# The role of amorphous precursors in the crystallization of La and Nd carbonates (SUPPLEMENTARY INFORMATION)

Beatriz Vallina[a,*], Juan Diego Rodriguez-Blanco[a,b], Andrew P. Brown[c], Jesus A. Blanco[d], Liane G. Benning[a,e,*]

[a] School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK

[b] Nano-Science Center; Department of Chemistry; University of Copenhagen H.C. Oersted Institute, C Bygn, 9 Universitetsparken 5, DK 2100 Copenhagen, Denmark

[c] Institute for Materials Research, SCaPE, Faculty of Engineering. University of Leeds, LS2 9JT, UK.

[d] Departamento de Física, Universidad de Oviedo, Oviedo, E-33007, Spain

[e] Research Center for Geosciences, GFZ, Interface Geochemistry Section, 14473, Potsdam, Germany.

* e-mail: earbv@leeds.ac.uk; l.g.benning@leeds.ac.uk

## FIGURE CAPTION (SUPPLEMENTARY INFORMATION)

**Figure SI-1.** a, b) Detailed indexing of the powder X-ray diffraction patterns of the solids obtained at wet-*ambient* conditions (21 °C) and during *hydrothermal* (95-220 ºC) treatments with conditions and name and formula of indexed phase shown at the top of each plot. The patterns could be indexed to: (Aa) La-$La_2(CO_3)_3 \cdot 8H_2O$, kozoite-(La) $LaCO_3(OH)$ and hydroxylbastnasite-(La) [$LaCO_3(OH)$] and (Bb) Nd-system with in both cases $Nd_2(CO_3)_3 \cdot 2\text{-}3H_2O$, $Nd_2(CO_3)_3 \cdot 8H_2O$, kozoite-(Nd) [$NdCO_3(OH)$], hydroxylbastnasite-(Nd) [$NdCO_3(OH)$]. Patterns have been vertically offset for clarity.

**Figure SI-2**. (A) FTIR spectra of amorphous lanthanum carbonate (ALC; bottom spectrum) and the crystalline end products of the hydrothermal treatment at 60 ºC (2nd spectrum from bottom), 95 ºC (3rd spectrum from bottom) and 220 ºC (top spectrum). (B) Detail of the FTIR bands between 650 and 900 $cm^{-1}$. Main molecular/lattice absorption bands are indicated by numbers above the spectra and band assignments are detailed in Table SI-2 and discussed in the text.

**Figure SI-3.** a) FTIR spectra of amorphous neodymium carbonate (ANC; bottom spectrum) and lanthanite-Nd ($2^{nd}$ spectrum from bottom) and tengerite-(Nd) ($3^{rd}$ spectrum) and the products of the hydrothermal experiment obtained at 60 ºC ($4^{th}$ spectrum from bottom), 95 ºC ($5^{th}$ spectrum) and 220 ºC (top spectrum). (B) Detail of the FTIR bands located between 650 and 900 $cm^{-1}$. Main molecular/lattice absorption bands are indicated by numbers above the spectra and band assignments are detailed in Table SI-2 and discussed in the text.

**Figure SI-4**. Secondary electron SEM image of kozoite-(Nd) [$NdCO_3(OH)$] crystallized directly from ANC after hydrothermal aging at 95 ºC for 1.5h.

**Table SI-1.** REE carbonate minerals and respective bibliography that describe various aspects related to these phases.

**Table SI-2**. Details of FTIR stretching (ν), bending (δ), and rocking (ρ) vibrational band assignments and corresponding references for the water and carbonate species in the lanthanum and neodymium carbonates produced in the current study with band numbers corresponding to those shown in the spectra in Figure SI-2 and SI-3.

**SUPPLEMENTARY INFORMATION**

**Fig. SI-1**

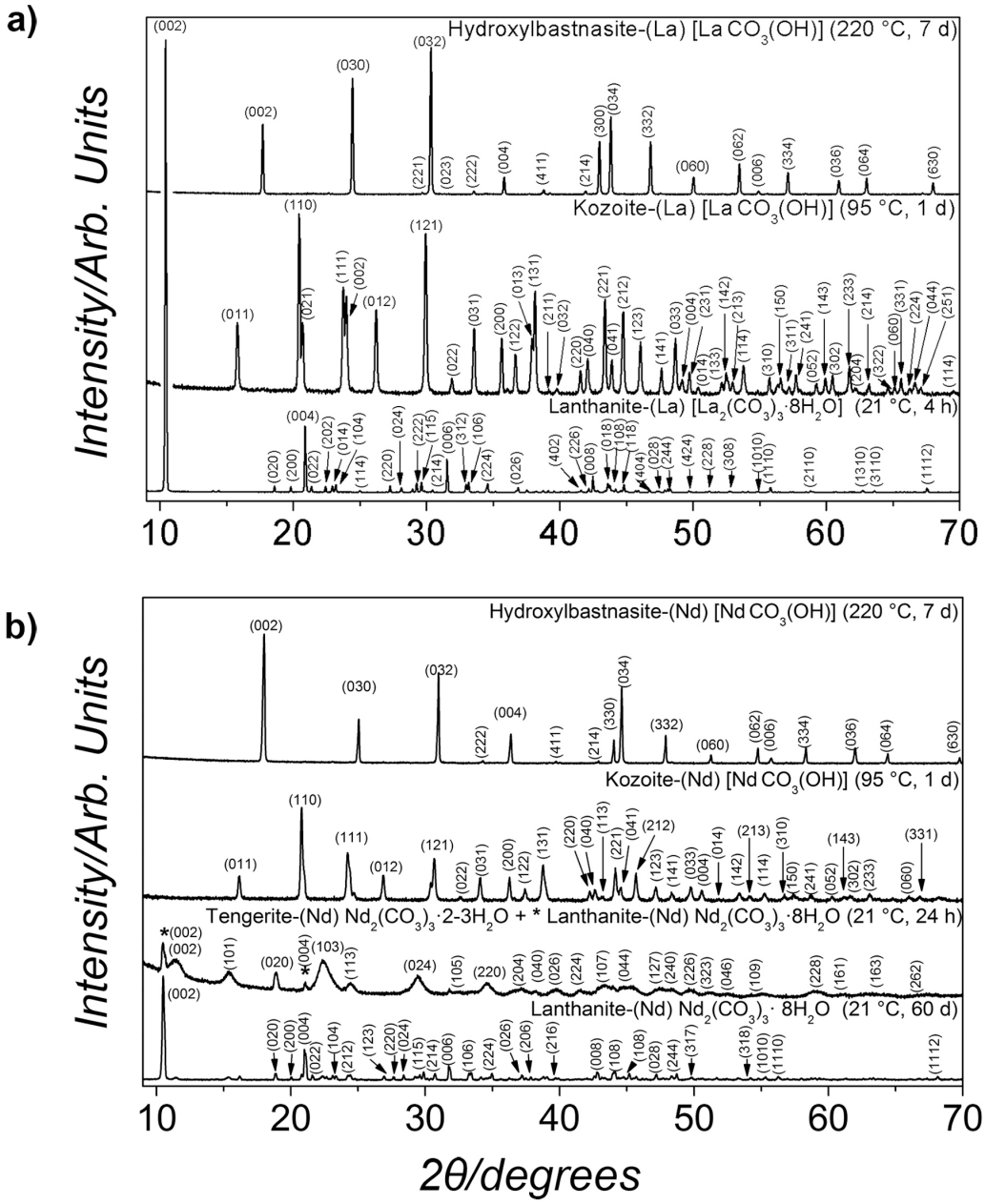

**Figure SI-2**

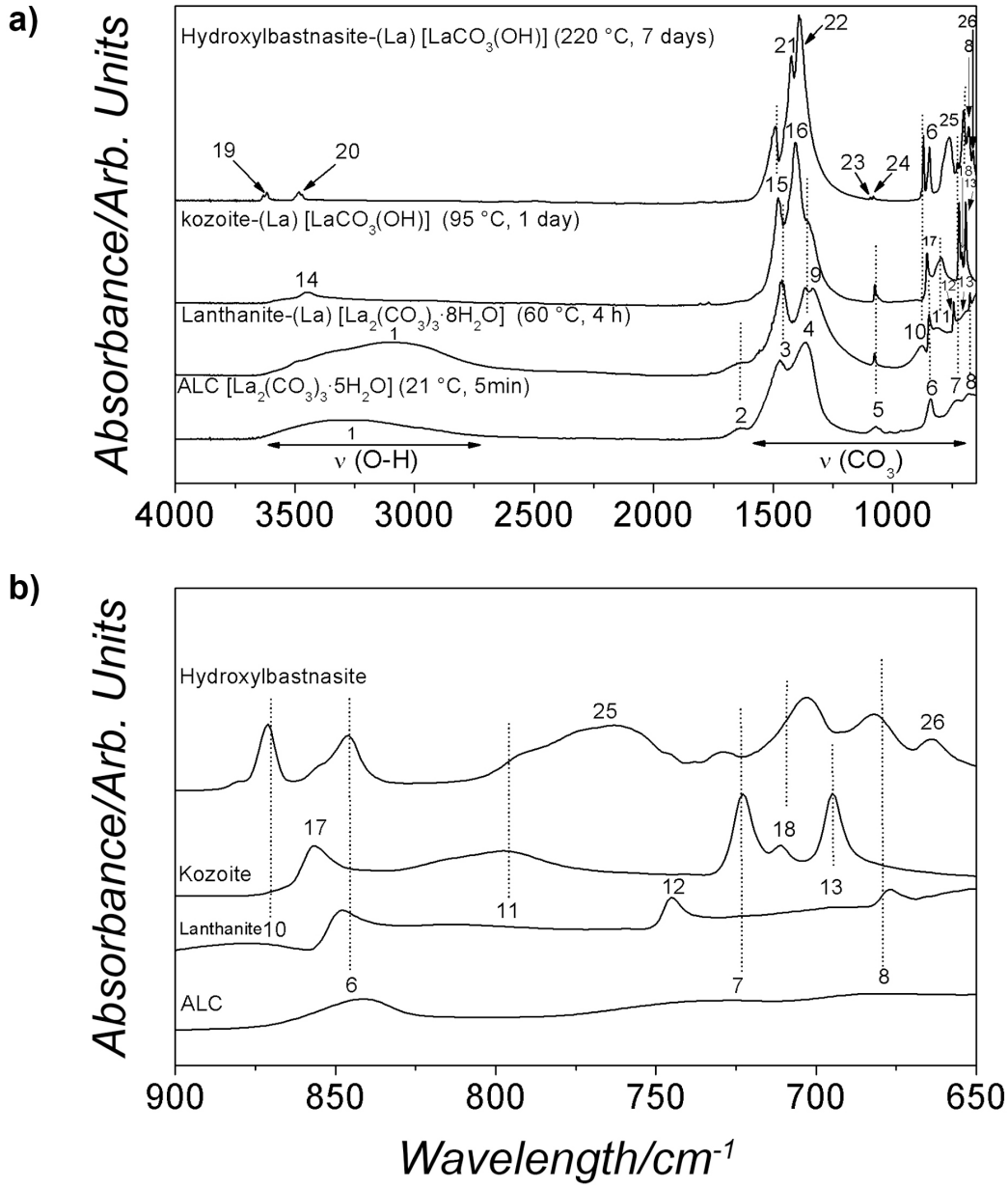
a)
Hydroxylbastnasite-(La) [LaCO3(OH)] (220 °C, 7 days)
kozoite-(La) [LaCO3(OH)] (95 °C, 1 day)
Lanthanite-(La) [La2(CO3)3·8H2O] (60 °C, 4 h)
ALC [La2(CO3)3·5H2O] (21 °C, 5min)
ν (O-H)
ν (CO3)
Absorbance/Arb. Units
4000 3500 3000 2500 2000 1500 1000
b)
Hydroxylbastnasite
Kozoite
Lanthanite
ALC
Absorbance/Arb. Units
900 850 800 750 700 650
Wavelength/cm-1

**Figure SI-3**

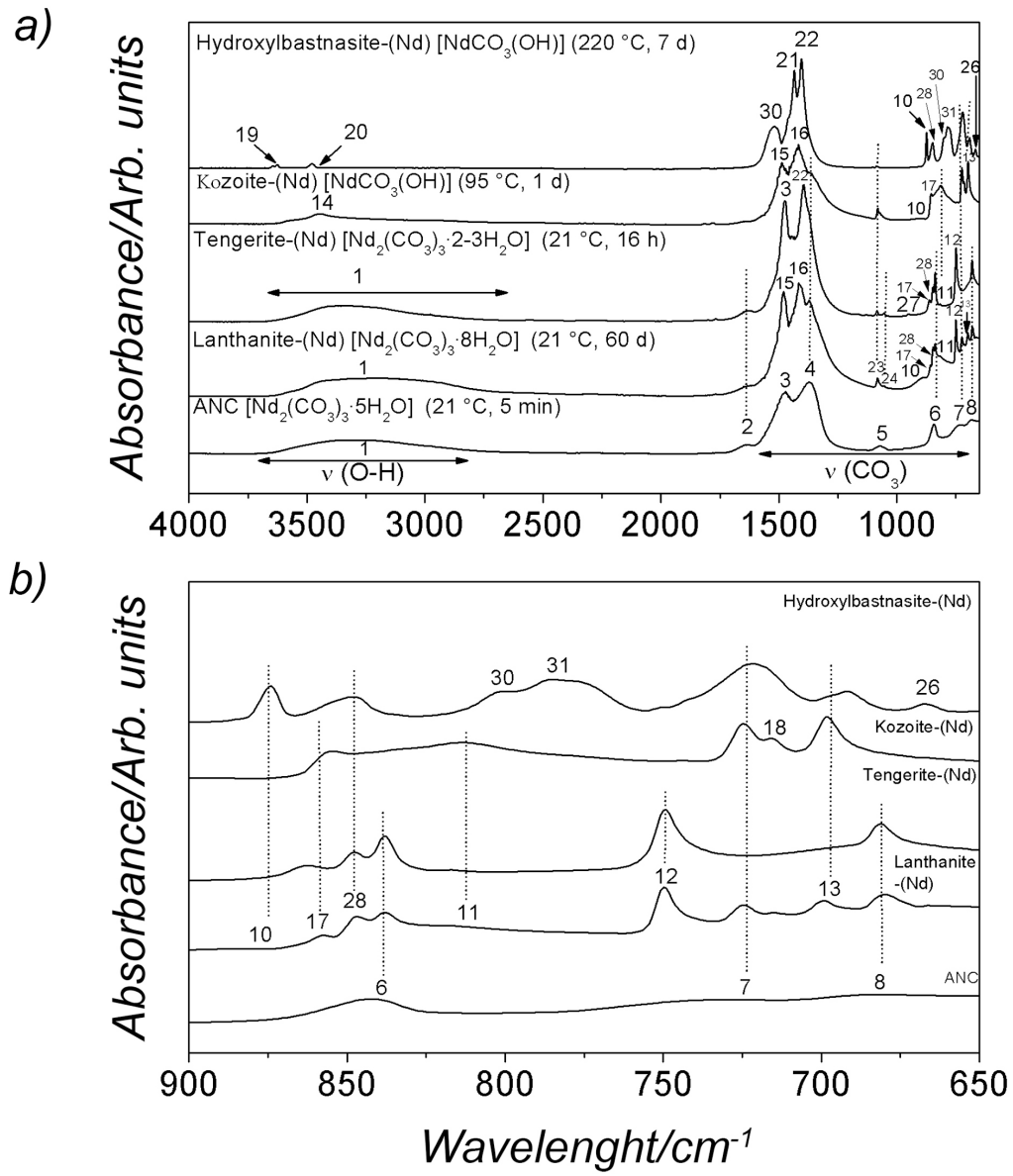
a)
Absorbance/Arb. units
Hydroxylbastnasite-(Nd) [NdCO3(OH)] (220 °C, 7 d)
Kozoite-(Nd) [NdCO3(OH)] (95 °C, 1 d)
Tengerite-(Nd) [Nd2(CO3)3·2-3H2O] (21 °C, 16 h)
Lanthanite-(Nd) [Nd2(CO3)3·8H2O] (21 °C, 60 d)
ANC [Nd2(CO3)3·5H2O] (21 °C, 5 min)
ν (O-H)
ν (CO3)
4000 3500 3000 2500 2000 1500 1000
b)
Absorbance/Arb. units
Hydroxylbastnasite-(Nd)
Kozoite-(Nd)
Tengerite-(Nd)
Lanthanite -(Nd)
ANC
900 850 800 750 700 650
Wavelenght/cm-1

**Fig SI-4**

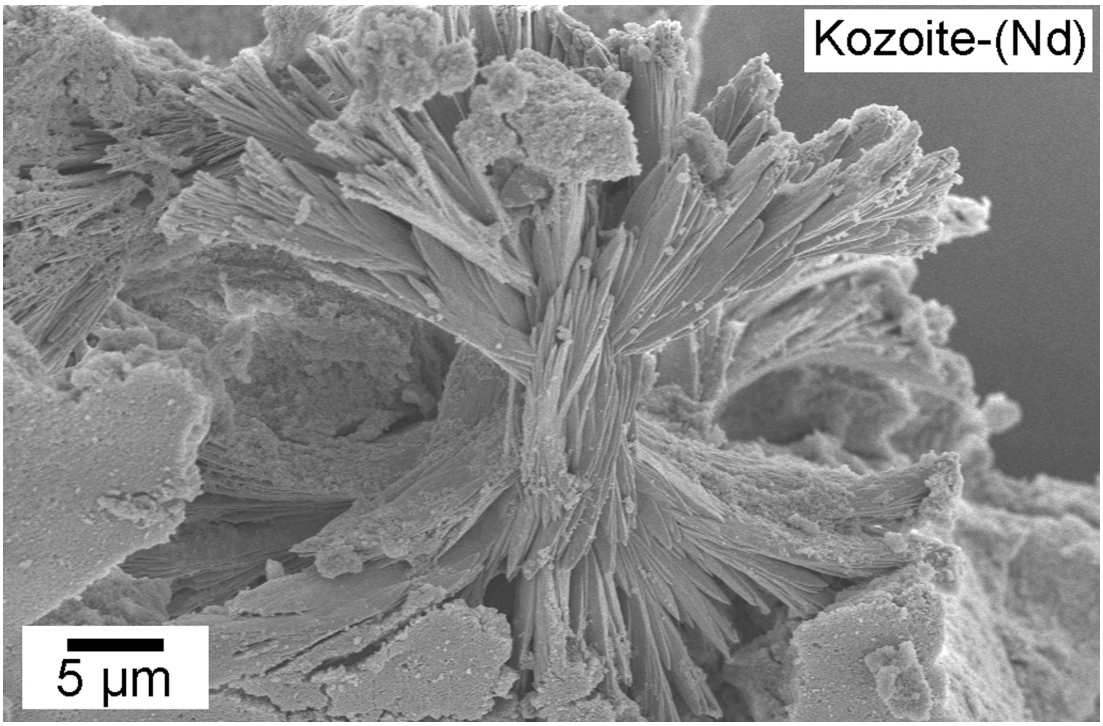

**Table SI-1**.

| Mineral | Bibliography |
|---|---|
| Lanthanite, [$REE_2(CO_3)_3 \cdot 8H_2O$] | 1-7 |
| Tengerite, [$REE_2(CO_3)_3 \cdot 2\text{-}3H_2O$] | 4,8 |
| Kozoite, [$REECO_3(OH)$] | 9-13 |
| Hydroxylbastnasite, [$REECO_3(OH)$] | 14-20 |
| Rare-earth dioxicarbonate, [$REE_2O_2CO_3$] | 16,21-25 |

**Table SI-2**.

| Band number | Wavelength ($cm^{-1}$) | Mode of vibration | Bibliography |
|---|---|---|---|
| 1 | 3700-2500 | $\nu$ (O-H) | 26 |
| 2 | 1633 | $\delta$ (O-H) | 27,28 |
| 3 | 1455 | $\nu_3$ asym. $CO_3$ | 29 |
| 4 | 1360 | $\nu_3$ asym. $CO_3$ | 30 |
| 5 | 1068 | $\nu_1$ sym. $CO_3$ | 7,11 |
| 6 | 841 | $\nu_2$ asym. $CO_3$ | 11 |
| 7 | 720 | $\nu_4$ asym. $CO_3$ | 11,18 |
| 8 | 679 | $\nu_4$ $CO_3$ | 7,11 |
| 9 | 1335 | $\gamma_1$ $CO_3$ | 28 |
| 10 | 878 | $\nu_2$ $CO_3$ | 7,18 |
| 11 | 818 | $\nu_2$ $CO_3$ | 11 |
| 12 | 745 | $\nu_4$ $CO_3$ | 31 |
| 13 | 693 | $\nu_4$ $CO_3$ | 7 |
| 14 | 3438 | $\nu$ (O-H) | 11 |
| 15 | 1479 | $\nu_3$ asym. $CO_3$ | 29 |
| 16 | 1409 | $\nu_3$ asym. $CO_3$ | 4,7 |
| 17 | 856 | $\nu_2$ $CO_3$ | 4 |
| 18 | 711 | $\nu_4$ asym. $CO_3$ | 11 |
| 19 | 3617 | $\delta$ (O-H) | 18 |
| 20 | 3482 | $\nu$ (O-H) | 18 |
| 21 | 1425 | $\nu_3$ asym. $CO_3$ | 7,18 |
| 22 | 1392 | $\nu_3$ asym. $CO_3$ | 4,11 |
| 23 | 1093 | $\nu_1$ sym. $CO_3$ | 11 |
| 24 | 1081 | $\nu_1$ sym. $CO_3$ | 11 |
| 25 | 763 | $\nu_2$ asym. $CO_3$ | 11 |
| 26 | 664 | $\rho$ $CO_3$ | 4 |
| 27 | 950 | $\nu_2$ $CO_3$ | 4 |
| 28 | 847 | $\nu_2$ $CO_3$ | 4,31 |
| 29 | 1519 | $\nu_3$ $CO_3$ | 18,31 |
| 30 | 800 | $\nu_2$ $CO_3$ | 32 |
| 31 | 784 | $\nu_3$ $CO_3$ | 8 |

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