragonite are routinely
44 used to inform about environmental changes of Earth's aquatic environments over the
45 geological past. For example, the ratios of divalent cations such as Ba, Mg and Sr in
46 biominerals such as foraminifera and corals have been used to assess variations in water
47 temperature (e.g. Beck et al., 1992; Nürnberg et al., 1996) or terrestrial input (Lewis et al.,
48 2018), among other parameters. Given the significant knowledge that can be extracted from
49 the trace element composition of CaCO₃ minerals, a large number of studies has been devoted
50 to understanding the parameters affecting trace element distribution in calcite and, to a lesser
51 extent, aragonite, since the '80s (e.g. Lorens, 1981; Mucci, 1986, 1987; Zhong and Mucci,
52 1989; Burton and Walter; 1991; Tesoriero and Pankow, 1996; Dietzel et al., 2004; Lee and
53 Reeder, 2006; Lakshtanov and Stipp, 2007; Balan et al., 2016; Mavromatis et al., 2022). In
54 the past two decades, owing to the technological ability to precisely measure the isotopic
55 compositions of trace elements in natural samples, experimental studies have also focused on
56 unravelling the role of physicochemical parameters on the isotope distribution between solid
57 and fluid (e.g. Tang et al., 2008, 2012; Immenhauser et al., 2010; Horner et al., 2011; Böhm et
58 al., 2012; Balan et al., 2018; Brazier et al., 2024). The interpretation of elemental distribution
59 between CaCO₃ mineral and aqueous fluid for divalent cations (Me²⁺) usually relies on an
60 ideal replacement of one Ca²⁺ ion in the solid with a Me²⁺ trace, leading to the formation of a
61 solid-solution. This approach is supported by synchrotron-based observations, which suggest
62 that the presence of Me²⁺ in calcite or aragonite yields a coordination of Me²⁺ to 6 or 9
63 oxygen atoms, respectively, denoting ideal replacement for Ca²⁺ ion (e.g. Reeder et al., 1999;
64 Allison et al., 2005; Finch and Allison, 2007; Finch et al., 2010).

65 Natural carbonates however, also contain monovalent ions such as sodium or lithium.
66 Specifically, the concentration and isotopic composition of lithium in natural carbonate

67 samples have been seen as an emerging paleo-proxy for a number of environmental
68 parameters. For example, changes in the isotopic composition of Li in carbonate rocks have
69 been used to assess paleo-weathering and hydrothermal processes, and to provide a direct
70 insight into the regulation of the global carbon cycle and Earth's climate over geological time
71 (Vigier et al., 2009; Misra and Froelich, 2012; Vigier and Godd ris, 2015; Chen et al., 2023).
72 Additionally, because Li does not directly participate in any biological processes, it has been
73 used to infer physicochemical parameters such as dissolved inorganic carbon concentration,
74 pH, degree of seawater saturation with respect to calcite, temperature, and growth rate (e.g.
75 Hall and Chan, 2004; Marriott et al., 2004; Millot et al., 2004; Bryan and Marchitto, 2008;
76 Lear et al., 2010; Lear et al., 2010; Vigier and Godd ris, 2015; Branson et al., 2024).

77 However, the mechanisms controlling the incorporation of the monovalent Li^+ in
78 calcite and aragonite lattice are still elusive, which is a serious obstacle to the use of Li as a
79 proxy tool. Previous experimental studies involving the co-precipitation of Li with CaCO_3 ,
80 have shown that lithium incorporation in these minerals is influenced by various factors
81 including temperature, fluid composition, growth rate and crystal structure (Marriott et al.,
82 2004; F ger et al., 2019; Seyedali et al., 2021; Brazier et al., 2024). Notably, F ger et al.
83 (2019) argued that incorporation of Li in calcite cannot be associated to only one coordination
84 environment in the solid, due to isotopic variations under different pH conditions. These
85 results have been further confirmed by Branson et al. (2024) who reported a correlation
86 between the Li partitioning coefficient and the solution pH. However, Branson et al. (2024)
87 did not identify any parameter controlling Li isotope fractionation. In this context, an atomic-
88 scale understanding of Li speciation in carbonates could bring important information about its
89 incorporation mechanism.

90 In this study, the local environment of ^7Li in two synthetic samples of Li-bearing
91 calcite and aragonite was probed by high-resolution solid-state ^7Li MAS NMR spectroscopy.

92 Solid-state NMR is a chemically selective technique that can provide detailed information on
93 the local chemical environment of elements, even to trace amount in crystal (Mavromatis et
94 al., 2015; Balan et al., 2016). NMR analyses was performed at a high magnetic field (17.6 T),
95 significantly increasing the sensibility and spectral resolution. In parallel, the structure and ^7Li
96 NMR spectroscopic properties of models of Li-bearing calcite and aragonite were analysed
97 using density functional theory. These models correspond to various schemes of Li
98 incorporation at the Ca structural site or at interstitial sites of the crystal structures. The
99 comparison of the theoretical results and NMR analytical data attests to the diversity of ^7Li
100 environments in the investigated calcite and aragonite samples.

101

102 **2. Materials and methods**

103 **2.1. Samples**

104 Two synthetic samples of Li-bearing aragonite and calcite containing 18 and 550
105 ppm of Li, respectively, were used for ^7Li NMR analyses. The aragonite sample LiAr-18 that
106 used in this study derived from the earlier work by Mavromatis et al. (2022) and additionally
107 contains ~100 ppm Mg. Briefly this sample was produced by co-precipitation of Li with
108 aragonite on Li free aragonite seeds. For details, we refer the reader to Mavromatis et al.,
109 (2022). Note here that in the analysed sample Li is incorporated solely in aragonite as
110 mentioned by Mavromatis et al. (2022) which is the only mineral precipitating in this
111 experiment as denoted by the lower abundance of calcite in the overgrowth compared to the
112 seed as quantified by XRD spectra and Rietveld refinement. The calcite sample was
113 synthesized by mixing equal volumes (i.e. 50mL) of a Li_2CO_3 and a CaCl_2 solution. The
114 concentrations of Ca^{2+} and CO_3^{2-} after mixing were 10 and 12 mM, respectively. The mixture,
115 incubated at 40°C for 7 days under continuous stirring. The precipitated solid was separated

116 from the fluid by suction filtration. The final solution had a pH of 6.5 and the concentration of
117 Ca and alkalinity were 8.0 and 10.0 mM, respectively.

118

119

120 **2.2. Solid characterization**

121 **2.2.1. Powder X-ray diffraction**

122 Powder X-ray diffraction (PXRD) patterns (Fig. S1) were recorded between 20° and
123 90° (2 θ) with a 0.02° step size using a Bruker D8 Advance laboratory diffractometer (Cu
124 K $\alpha_{1,2}$ radiation) equipped with a LynxEye XE detector in Bragg–Brentano geometry.

125

126 **2.2.2 ⁷Li MAS NMR analyses**

127 Solid state ⁷Li NMR spectra were obtained using a Bruker AVANCE NEO 750 (17.6
128 T) NMR spectrometer operating at 291.5 MHz at spinning frequencies ranging from 5 to 14
129 kHz, using a 4 mm Bruker MAS probe. A ⁷Li radiofrequency field strength of 50 kHz was
130 used and a small flip angle ($\pi/6$) was utilized with recycle delays of 30 s to ensure complete
131 magnetisation for the ⁷Li MAS NMR analyses. The rotors were filled up in a glove-box under
132 dried Ar atmosphere and approximately 2000 scans were accumulated during each
133 acquisition. NMR MAS measurements were performed at -28, +22 and +65 °C. Temperature
134 was controlled and measured using thermocouples inserted in the NMR probe and the
135 temperature calibration was performed through the ⁷⁹Br shift of KBr (Thurber and Tycko,
136 2009). The ⁷Li chemical shifts were referenced to a 1M LiCl solution.

137

138 **2.3 Theoretical modelling**

139 In the past thirty years, theoretical methods based on the density functional theory
140 (DFT) have reached a level of accuracy high enough to predict the properties of
141 geochemically relevant systems (e.g., Cygan and Kubicki, 2001). In the present study, the
142 theoretical properties of models of Li-bearing calcium carbonates were investigated at the
143 DFT level, following an approach similar to that previously used to investigate the boron and
144 sulphate environment in calcite and aragonite (Balan et al. 2014; 2016). The generalized
145 gradient approximation (GGA) to the exchange-correlation functional as proposed by Perdew,
146 Burke, and Ernzerhof (PBE) (Perdew et al. 1996). was used and calculations were performed
147 with the QUANTUM ESPRESSO package (Giannozzi et al., 2009). The ionic cores were
148 described using norm-conserving pseudopotentials from the Optimized Norm-Conserving
149 Vanderbilt (ONCV) library (Hamann, 2013). Electronic wave-functions and charge density
150 were expanded with plane-wave basis sets with cutoffs 80 and 480 Ry, respectively,
151 corresponding to a total energy convergence better than 1 mRy/atom.

152 Periodic models of Li-bearing calcium carbonates were built for the two common
153 CaCO_3 polymorphs: calcite (space group $R\bar{3}c$, $Z=2$) and aragonite ($Pmcm$, $Z=4$). The models
154 were built by inserting one or two Li atoms in $2\times 2\times 2$ supercells of calcite (rhombohedral cell,
155 80 atoms) or aragonite (160 atoms). The sampling of the reciprocal space for the electronic
156 integration was restricted to the centre of the Brillouin zone (Γ point). Cell parameters of the
157 pure phases ($a = 12.83 \text{ \AA}$, $\alpha = 46.28^\circ$ for the rhombohedral supercell of calcite; $a = 10.03 \text{ \AA}$, b
158 $= 16.02 \text{ \AA}$, $c = 11.63 \text{ \AA}$ for the orthorhombic supercell of aragonite) were optimized at zero
159 pressure and were used without further relaxation to produce the Li-bearing supercells. The
160 relaxation of atomic internal coordinates was performed until the residual forces were $<10^{-4}$
161 Ry per atomic unit. The structure files (.cif) of the models are provided as Supplementary
162 Information.

163 The NMR properties of ${}^7\text{Li}$ (nuclear spin $I = 3/2$) involve both the Zeeman effect and
164 the interaction of the nuclear quadrupolar moment with the electric field gradient (EFG) at the
165 nucleus. Accordingly, the ${}^7\text{Li}$ NMR spectra are characterized by three parameters: the
166 chemical shift δ_{iso} , the quadrupolar coupling constant C_Q and the asymmetry parameter η .

167 The NMR chemical shift δ_{iso} is defined as $\delta_{\text{iso}} = -(\sigma - \sigma^{\text{ref}})$, where σ is the isotropic
168 shielding (one-third of the trace of the NMR shielding tensor) and σ^{ref} is the isotropic
169 shielding of the same nucleus in a reference system. It can be obtained from the structural
170 models by calculating the shielding of the nuclei relative to the electronic current induced by
171 the external magnetic field, using the Gauge Including Projector Augmented Waves (GIPAW)
172 approach, which allows reconstructing the all-electron magnetic response from the pseudo-
173 wave-functions (Pickard and Mauri, 2001; Charpentier, 2011; Bonhomme et al., 2012). For
174 this calculation, GIPAW pseudopotentials (Giannozzi et al., 2009) were used with cutoffs of
175 80 and 480 Ry for the wave-functions and charge density, respectively. The conversion of
176 absolute shielding tensors in isotropic chemical shifts was done using a calibration curve
177 relating the ${}^7\text{Li}$ chemical shift δ_{iso} and the calculated magnetic shielding σ_{iso} for a series of Li-
178 bearing compounds (Fig 1; Tables S1 and S2). The corresponding best linear fit is expressed
179 as $\delta_{\text{iso}} = -0.7532\sigma_{\text{iso}} + 67.19$ with a regression factor 0.9784. Crystallographic data and
180 isotropic chemical shifts δ_{iso} used in these benchmarking calculations were taken from Köcher
181 et al. (2018). On average, the difference between measured and calculated ${}^7\text{Li}$ chemical shifts
182 is $\Delta\delta_{\text{iso}} = \pm 0.3$ ppm. The C_Q and η parameters are related to the eigenvalues (V_{zz} , V_{xx} and V_{yy})
183 of the electric field gradient. V_{zz} has the largest magnitude, while V_{xx} and V_{yy} correspond to
184 the other two eigenvalues, ordered such that $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. The asymmetry parameter
185 $\eta_Q = (V_{xx} - V_{yy})/V_{zz}$ describes the deviation of the EFG from axial symmetry, tensor and reflect
186 the symmetry of the Li site. These quantities were calculated for all the models.

187 3. Results

188 3.1. ⁷Li MAS NMR of calcite and aragonite

189 The ⁷Li MAS NMR spectra of calcite and aragonite samples obtained at room
190 temperature (Fig. 2) included the central transition as well as the complete set of spinning
191 sidebands corresponding to the $\langle \pm 1/2, \pm 3/2 \rangle$ satellites. The spectra of the two samples were
192 recorded at various spinning speeds but only the most informative spectra, recorded at 5 kHz,
193 are reported here and analysed. These spectra were chosen due to the full presence of spinning
194 sidebands, which is a prerequisite for determining the quadrupolar coupling constant C_Q . The
195 central line in calcite is dominated by an asymmetric contribution with a maximum at 0.20
196 ppm and several shoulders at 0.87, -0.33 and -1.13 ppm. A weaker but well-defined peak is
197 observed at -1.87 ppm. In aragonite, the central line corresponds to a single peak at -0.50 ppm
198 with a slight asymmetry on the negative chemical shifts side. The asymmetric and structured
199 shape of these spectra reflects the presence of several overlapping contributions, attesting to
200 the occurrence of different lithium environments in the samples. At this stage, an
201 unambiguous decomposition of the spectrum into individual contributions cannot be achieved
202 solely based on the room temperature (22 °C) spectral data.

203 To better identify individual contributions present in the NMR spectra, the ⁷Li NMR
204 spectra of calcite and aragonite samples were recorded at different temperatures (65, 22, -28
205 °C) (Fig. 3). In both polymorphs, the position of the main line shifts by approximately +0.52
206 ppm from -28 °C to 65 °C. In calcite, the narrow signal at -1.87 ppm also displays a notable
207 shift with temperature. In addition, a significant broadening of the main line is observed in the
208 spectra recorded at -28 °C. While a detailed analysis of the evolution of the full width at half
209 maximum (FWHM) of the individual peaks is not possible, the observed changes suggests
210 that a broader static distribution of sites occurs at lower temperature while the lines are
211 narrowed at higher temperature (Massiot, 1990; Wagemaker et al., 2001).

212 3.2. Analysis of NMR spectra

213 A deconvolution of the collected spectra (Fig. 4), including all spinning sideband
214 patterns, was performed using the “disperse” model integrated in Dmfit software (Massiot et
215 al., 2002). This model enables the determination of the ^7Li chemical shift δ_{iso} and quadrupolar
216 coupling constant (C_Q), allowing for a quantitative analysis of the proportion of different
217 contributions. It assumes a Gaussian distribution of the V_{zz} component in the electric field
218 gradient (EFG) tensor, leading to a distribution of C_Q . However, V_{xx} and V_{yy} are held
219 constant, which prevents the determination of the asymmetry parameter (η_Q).

220 The fitting of spectra at different temperature was carried out using the same C_Q
221 values and the same proportion of lithium sites, while the chemical shift ^7Li and FWHM of
222 each line were allowed to vary.

223 The best fit accounting for both the central and the satellite transitions required seven
224 different ^7Li structural environments for the calcite samples (Fig. 4). For the aragonite sample,
225 only two contributions were required (Fig. 4). The different ^7Li contributions identified in
226 calcite are labelled as Li_x ($x=1,\dots,7$) and cover a chemical shift range of ~ 2.74 ppm. A strong
227 overlap is however observed between the Li_1 , Li_2 and Li_3 contributions ($\sim 76\%$ of the
228 spectrum area) and the Li_4 and Li_5 contributions ($\sim 17\%$ of the spectrum area). The chemical
229 shifts of all these contributions exhibit a similar temperature dependence (Fig. 5).

230 For the aragonite sample, only two contributions were required to fit the spectra at
231 22°C and 65°C (Fig. 4). In the spectrum at 22°C , the Li_1 contribution is dominant and
232 accounts for 93% of the total area. It was necessary to add a third contribution (Li_3) to
233 account for the broadening of the spectrum at -28°C compared to the spectra recorded at
234 higher temperatures (Fig. 4). The NMR parameters determined at different temperatures are
235 reported in Tables 1 and S3. The ^7Li chemical shifts in the aragonite sample cover a smaller
236 range (~ 0.45 ppm) than in the calcite sample. The Li_1 contribution in aragonite is more
237 sensitive to the temperature change than the Li_2 contribution (Fig. 5)

238 In the calcite and aragonite samples, the average value of the ^7Li quadrupolar coupling
 239 constants (C_Q) is 0.06 MHz, while the C_Q values determined for the various sites do not
 240 display significant variations with respect to the corresponding uncertainty range (± 0.05
 241 MHz) (Table 1).

242 **Table 1.** ^7Li isotropic chemical shifts (δ_{iso}), quadrupolar coupling constants (C_Q),
 243 FWHM and Integral intensities (I) obtained from the simulation of the ^7Li MAS NMR spectra
 244 calcite and aragonite obtained at 22 °C.

<i>Sample</i>	<i>Lithium site</i>	δ_{iso} , ppm (± 0.02 ppm)	C_Q , MHz (± 0.05 MHz)	FWHM (Hz) (± 10 Hz)	I, % ($\pm 1\%$)
<i>Calcite</i>	Li1	0.87	0.08	120	8
	Li2	0.33	0.06	230	53
	Li3	0.17	0.01	130	15
	Li4	-0.33	0.09	175	12
	Li5	-0.68	0.06	170	5
	Li6	-1.13	0.09	140	2
	Li7	-1.87	0.04	100	5
<i>Aragonite</i>	Li1	-0.50	0.05	150	93
	Li2	-0.95	0.10	200	7

245

246 3.3 Theoretical models of Li sites in calcite and aragonite

247 The NMR properties of selected models of Li bonding environments in calcite and
 248 aragonite have been considered to support the interpretation of experimental spectra (Fig. 6).
 249 The .cif files of these models are provided as supplementary information.

250 The model “Li_{sub}” was obtained by substituting one Li⁺ for one Ca²⁺ ion in the
251 supercells, using a homogeneous electrostatic background to ensure the electrostatic neutrality
252 of the system. Such model is expected to mimic a relatively remote charge compensation, in
253 which the macroscopic neutrality of the crystal is ensured by impurities or defects which are
254 located sufficiently far apart from the substituted site to leave its local structure unaffected. In
255 calcite, the coordination of Li is similar to that of Ca and corresponds to a weakly distorted
256 octahedron with Li-O bond lengths ranging between 2.32 and 2.35 Å. In aragonite, the nine-
257 fold coordination of Ca corresponds to a more complex and elongated geometry with varying
258 Ca-O bond lengths and angles (Finch and Allison, 2007). The corresponding atomic-scale
259 environment of substitutional Li in aragonite is significantly distorted with Li-O bond lengths
260 ranging between 2.0 and 3.3 Å.

261 The model “Li_{int}” was obtained by setting the Li atom at the most probable interstitial
262 site position. In calcite, this interstitial site lies between carbonates groups CO₃²⁻ groups and
263 the CaO₆ coordination polyhedra along the c-axis, with a radius of approximately 0.86 Å
264 (Ishikawa and Ichikuni, 1984). This site has been identified as a potential incorporation site
265 for monovalent cations such as Na⁺ and K⁺ (Ishikawa and Ichikuni, 1984). The Li is in 6-fold
266 coordination with Li-O bond lengths ranging between 1.92 and 2.42 Å. In the denser structure
267 of aragonite, the interstitial environment of Li corresponds to a four-fold coordination with
268 Li-O bond lengths ranging between 1.8 and 2.0 Å.

269 The “Li_{sub}+Li_{int}” model combines the two previous configurations, leading to an
270 electrostatically neutral configuration. In this case, it was assumed that electrostatic
271 interactions favour the configuration corresponding to the shortest distance between Li_{sub} and
272 Li_{int}. In calcite, the two Li ions display an almost regular triangular coordination with a Li-O
273 bond length of 1.877 Å, forming nearly parallel and off-centered LiO₃ triangles. In aragonite,
274 the two Li atoms occupy the opposite faces of the vacant 9-fold Ca site. They display different

275 atomic-scale environments, with 4-fold (Li-O bond lengths between 1.9 and 2.15 Å) and 5-
 276 fold (Li-O bond length between 1.89 and 2.12 Å) coordinations.

277 Finally, two “Li_{sub}+H” models have been considered. They correspond to a Li⁺ for
 278 Ca²⁺ substitution with an electrostatic charge compensation ensured by a proton bonded to a
 279 neighbouring CO₃ group. In this case, a position closer to the charge-deficient Li site was
 280 selected. In both polymorphs the OH group points out of the CO₃ triangle, sharing a
 281 moderate-strength H-bond with an oxygen atom belonging to an adjacent carbonate group. In
 282 calcite, the Li atom is in 3-fold coordination and located on the opposite face of the octahedral
 283 site, while it occurs in a distorted 4-fold coordination in aragonite (Fig. 6).

284

285 **Table 2.** Theoretical ⁷Li isotropic chemical shifts (δ_{iso}), quadrupolar coupling
 286 constants (C_Q), and shortest Li-O bond length, predicted by the density functional theory
 287 calculations for the different Li-bearing calcite and aragonite models.

<i>Mineral</i>	<i>Model</i>	<i>Li site</i>	<i>shortest Li-O bond length (Å)</i>	δ_{iso} (ppm)	C_Q (MHz)
<i>Calcite</i>	Li _{sub}	Li _{sub}	2.328	-2.28	0.06
	Li _{int}	Li _{int}	1.923	0.00	0.32
	Li _{sub} +H	Li _{sub} +H	1.919	-0.18	0.35
	Li _{sub} +Li _{int}	Li _{sub}	1.877	0.86	0.56
			Li _{int}	1.877	0.86
<i>Aragonite</i>	Li _{sub}	Li _{sub}	2.019	-1.38	0.22
	Li _{int}	Li _{int}	1.797	0.14	0.18
	Li _{sub} +H	Li _{sub} +H	1.974	-1.04	0.22
	Li _{sub} +Li _{int}	Li _{sub}	1.917	-0.61	0.22

Li_{int}	1.887	-0.40	0.46
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288

289 Significant variations (~3.14 ppm) are observed in the theoretical ^7Li chemical shift
 290 across the different Li-bearing calcite models (Table 2). These variations are enough to be
 291 observed. In particular, the Li_{sub} substitutional model leads to a theoretical chemical shift at -2
 292 ppm while the other models lead to theoretical chemical shifts ranging between -0.2 and 0.9
 293 ppm. For aragonite, the range of theoretical ^7Li chemical shifts is about half as large as that
 294 obtained for calcite (Table 2), which could make distinguishing signals in the acquired NMR
 295 spectrum of aragonite more challenging. However, it is noteworthy that the simple
 296 substitutional model leads to the more negative value, as in calcite. The range of calculated
 297 quadrupolar coupling constants (C_Q) observed for the different types of lithium environments
 298 does not exceed 0.6 MHz (Table 2), indicating weakly distorted Li environments. The
 299 significant discrepancy between the fitted (Table 1) and calculated (Table 2) C_Q parameters
 300 may stem from dynamic effects (Dunstan et al., 2015) that are not accounted for in the static
 301 GIPAW calculations.

302 Although it is difficult to precisely determine the leading structural parameter
 303 controlling the ^7Li chemical shift, it can be noticed that the theoretical ^7Li chemical shifts in
 304 calcite and aragonite (Fig. 7) define two almost parallel trends when plotted as a function of
 305 the shortest Li-O bond length of the Li site. The relation with the other Li-O bond lengths
 306 (Table S3), or with the average Li-O bond length of the corresponding sites, is poorer. In
 307 calcite, a difference in Li-O bond length of 0.451 Å results in a difference larger than 2 ppm
 308 in the ^7Li chemical shift. The “ $\text{Li}_{\text{sub}}+\text{Li}_{\text{int}}$ ” model displays similar values for the shortest Li-O
 309 bond length of the two site, leading to a similar ^7Li chemical shift value for both lithium
 310 atoms. In the “ $\text{Li}_{\text{sub}}+\text{H}$ ” model, the presence of hydrogen modifies the local environment of
 311 lithium, leading to a decrease in the shortest Li-O bond length compared to the more

312 symmetric substitutional “Li_{Ca}” model. Compared with the Li_{sub} (-2.28 ppm) this structural
313 change induces a significant change in ⁷Li chemical shift which is close to 0 ppm.

314 Regarding aragonite, the shortest Li-O bonds are found for the interstitial Li model
315 (Table 2). Protonation of CO₃²⁻ group close to the substitutional lithium has a similar effect to
316 that observed in calcite, i.e. a shortening of Li-O bond lengths and an increase of the Li
317 chemical shift toward positive values. In the “Li_{sub}+Li_{int}” model, the shortest Li-O bond
318 length of the interstitial lithium is shorter than that observed on the substitutional Li in the
319 same model. This difference induces a slight difference in the ⁷Li chemical shift of the two
320 atoms; while the equivalent model in calcite provided an identical value for the two atoms in
321 triangular coordination (Table 2).

322

323 4. Discussion

324 4.1 Li environment in calcite

325 The ranges of theoretical ⁷Li chemical shifts are well consistent with those observed
326 on the calcite sample (Fig. 8; Table 2).

327 In calcite, the theoretical ⁷Li NMR chemical shift of the “Li_{sub}” model determined at -
328 2.28 ppm occurs within 0.5 ppm of the acquired value determined for the well-defined narrow
329 peak observed on the more negative side of the spectrum (Li7 contribution, -1.87; Table 1).
330 Accordingly, the Li7 contribution most likely correspond to Li atoms substituted at the
331 symmetric 6-fold Ca sites (“Li_{sub}” model). In this case, the charge compensation should be
332 ensured by a relatively more remote mechanism than in the other models. For instance,
333 macroscopic electroneutrality of the crystal can be given by impurities or defects located
334 sufficiently far apart from the substituted site. Based on this assignment and considering the
335 relative variations in the theoretical chemical shifts of the different models, the Li4 (-0.33

336 ppm) and Li5 (-0.68 ppm) contributions could correspond to substitutional Li atoms locally
337 compensated by the presence of protons in their local environment. The “Li_{sub}+H” model
338 leads to a slightly negative calculated shift of -0.18 ppm which is in an acceptable range
339 compared to the Li4 and Li5 values. In this case, the charge compensation is ensured by the
340 presence a nearby HCO₃⁻ group. Such a local mechanism induces a stronger site distortion and
341 potentially multiple configurations depending on the location and orientation of the OH
342 group. The potential occurrence of several configurations is consistent with the observation of
343 several overlapping contributions appearing on the low chemical shift side of the main band.
344 The interstitial Li model “Li_{int}” yields a theoretical shift of 0 ppm, consistent with the
345 acquired Li2 (0.33 ppm) and Li3 (0.17 ppm) signals which correspond to the main band,
346 which could suggest that the incorporation mechanism of Li in calcite predominantly involves
347 interstitial Li ions. However, it cannot be excluded that these signals also correspond to
348 Li_{sub}+H type environments, considering the proximity of the theoretical chemical shifts
349 determined for the Li_{sub}+H and Li_{int} models. Finally, the “Li_{sub}+Li_{int}” model, displaying both
350 substitutional and interstitial lithium, corresponds to a theoretical ⁷Li chemical shift of 0.86
351 ppm for both lithium sites. In this case, the interstitial Li⁺ cation ensures the local charge
352 balance of the neighbouring Li⁺ for Ca²⁺ substitution. This specific Li environment could
353 correspond to the shoulder clearly observed on the high chemical shift side of the main
354 resonance (Li1 contribution, 0.87 ppm). This suggests that even at low Li concentrations,
355 electrostatic constraints can favour a coupled incorporation of interstitial and substitutional Li
356 in calcite.

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358 **4.2 Li environment in aragonite**

359 In aragonite, the measured values range between -0.50 ppm for the dominant Li1
360 contribution and -0.95 ppm for the Li2 contribution at room temperature (Table 1).

361 Consistently, the range covered by the theoretical chemical shifts is smaller than in calcite,
362 from -1.38 ppm to 0.14 ppm for substitutional and interstitial lithium, respectively. By
363 comparison with the assignments proposed on calcite, the minor signal (Li2) could correspond
364 to substitutional lithium, either with remote charge compensation (“Li_{sub}” model, -1.38 ppm)
365 or more local charge compensation by H atoms (“Li_{sub}+H” model, -1.04 ppm). Due to the
366 proximity of the theoretical values and strong overlap of the bands, it is not possible to assign
367 the observed signals more precisely from the present data. The dominant contribution at -0.50
368 ppm actually corresponds to two components of similar intensity, which are resolved in the
369 spectrum recorded at -28 °C and differ by 0.27 ppm (Table S3). These properties are
370 consistent with those of the coupled incorporation “Li_{sub}+Li_{int}” model, which displays two Li
371 sites with slightly different theoretical chemical shifts at -0.61 and -0.40 ppm (Table 2). A
372 quantification based on the spectra at -28 °C (Table S3) suggests that, in the investigated
373 aragonite sample, about half of the lithium occupies a substitutional position and half is
374 located at the interstitial site, acting as charge compensator of the substitutional Li.

375

376 **4.3 Implications for the Li incorporation in calcium carbonates**

377 The obtained results offer insights into Li environment in carbonate group minerals.
378 This is of significant importance because Li and its isotopes in carbonates have been proposed
379 as emerging paleoenvironmental tools (e.g. Hall et al., 2004; Pogge von Strandmann et al.,
380 2019; 2020). Understanding however how physicochemical parameters affect the
381 concentration and isotope composition of Li in CaCO₃ minerals requires characterization of
382 bonding environment. This is because coordination and metal-oxygen (Me-O) bond length of
383 trace metal in the solid, can assist interpretations on trace metal concentration and isotope
384 fractionation. For example, the incorporation of Ba in aragonite is hindered due to its large
385 size compare to Ca in 9-fold coordination. However, the distribution coefficient of Ba in

386 aragonite is significantly larger compared to that in calcite, because Ba^{2+} (aq) has to reduce its
387 coordination number to 6 (Dietzel et al., 2004; Mavromatis et al., 2018). Moreover,
388 information of Me-O difference between a mineral and a fluid can be used to assess
389 enrichment or depletion of an isotope **under thermodynamics**. For example, the shorter/stiffer
390 Ba-O bond length in aragonite compared to Ba^{2+} (aq) suggest enrichment of the heavier
391 isotope in the solid (e.g. Schauble, 2004; Blanchard et al., 2017). These predictions have been
392 recently confirmed in synthetic samples and modelled using first-principle calculations
393 (Mavromatis et al., 2020). However, the variations of Li environment probed by NMR at
394 different temperatures suggest a significantly enharmonic behaviour confirming that the
395 relation of the Li bonding to its isotopic fractionation properties **could be** less straightforward
396 than for other chemical elements (Dupuis et al. 2017).

397 The challenge of characterizing Li environments in CaCO_3 minerals is not easy to
398 resolve because the spectroscopic techniques available are limited. Here for the first time we
399 show that ^7Li NMR spectroscopy can be used to assess environments of traces of Li in calcite
400 and aragonite. Note that earlier NMR spectroscopy has been successfully used to explore the
401 presence of B at low concentration in calcite and aragonite (e.g. Noireaux et al., 2015;
402 Mavromatis et al., 2021). Despite the limited number of investigated samples, the present
403 results offer a direct insight into Li environment in carbonate group minerals. The occurrence
404 of interstitial and substitutional Li in both calcite and aragonite samples confirms that
405 interstitial sites can play a key role in the incorporation of alkali ions in calcite (Ishikawa and
406 Ichikuni, 1984; Okumura and Kitano, 1986). The presence of several Li environments in a
407 single calcite sample is also consistent with the previous proposal that incorporation of Li in
408 calcite is likely associated to more than one coordination environments (Füger et al., 2022). In
409 contrast, the incorporation of Li in the investigated aragonite sample is dominated by a
410 coupled mechanism where Li occupies neighbouring substitutional and interstitial sites,

411 corresponding to incorporation as Li_2CO_3 . We acknowledge here that analyses of only one
412 sample for calcite and one for aragonite cannot provide concrete arguments for the differences
413 observed in Li concentration and isotope fractionation among synthetic samples of different
414 studies (e.g. Fuger et al., 2022 vs. Branson et al., 2024). Yet additional NMR measurements
415 together with the possible Li-O bond lengths presented in Table 2 can act as the basis for the
416 interpretations of Li isotope compositions in these samples in the future.

417 Overall the differences between aragonite and calcite, as well as the relatively complex
418 Li environment observed in each sample, underline the need of systematic analyses a series of
419 samples, aiming at identifying specific relations between the proportion of Li environments
420 and specific parameters such as the degree of fluid saturation and respective growth rate,
421 solution pH and mineral growth mechanisms. However, it has to be emphasized that the
422 incorporation of Li in natural carbonates could differ from those corresponding to inorganic
423 precipitation experiments. In Earth's aquatic environments CaCO_3 minerals may also form via
424 an amorphous precursor (Gilbert et al., 2022) a mineral formation pathway that can result in
425 trace element composition different from that expected during classical growth (e.g. Loste et
426 al., 2003; Littlewood et al., 2017; Purgstaller et al., 2017). As such, it should be considered
427 that Li bonding environments may be different in crystalline solids formed via an amorphous
428 precursor as for example it has been shown for Sr in calcite formed via ACC compared to
429 typical overgrowth by Littlewood et al. (2017). Moreover, it has to be pointed out that recent
430 works examining the role of mineral growth from solution enriched in SO_4^{2-} (aq) on uptake of
431 traces such as Mg or B have shown significant variations in distribution coefficients (e.g.
432 Goetschl et al., 2019; 2021; Uchikawa et al., 2023) associated with presence of sulphate in the
433 solid, but also in Mg isotope fractionation (e.g. Mavromatis et al., 2025). Considering that Li
434 occupies both substitutional positions and interstitial sites in both calcite and aragonite, as
435 shown above, presence of sulphate may as well produce additional Li bonding environments.

436 These observations suggest that the investigation of natural samples, and potential
437 identification of specific ^7Li NMR signatures, could bring new information about the
438 physicochemical conditions which prevailed during calcite or aragonite formation.

439 **5. Conclusions**

440 In this study we have for the first time shown that ^7Li MAS NMR spectroscopy can
441 differentiate Li bonding environments. Here we couple NMR analyses of two synthetic
442 samples with DFT calculations and show that Li in CaCO_3 minerals can occupy both
443 substitutional and interstitial sites. For aragonite NMR spectra show only two sites to occur,
444 one substitutional and one interstitial. In contrast in calcite 7 different sites have been
445 identified in which Li resides obtaining charge compensation with H^+ , OH^- and HCO_3^-
446 groups. Overall, this study provides the first characterization of Li bonding environment in the
447 two most abundant CaCO_3 polymorphs and sets the basis for additional work with NMR
448 spectroscopy as a tool for the interpretation of Li chemical and isotopic composition in natural
449 CaCO_3 minerals.

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